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Solubility of Gaseous Carbon Dioxide in Molten LiCl-Li₂O

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Abstract

Carbonate ions in LiCl-Li₂O salt are a source of carbon contamination in the electrolytic refining of metal oxides, and their concentration is also essential information for understanding the CO₂ decomposition process. In this study, the solubility of gaseous CO₂ in molten LiCl-Li₂O was studied, with the goal of developing processes to decompose the oxides effectively. Ar-CO₂ gas mixtures were dissolved in molten salts containing various amounts of Li₂O, and the solubility of the CO₂ gas was calculated by measuring the mass difference between the molten salts before and after the CO₂ dissolution. The molar amount of dissolved CO₂ gas was almost as large as the molar
quantity of Li$_2$O when the partial pressure of CO$_2$ was 1.0 or 0.5 atm for Li$_2$O concentrations in the range of 0–60 mol%. This confirms that a large quantity of the oxide ions reacted with the CO$_2$ gas, resulting in the generation of carbonate ions.

**Keywords**: molten salt; solubility; phase diagram; carbon dioxide

1. **Introduction**

Several methods for the electrochemical reduction of metal oxides using molten salts have been actively developed in the past decades [1-9]. For example, the OS (Ono-Suzuki) process and the FFC (Fray-Farthing-Chen) process have become well known methods for reducing titanium oxide in CaO-CaCl$_2$ [2,4]. In the OS process, the metallic calcium electrodeposited on the cathode dissolves into the molten salt to create an environment that can reduce metallic oxides such as TiO$_2$. Subsequently, calcium oxide is formed as a product of a calciothermic reaction and is electrolyzed in the molten salt. At the anode, carbon reacts with oxide ions and forms carbon dioxide or carbon monoxide, which removes oxygen from the molten salt [2]. On the other hand, the FFC process is a direct reaction in which a metallic oxide is used as the cathode, where it is reduced electrochemically to remove oxygen ions [4].

The electrochemical and thermochemical reactions involved in these mechanisms can
be summarized as follows:

**OS process**

4. $Ca^{2+} + 2e^- \rightarrow Ca$ (at the cathode) \hspace{1cm} (1)

5. $Ca \rightarrow Ca$ (dissolution to molten salt) \hspace{1cm} (2)

6. $nCa + M_mO_n \rightarrow mM + nCaO$ (reduction) \hspace{1cm} (3)

7. $CaO \rightarrow Ca^{2+} + O^{2-}$ (ionization) \hspace{1cm} (4)

8. $nO^{2-} + C \rightarrow CO_n + 2ne^-$ \hspace{1cm} \((n = 1 \text{ or } 2) \) (at the anode) \hspace{1cm} (5)

**FFC - Cambridge process**

11. $M_mO_n + 2ne^- \rightarrow mM + nO^{2-}$ (electroreduction at the cathode) \hspace{1cm} (6)

12. $nO^{2-} + C \rightarrow CO_n + 2ne^-$ \hspace{1cm} \((n = 1 \text{ or } 2) \) (at the anode) \hspace{1cm} (7)

In both processes, the dissolution of $O^{2-}$ in the chloride melt is critically important to reduce the metallic oxide $M_mO_n$, and a high solubility of metallic Ca in the melt is also critical to realize good reactivity. The two molten salts, CaCl$_2$-CaO and LiCl-Li$_2$O, can reduce metallic oxides more efficiently than other combinations of oxides and chlorides.

The key advantage of both methods is that they enable the direct reduction of the
oxides. This is not true for the Kroll process conventionally used in industry, and thus
these methods have the potential to replace it. However, the product is occasionally
contaminated with carbon when the CaCl$_2$-CaO system is used [10], because the CO$_2$
gas evolved at the carbon anode partially dissolves into the salt as CO$_3^{2-}$ and is reduced
to carbon at the cathode. The resulting carbon deposits may react with the metallic
particles, and produce a carbon solid solution or a carbide. Thus, it is very important to
quantify the solubility of CO$_2$ in the molten salt in order to develop techniques to
suppress the carbide formation and the carbonate reduction.

