Dissolution Behavior of Lithium Oxide in Molten LiCl−KCl Systems

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The solubility of lithium oxide was measured in molten LiCl−KCl containing (58.5, 75, 90, and 100) mol % LiCl in the temperature range of (673 to 923) K. The melt with a higher content of LiCl has a higher solubility of Li_2O. The pure LiCl has the highest solubility of Li_2O, (12.0 ± 0.2) mol % at 923 K. The estimated standard formal potential of O_2/O^{2-} increases linearly as the temperature decreases and as the mole fraction of LiCl increases.

Introduction

Electrochemical reduction processes in molten salts have been studied for metal refining and nuclear fuel reprocessing.[1,2] One of the most important achievements expected for the improvement of the efficiency of the process is the development of an inert anode. In our previous study, a boron-doped diamond (BDD) electrode was found to possess excellent properties for this purpose.[3] In addition to the electrode materials, high solubility of oxides in the melts is essential for fast electrochemical reduction of metal oxides with high efficiency.[4] Molten LiCl and $CaCl_2$ are strong candidates of the melts that satisfy the above requirement. Because of their high solubilities as oxides,[2,5] reduction of metal oxides has been achieved chemically and electrochemically in these melts.[2,6] However, the high melting temperatures of LiCl and $CaCl_2$ are disadvantageous for the process. Lower temperature operation has advantages such as lower corrosive and thermal damage to the vessels and electrode materials. Therefore, molten salts that have high solubilities as oxides at lower temperatures are indispensible for the reduction processes of metal oxides, although few reports are currently available on this subject. In this study, the temperature dependence of solubilities was investigated in molten LiCl−KCl systems with an electrochemical method. We selected the compositions of LiCl−KCl melts by referring to the reported binary phase diagram.[7]

Experimental Section

A glassy carbon rod (Tokai Carbon) was used as an anode material for cyclic voltammetry. The cathode materials were also glassy carbon rods at temperatures higher than 823 K, whereas aluminum plates (99.2 %, Nilako) were used at temperatures lower than 823 K. The reference electrode was an Ag^+/Ag electrode. A silver wire (99.99 %, Japan Metal Service) was immersed in the LiCl−KCl melt of each composition containing 0.5 mol % AgCl (99.5 %, Wako Pure Chemical), which was set in a Pyrex glass or mullite tube. The potential of the reference electrode was standardized against the Li^+/Li. A nickel wire was used as a current collector and was immersed in molten lithium metal to measure the potential of Li^+/Li against Ag^+/Ag.

Reagent grade LiCl (Aldrich-APL, 99.99 %), KCl (Aldrich-APL, 99.99 %), and a eutectic mixture of LiCl−KCl (Aldrich-APL, 99.98 %) were used for the melt. The solubility of lithium oxide (Li_2O, Aldrich, 97 %) was measured in LiCl and LiCl−KCl mixtures of following compositions: LiCl:KCl = 90:10, 75:25, 58.5:41.5 (eutectic). The experimental temperature range was (673 to 923) K. All experiments were conducted in a glove box filled with Ar gas dried and deoxygenated by a gas purifier (MIWA, MS3-H60SN). The concentration of water and oxygen gas in the atmosphere were kept at less than 1 ppm.

Electrochemical measurements were performed using an electrochemical measurement system (HZ-3000, Hokuto Denko).