The CO$_2$ solubility in molten salts has been previously studied in order to understand
the slag basicity in non-SiO$_2$-based fluxes [11-13]. Hashizume et al. [10] studied the
solubility of CO$_2$ in the CaCl$_2$-CaO-CaCO$_3$ system from the viewpoint of phase
equililibria and concluded that carbon contamination of the reduction product is caused
by the following reaction (8):

$$\text{CO}_3^{2-} + 2\text{Ca} \rightarrow \text{C} + 3\text{O}^{2-} + 2\text{Ca}^{2+} \quad (8)$$

Oxide reduction in a LiCl-Li$_2$O melt is also popular, because it works even at low
temperatures, but the CO$_2$ solubility and the concentration of CO$_3^{2-}$ in this system have
not been well examined. Therefore, the possibility of the occurrence of the following
reaction (9) is considered in this study:
Otake et al. reported that CO₂ gas decomposes to carbon and oxygen in CaCl₂-CaO and LiCl-Li₂O melts [14]. The decomposition of the carbonate ions in the molten salt has also been examined and was found to be one of the reasons for the reduction of carbon from CO₂ gas [14, 15]. However, the dependence of the CO₃²⁻ concentration in molten LiCl-Li₂O on the melt composition, which is a fundamental property necessary for minimizing the contamination of the reduced product, has not been investigated in detail. In particular, melts in the LiCl-Li₂O system can decompose CO₂ at lower temperatures than those in the CaCl₂-CaO system, and a detailed study on CO₂ gas solutions in LiCl-Li₂O is desired both to analyze the decomposition process of CO₂ gas and to minimize the carbon contamination in the fresh product from the metallic oxide.

Therefore, the present study aims to determine the solubility of CO₂ in molten LiCl-Li₂O and analyze the mechanism of CO₂ decomposition.

A temperature of 923 K was chosen for this study because evaporation is more significant above this temperature. Reliable and reproducible data have been obtained previously at 923 K, well above the melting temperature [25]. For example, Usami et al. [17] reported that 12 mol%Li₂O can dissolve in the LiCl melt at 923 K. Sanster et al. [16] measured the phase diagram of the LiCl-Li₂CO₃ system and found that the liquid
can exist at 923 K in a composition ranging between pure LiCl and 70 mol% Li₂CO₃.

Assuming that the entire amount of Li₂O reacts with CO₂ to form Li₂CO₃, the solubility of Li₂CO₃ in LiCl is limited to 70 mol% at 923 K. Therefore, LiCl-Li₂O melts with various concentrations of Li₂O from pure LiCl to LiCl-70 mol% Li₂O were studied in this work.

2. Materials and methods

LiCl (99.0% purity, Wako Chemical Co.) and Li₂O (99.5% purity, Strem Chemicals Co.) were mixed to obtain the desired composition in the range of 0–60 mol% Li₂O and placed in an Al₂O₃ crucible with an inner diameter of 17 mm and height of 100 mm. The mass of the crucible after the mixture of salt and oxide was added was measured precisely before it was set inside the furnace. The crucible was fixed to a titanium rod and set inside the furnace, as shown in Fig. 1. The temperature of the furnace was controlled with an accuracy of ±1 K. The sample was dehydrated by continuous evacuation at 723 K. Then, the furnace was heated up to 923 K and filled with Ar gas. While this temperature was maintained, a gaseous Ar-CO₂ mixture was flowed through the furnace to dissolve into the molten salt for a predetermined time. The partial pressures of Ar and CO₂ gas in the mixture could be controlled in a range of...
±0.004 atm. The crucible was retracted after the CO₂ flow was halted, and the crucible was cooled rapidly at the low-temperature zone in the upper part of the furnace. After the crucible cooled to room temperature, the mass of the crucible with the solidified salt was measured. The products in the crucible were characterized by powder X-ray diffraction (XRD) using CuKα radiation. The data processing procedures in this work are based on the general design of the experiments [24].

3. Results

Table 1 shows the experimental conditions and the results obtained.