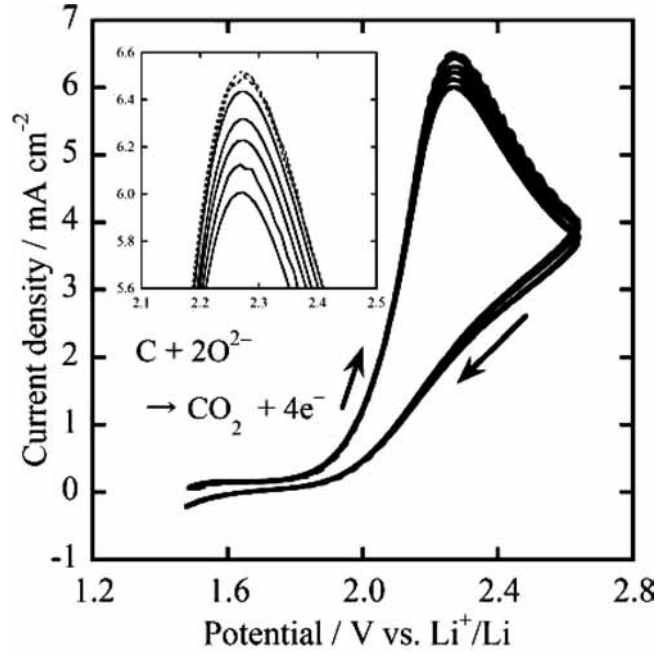

Figure 1. Cyclic voltammograms of a glassy carbon rod in eutectic LiCl−KCl (58.5:41.5) with the addition of Li_2O (solid line, (0.975, 1.000, 1.025, 1.050, and 1.100) mol %; dotted line, (1.150, 1.200, and 1.225) mol %) at 773 K. Scan rate is 0.2 $V \cdot s^{-1}$. The inset is the close-up drawing around the current density peaks.

Results and Discussion

Temperature Dependence of the Solubility of Lithium Oxide in Molten LiCl−KCl. Figure 1 shows the cyclic volta-

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Table 1. Temperature Dependence of the Solubility Products of Li_2O in Molten LiCl−KCl Systems[a]

LiCl:KCl	T/K	ln K_{sp}
100:0	873 to 923	$-(2.44 \pm 0.47)\cdot 10^3 T^{-1} + 0.52 \pm 0.01$
90:10	823 to 923	$-(0.41 \pm 0.14)\cdot 10^3 T^{-1} - 2.17 \pm 0.01$
75:25	773 to 873	$-(1.79 \pm 0.35)\cdot 10^3 T^{-1} - 1.46 \pm 0.03$
58.5:41.5	673 to 823	$-(2.39 \pm 0.29)\cdot 10^3 T^{-1} - 2.43 \pm 0.03$

[a] Error values are the 95 % confidence intervals.

mmogram in the positive potential region obtained in a eutectic LiCl−KCl (58.5:41.5) melt containing various amounts of Li_2O at 773 K using a glassy carbon rod electrode. A sharp increase in anodic currents was observed at about 2.0 V (vs Li^+/Li). This current is attributed to the evolution of carbon dioxide.[8]

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \quad (1)$$

The peak currents corresponding to CO_2 evolution plotted against the amount of Li_2O added to the melt are shown in Figure 2. The current increased almost linearly as the amount of Li_2O added increased and finally showed a constant value when the melt was saturated with Li_2O. As a result, the solubility of Li_2O in eutectic LiCl−KCl at 773 K was determined to be 1.12 mol %. The intersecting point of the two lines shown in the Figure was chosen to be a saturation point. In the same manner, the solubilities of Li_2O were determined at (673, 723, 773, and 823) K. They were (0.708 ± 0.055, 0.966 ± 0.031, 1.14 ± 0.05, and 1.32 ± 0.53) mol %, respectively. The error value denotes the 95 % confidence interval. The solubility of Li_2O was also determined in the pure LiCl and LiCl−KCl mixtures; LiCl:KCl = 90:10 and 75:25. The results are summarized in Figures 3 and 4. The temperature dependence of the solubility product, K_{sp}, is given by the empirical equations in Table 1, where T is the absolute temperature. K_{sp} is determined from eq 2 by using the mole fraction of lithium ion, X_{Li^+}, and that of the oxide ion, $X_{O^{2-}}$. The solubility of Li_2O increases with an elevation of the temperature of the melt and an increase in the mole fraction of LiCl in the melt.

$$K_{sp} = X_{Li^+}^2 \cdot X_{O^{2-}} \quad (2)$$

Thermodynamical Study on the Standard Formal Potential of O_2/O^{2-}. The standard formal potential of O_2/O^{2-}, $E^{0\prime}_{O_2/O^{2-}}$, was calculated and estimated from the results obtained from the measurement of the solubility. The oxygen electrode reaction and the Nernstian equation in molten salts are described as follows

$$\frac{1}{2}O_2 + 2e^- = O^{2-} \quad (3)$$

$$E_{O_2/O^{2-}} = E^0_{O_2/O^{2-}} + \frac{RT}{2F} \ln \frac{f_{O_2}^{1/2}}{a_{O^{2-}}} \quad (4)$$

where R is the gas constant, F is the Faraday constant, f_{O_2} is the fugacity of O_2, $a_{O^{2-}}$ is the activity of O^{2-}, and $E^{0\prime}_{O_2/O^{2-}}$ is

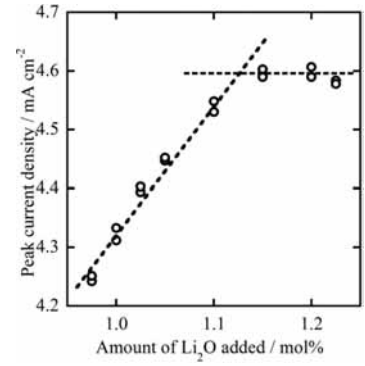

Figure 2. Peak currents against the amount of Li_2O added to the melt determined from cyclic voltammograms of a glassy carbon electrode in eutectic LiCl−KCl (58.5:41.5) at 773 K.

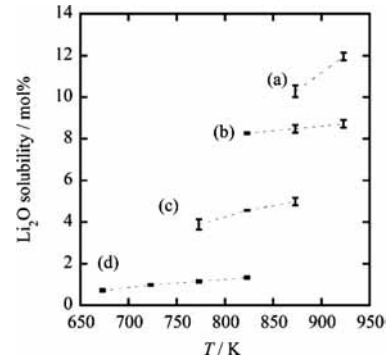

Figure 3. Solubilities of Li_2O in molten LiCl−KCl systems. LiCl:KCl = (a) 100:0, (b) 90:10, (c) 75:25, and (d) 58.5:41.5.

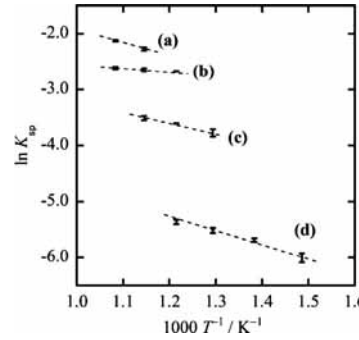

Figure 4. Relationship between temperature and the solubility products of Li_2O in molten LiCl−KCl systems. LiCl:KCl = (a) 100:0, (b) 90:10, (c) 75:25, and (d) 58.5:41.5.

the standard potential of O_2/O^{2-}. Equation 4 is described below using the fugacity coefficient of O_2 (γ_{O_2}) the activity coefficient of the O^{2-} anion ($\gamma_{O^{2-}}$), and the pressure of O_2 (P_{O_2})

$$E_{O_2/O^{2-}} = E^0_{O_2/O^{2-}} + \frac{RT}{2F} \ln \frac{(\gamma_{O_2} P_{O_2})^{1/2}}{(\gamma_{O^{2-}})(X_{O^{2-}})} \quad (5)$$

Consequently, $E^{0\prime}_{O_2/O^{2-}}$ is given by the equation

Table 2. Thermodynamic Data for Equation 14: $2Li(l) + {}^1/_2O_2(g) \rightarrow 2Li^+ + O^{2-}$[a]