3.1. Characterization of the products

Two samples with identical initial compositions of 30 mol% Li₂O were cooled and analyzed by XRD. To investigate the formation of carbonate in the presence of gaseous CO₂, two samples labeled #A and #B were prepared. Sample #A was heated without CO₂ even after the temperature reached 923 K. For sample #B, CO₂ was dissolved after the temperature was stabilized at 923 K. Fig. 2 shows the XRD patterns of these samples. Lithium oxide, lithium chloride, and lithium chloride hydrate were present in sample #A, as shown in Fig. 2(a). The hydrate was formed at room temperature because the lithium chloride easily reacts with moisture in the atmosphere during sample
handling for the XRD experiments. Although the intensities of the diffraction peaks of
the hydrate increased when the sample was exposed to the atmosphere for a longer
period, the initial constituents of sample #A, i.e., LiCl and Li₂O, did not change after the
experiments, except for the formation of the LiCl hydrate. However, Li₂CO₃ was clearly
generated because of the dissolution of CO₂ in sample #B, as shown in Fig. 2(b).
Interestingly, peaks corresponding to lithium oxide disappeared in the XRD patterns of
sample #B. The alumina peaks originated from the broken crucible.
Since the molten salt used in this study did not include network-forming entities such
as SiO₂, lithium chloride and lithium oxide were completely ionized. Li₂CO₃ consists of
lithium and carbonate ions, so the following reaction (10) takes place when CO₂ gas
dissolves into the molten salt during heating [18-21]:

\[
\text{CO}_2 + \text{O}^{2-} \rightarrow \text{CO}_3^{2-} \tag{10}
\]

3.2. CO₂ saturation time
Even when a sufficient amount of CO₂ gas was introduced to the melt, the mole
fraction of CO₃²⁻ was lower than that of Li₂O. Therefore, we can neglect any gas
dissolution not leading to the formation of carbonate ions and hypercarbonates such as
Li$_2$(CO$_3$)$_n$ ($n > 1$). The CO$_2$ solubility ($X_{CO2}$) was evaluated by using equations (11) and (12):

\[ X_{CO2} = N_{CO2} / (N_{Li2O} + N_{LiCl}) \quad (11) \]

\[ N_{CO2} = \Delta w / M_{CO2} \quad (12) \]

In the above equation, $N_{Li2O}$ and $N_{LiCl}$ are the initial molar quantities of Li$_2$O and LiCl added to the crucible, respectively, and $\Delta w$ (g) is the mass difference caused by the dissolution of CO$_2$ gas. $N_{CO2}$ is the molar quantity of dissolved CO$_2$, and $M_{CO2}$ (g/mol) is the molecular weight of CO$_2$.

To measure the maximum solubility of CO$_2$, CO$_2$ should be saturated in the molten salt. Therefore, Fig. 3 shows the relationship between the exposure time and CO$_2$ concentration to allow an estimation of the CO$_2$ saturation time. When $X_{Li2O}$ is 0.2, $X_{CO2}$ should also be 0.2 at a holding time of 14.4 ks. However, $X_{CO2}$ slightly decreased when the holding time was increased to 172.8 ks. Because a small amount of LiCl was deposited on the colder part of the reaction vessel, mass loss due to vaporization of the molten salt could not be neglected. When $X_{Li2O}$ was 0.6, $X_{CO2}$ increased from a holding time of 14.4 ks to a holding time of 32.4 ks, but decreased when the holding time
further increased 172.8 ks because of the considerable mass loss. Therefore, 86.4 ks was chosen for further analysis as a dissolution time at which CO₂ gas was saturated but the effect of the vaporization was insignificant as compared to that observed at a holding time of 172.8 ks. The mass loss due to the evaporation of the molten salt was corrected for as described in the next section.

3.3. Effect of salt evaporation

Because the sample in the crucible constantly loses mass when the molten salt is kept at a high temperature, it is necessary to evaluate the mass loss due to the molten salt vaporization at 923 K. The mass loss was experimentally measured by keeping the samples at 923 K under an Ar atmosphere.