	T	$\Delta G^{0\prime}$ (13)	$\Delta S^{0\prime}$ (13)	$\Delta H^{0\prime}$ (13)
LiCl:KCl	K	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	kJ·mol^{-1}
100:0	873 to 923	$(-586.9 \pm 0.1) + (137 \pm 4)\cdot 10^{-3} T$	-137 ± 4	-586.9 ± 0.1
90:10	823 to 923	$(-602.7 \pm 0.1) + (158 \pm 1)\cdot 10^{-3} T$	-158 ± 1	-602.7 ± 0.1
75:25	773 to 873	$(-591.4 \pm 0.2) + (152 \pm 4)\cdot 10^{-3} T$	-152 ± 4	-591.4 ± 0.2
58.5:41.5	673 to 823	$(-586.5 \pm 0.2) + (160 \pm 3)\cdot 10^{-3} T$	-160 ± 3	-586.5 ± 0.2

[a] Error values are the 95 % confidence intervals.

$$E^{0}_{O_2/O^{2-}} = E^{0'}_{O_2/O^{2-}} + \frac{RT}{2F} \ln \frac{P^{1/2}_{O_2}}{X_{O^{2-}}} \quad (6)$$

where $E^{0'}_{O_2/O^{2-}}$ is the standard fromal potential of O_2/O^{2-} which is given by the following equation

$$E^{0'}_{O_2/O^{2-}} = E^{0}_{O_2/O^{2-}} + \frac{RT}{2F} \ln \frac{\gamma^{1/2}_{O_2}}{\gamma_{O^{2-}}} \quad (7)$$

The solution equilibrium of Li_2O is described by eq 8, and the free energy change is given by eq 9. When a LiCl−KCl melt is saturated with Li_2O, the solution equilibrium is achieved and the free energy change of eq 8 is zero. Therefore, the standard free energy change of eq 8, ΔG^0 (8), can be shown by eq 10 using the activity of the Li^+ cation, a_{Li^+}

$$2Li^+ + O^{2-} = Li_2O\ (s) \quad (8)$$

$$\Delta G\ (8) = \Delta G^0\ (8) - RT \ln\left(a^2_{Li^+} \cdot a_{O^{2-}}\right) \quad (9)$$

$$\Delta G^0\ (8) = RT \ln\left(a^2_{Li^+} \cdot a_{O^{2-}}\right) \quad (10)$$

Here we introduce the standard formal free energy, $\Delta G^{0'}$ (8), described by the equation

$$\Delta G^{0'}\ (8) = \Delta G^0\ (8) - RT \ln\left(\gamma^2_{Li^+} \cdot \gamma_{O^{2-}}\right) \quad (11)$$

where γ_{Li^+} is the activity coefficient of the Li^+ cation.[9] Therefore, $\Delta G^{0'}$ (8) is given by the following equation using the mole fraction of the Li^+ cation

$$\Delta G^{0'}\ (8) = RT \ln\left(X^2_{Li^+} \cdot X_{O^{2-}}\right) \quad (12)$$

This concept is similar to that of the standard formal potential in eq 7. Also, the standard formal free energy of the following reaction, $\Delta G^{0'}$ (13), is available from reported thermodynamical data.[10]

$$Li\ (1) + \frac{1}{2}O_2\ (g) = Li_2O\ (s) \quad (13)$$

The free energy of the reaction shown in eq 14, $\Delta G^{0'}$ (14), is calculated using $\Delta G^{0'}$ (8) and $\Delta G^{0'}$ (13).

Table 3. Standard Formal Potential of O_2/O^{2-} in Molten LiCl−KCl Systems[a]

LiCl:KCl	T/K	$E^{0'}_{O_2/O^{2-}}$ /V vs Li^+/Li
100:0	873 to 923	$(-7.08 \pm 0.24)\cdot 10^{-4}T + (3.042 \pm 0.001)$
90:10	823 to 923	$(-8.11 \pm 0.10)\cdot 10^{-4}T + (3.124 \pm 0.001)$
75:25	773 to 873	$(-7.70 \pm 0.21)\cdot 10^{-4}T + (3.078 \pm 0.001)$
58.5:41.5	673 to 823	$(-7.90 \pm 0.16)\cdot 10^{-4}T + (3.042 \pm 0.001)$

[a] Error values are the 95 % confidence intervals.