Fig. 4 shows the amount of salt that evaporates within 86.4 ks as a function of the Li₂O concentration. The amount of evaporation was independent of the Li₂O concentration over a wide range, as long as the crucible was the same size. The correction value \( \Delta w_{\text{cor.}} \) (g) was determined by taking the average of the amounts of evaporated salt for the different experiments. The following compensating equation (13) was deduced from equation (12):
The compensated solubility of the CO₂ gas in the molten salt, $X_{\text{CO}_2, \text{meas.}}$, was thus calculated by considering the amount of salt that evaporated. However, this compensation hardly affected the CO₂ solubility: its contribution was less than 1%.

3.4. Solubility of CO₂ gas in molten LiCl

Table 2 shows the CO₂ solubility data. $X_{\text{Li}_2\text{O,id.}}$ is the target composition before weighing, and $X_{\text{Li}_2\text{O,meas.}}$ is the measured composition calculated from the amounts of LiCl and Li₂O. $X_{\text{CO}_2}$ is the molar fraction of dissolved CO₂ calculated by neglecting the error of the electric balance and the amounts of evaporated salt. $X_{\text{CO}_2,\text{high}}$ and $X_{\text{CO}_2,\text{low}}$ are the maximum and minimum values when the error of electric balance and the amounts of evaporated salt were taken into consideration. $X_{\text{CO}_2,\text{ave}}$ is the average of $X_{\text{CO}_2,\text{high}}$ and $X_{\text{CO}_2,\text{low}}$. The difference between $X_{\text{CO}_2,\text{high}}$ and $X_{\text{CO}_2,\text{low}}$ was very small, less than 1%.

Fig. 5 shows the relationship between the compensated CO₂ solubility and the measured concentration of Li₂O at 923 K for an exposure duration of 86.4 ks. Three partial pressures of CO₂ ($P_{\text{CO}_2}$) were selected: 1.0, 0.5, and 0.1 atm. The CO₂ solubility
increases linearly with increasing initial Li$_2$O concentration at $P_{CO_2} = 1.0$ and 0.5 atm. The broken line in Fig. 5 represents the ideal CO$_2$ solubility when all the O$^{2-}$ in the molten salt reacts with the CO$_2$ gas. As discussed in section 3.2, the CO$_2$ gas was saturated for a wide range of Li$_2$O concentrations. When $P_{CO_2}$ was 1.0 and 0.5 atm, the CO$_2$ solubility also approached the ideal solubility for a wide range of Li$_2$O concentrations, as shown in Fig. 5. There is a strong positive correlation between the CO$_2$ solubility and Li$_2$O concentration, with a correlation coefficient of 0.9998. Regression analysis revealed that the slope of the straight line showing the proportional relationship between the two variables was 95% of the slope for the ideal relationship. Thus, 95% of the initial amount of O$^{2-}$ in the molten salt well reacted with CO$_2$ gas to form CO$_3^{2-}$. However, when $P_{CO_2}$ was 0.1 atm, the solubility of CO$_2$ was clearly different from the other partial pressures of CO$_2$. The equilibrium constant of reaction (8) thermodynamically depends only on the temperature, not on $P_{CO_2}$. Therefore, the decrease in CO$_2$ solubility corresponds to a change in the ratio between the thermochemical activities of CO$_3^{2-}$ and O$^{2-}$ with decreasing $P_{CO_2}$.

The reason why the CO$_2$ solubility was constant over a wide range of Li$_2$O at $P_{CO_2} =$ 0.1 atm is explained below. According to Usami et al., the solubility of Li$_2$O in the
LiCl melt is only about 12 mol% at 923 K [17]. Thus, the residual Li₂O exists as a solid when more than 12 mol% Li₂O is present. In this study, the concentration of Li₂O initially ranged between 0 and 60 mol%, and some portion of Li₂O existed as a solid prior to the injection of the gas and in the initial stages of CO₂ dissolution. Li₂O could turn into Li₂CO₃ and then form a LiCl-Li₂CO₃ molten salt. However, when $P_{\text{CO₂}}$ is as low as 0.1 atm, the CO₂ gas may not be well saturated in the molten salt, and a small amount of undissolved Li₂O may remain unreacted. This problem is challenging to solve, because, for example, extending the CO₂ dissolution time causes an increase in mass loss due to vaporization of the molten salt.

4. Discussion

When the Li₂O content is 60 mol% at $P_{\text{CO₂}} = 1.0$ and 0.5 atm, more than 95% of the reacted Li₂O can be expected to exist as CO₃²⁻, as shown in Fig. 5. Similar works on the dissolution of CO₂ gas in a mixture of a chloride and an oxide were reported by Maeda and Ikeda [22] and by Hashizume et al. [10]. They found that the CO₂ solubility in the CaCl₂-CaO melt followed a linear relationship with the initial amount of CaO. A similar linear relationship was also found in the present study on the LiCl-Li₂O system, as shown in Fig. 5. Whereas thermogravimetry was used to measure the mass
difference in previous work [7], the work presented here proves that similar results can be obtained by using a simple apparatus. The data accumulation method developed in this study can also be applied at the other temperatures and pressures to study oxide reduction using molten salt electrolysis in expanded temperature or pressure ranges.

For example, Ijije et al [26] recently reported the CO$_2$ decomposition using the molten salts containing Li$_2$CO$_3$. Their operating temperature is in the range of 723K and 1173 K by mixing with Na$_2$CO$_3$ and K$_2$CO$_3$. The CO$_2$ dissolution data for the wider temperature range and at the various mixtures are required for the further precise operation of CO$_2$ decomposition.

It is noted that the maximum solubility of CO$_2$ in the LiCl-Li$_2$O melt is significantly higher than the values reported in previous studies for the CaCl$_2$-CaO melt. This indicates a strong affinity between Li$_2$O and CO$_2$ gas at 923 K. The solubility of CO$_2$ in the CaCl$_2$-CaO melt was also studied at temperatures higher than 923 K, at which the thermal stability of CaCO$_3$ is weaker. The solubility at $P_{CO_2}=1$ atm is useful for evaluating the concentration of CO$_2$ close to the anode in the OS and FFC processes, because $O^{2-}$ at the carbon anode reacts with carbon to form CO$_2$ gas bubbles at $P_{CO_2}=1$.

When the metallic oxide is reduced at the cathode in carbonate ion-rich molten salt in
the OS method, carbon contamination of the reduction product may be driven by reactions (8) and (14) [15, 26]:

$$\text{CO}_3^{2-} + 4e^- = C + 3\text{O}_2^2$$  \hspace{1cm} (14)

Therefore, the cathodic potential in this process must be kept at the voltage that carbonate ions cannot decompose to contaminate the product as carbon or a carbide. In contrast, the data obtained at $P_{\text{CO}_2} < 1\text{ atm}$ are informative about the CO$_2$ decomposition process at low temperatures such as 923 K. When the gaseous CO$_2$ is decomposed in the OS method, a mixture of CO$_2$ and Ar gas is introduced at the cathode that forms carbon, and the partial pressure of CO$_2$ in the gas bubbles is lower than 1 atm [14]. When LiCl-Li$_2$O molten salt is used to decompose gaseous CO$_2$, the CO$_2$ gas bubbling changes the composition of the residual molten salt from LiCl-Li$_2$O to LiCl-Li$_2$O-Li$_2$CO$_3$. In this context, the CO$_2$ solubility obtained in this work will be valuable for future applications.

Supposing that the decrease in CO$_2$ solubility at $P_{\text{CO}_2} = 0.1\text{ atm}$ is due to the precipitation of Li$_2$O(s), the phase equilibria in the LiCl-Li$_2$O-Li$_2$CO$_3$ ternary system were predicted, as shown in Fig. 6. The maximum solubilities of Li$_2$CO$_3$ and Li$_2$O in liquid LiCl correspond to the compositional points A and B in Fig. 6, respectively. Assuming that the maximum solubility of CO$_2$ in liquid LiCl at $P_{\text{CO}_2} = 0.1\text{ atm}$ is given
by point C, three-phase equilibrium among the LiCl-rich liquid, solid Li₂O, and solid Li₂CO₃ is predicted as the shaded triangle in Fig. 6. The solidus line is shown as a broken line. From the experimental results, at $P_{CO2} > 0.5$ atm, the two-phase equilibrium between the LiCl melt and Li₂CO₃ is achieved. When $P_{CO2} < 0.1$ atm, the LiCl melt should form an equilibrium with Li₂O(s). Therefore, the three-phase equilibrium can exist when $P_{CO2}$ is between 0.1 and 0.5 atm. Since the pressure required to decompose Li₂CO₃ to CO₂ gas and Li₂O is evaluated as $2.2 \times 10^{-5}$ atm from the thermodynamic data [23], the $P_{CO2}$ for the three-phase equilibrium is higher than $2.2 \times 10^{-5}$ atm. Therefore, the isobars of oxygen between $2.2 \times 10^{-5}$ and 0.1 atm in the LiCl-rich liquid connect with the solid solution of Li₂O and enter into the single-phase region of Li₂O. These isobars also finally enter the region of the Li₂CO₃ solid solution. A phase equilibrium between Li₂CO₃ and Li₂O should exist over a wide range of Li₂CO₃ and Li₂O contents, as shown by regions I and II in Fig. 6. Such an Li₂CO₃(s)-Li₂O(s) equilibrium cannot exist if Li₂CO₃ and Li₂O are insoluble. The existence of this equilibrium over a wide range of Li₂CO₃ and Li₂O contents may cause the inversion in the relationship between CO₂ solubility and $P_{CO2}$ close to the Li₂CO₃-Li₂O quasi-binary system.
5. Conclusions

The solubility of CO$_2$ gas in LiCl-Li$_2$O was determined experimentally by measuring the mass change due to CO$_2$ gas dissolution. A small amount of molten salt was evaporated when the melt was held at 923 K, which influenced the mass change measured for the compositional range considered here. This mass change was subtracted from the measured mass change, and the measured data were well compensated, although this correction to the CO$_2$ solubility was less than 0.1%. After this correction, it was found that a molar quantity of CO$_2$ gas as large as 95% of the molar quantity of Li$_2$O could dissolve into the molten salts in the compositional range 0–60 mol% Li$_2$O.

The formation of Li$_2$CO$_3$ due to CO$_2$ dissolution and its dissolution into the LiCl melt were observed by XRD analysis. The dissolution behavior of CO$_2$ gas is identical at $P_{CO_2} = 1.0$ and 0.5 atm. However, the possible precipitation of Li$_2$O at $P_{CO_2} = 0.1$ atm was discussed on the basis of the ternary phase equilibrium.

List of symbols

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<td>$T$</td>
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1 \( X_{\text{CO2}} \)  Mole fraction of dissolved CO₂

2 \( N_i \)  Molar quantities of chemical species “\( i \)”

3 \( M_i \)  Molecular weight of chemical species “\( i \)”

4 \( \Delta w \)  Amount of evaporated salt

5 \( P_{\text{CO2}} \)  Partial pressure of CO₂

6 **Subscripts**

7 cor.  corrected

8 ave.  averaged

9 id.  ideal

10 meas.  Measured

11

12 **6. Acknowledgements**

13 The authors thank Ms Mika Kitamura of Hokkaido University for her experimental assistance. They also appreciate financial support from the Japan Science and Technology Agency (JST) – Advanced Low Carbon Technology Research and Development Program (ALCA).

14

15 **References**


Table caption

1 Table 1 Chemicals description.

2 Table 2 Experimental results for each condition.\(^a\)

5 Figure captions

6 Fig. 1 Experimental set-up used in the present study.

8 Fig. 2 (a) XRD pattern of the sample not subjected to CO\(_2\) dissolution.

9 (b) XRD pattern of the sample after dissolution of CO\(_2\).

11 Fig. 3 Time-dependent change of the mass difference of the crucible.

13 Fig. 4 Amount of the evaporated salt evaluated by mass loss during heating in Ar gas at 923 K for 86.4 ks.

16 Fig. 5 Amount of dissolved CO\(_2\) at three conditions.

18 Fig. 6 Phase equilibria in the LiCl-Li\(_2\)O-Li\(_2\)CO\(_3\) ternary system.
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</table>

- Not measured

a An uncertainties are \(U(P_{\text{CO}_2}) = \pm 0.004\) atm, \(U(T) = \pm 1\) K.