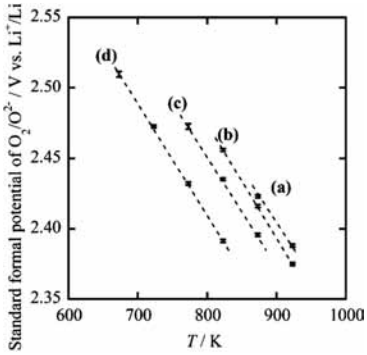

Figure 5. The standard formal potential of O_2/O^{2-} in molten LiCl−KCl systems. LiCl:KCl = (a) 100:0, (b) 90:10, (c) 75:25, and (d) 58.5:41.5.

$$2Li\ (1) + \frac{1}{2}O_2\ (g) = 2Li^+ + O^{2-} \quad (14)$$

$$\Delta G^{0'}\ (14) = \Delta G^{0'}\ (13) - \Delta G^{0'}\ (8) \quad (15)$$

$\Delta G^{0'}$ (14) is therefore obtained from experimental data of $\Delta G^{0'}$ (8). In addition, the standard formal entropy of formation, $\Delta S^{0'}$ (14), and the standard formal enthalpy of formation, $\Delta H^{0'}$ (14), are is calculated according to eqs 16 and 17

$$\Delta S^{0'}\ (14) = -\left(\frac{\partial\ \Delta G^{0'}(14)}{\partial\ T}\right)_p \quad (16)$$

$$\Delta H^{0'}\ (14) = \Delta G^{0'}(14) + T\Delta S^{0'}(14) \quad (17)$$

The obtained formal thermodynamic quantities are shown in Table 2. The error values are the 95 % confidence intervals. Table 2 shows that $\Delta H^{0'}$ (14) is almost constant in all systems. However, $\Delta S^{0'}$ (14) obtained in the pure LiCl is remarkably different from that in the melt containing KCl, which is attributed to the difference in the structure of the oxide ion in the melts.

Equation 14 is divided into the following two half-equations

$$\text{Anode}: \frac{1}{2}O_2 + 2e^- = O^{2-} \quad (18)$$

$$\text{Cathode}: Li^+ + e^- = Li \quad (19)$$

Therefore, the standard free energy of eq 14 is given by the equation

$$\Delta G^0\ (14) = -2F\left(E^0_{O_2/O^{2-}} - E^0_{Li^+/Li}\right) \quad (20)$$

where $E^0_{Li^+/Li}$ is the standard potential of Li^+/Li. However, those values cannot be experimentally measured. Here standard formal free energy, $\Delta G^{0'}$ (14), is expressed by eq 21[9]

$$\Delta G^{0'}\ (14) = \Delta G^0\ (14) - RT \ln \frac{\gamma^{1/2}_{O_2}}{\gamma_{O^{2-}} \cdot \gamma^2_{Li^+}} \quad (21)$$

Therefore, $\Delta G^{0'}$ (14) is given by the equation

$$\Delta G^{0'}\ (14) = -2F\left(E^{0'}_{O_2/O^{2-}} - E^{0'}_{Li^+/Li}\right) \quad (22)$$

where $E^{0'}_{Li^+/Li}$ is the standard formal potential of Li^+/Li, which is given by the following equation

$$E^{0'}_{Li^+/Li} = E_{Li^+/Li} - \frac{RT}{F} \ln X_{Li^+}$$

$$= -\frac{RT}{F} \ln X_{Li^+} \quad (23)$$

E_{Li^+}/Li is defined to be zero in this study.

Consequently, the standard formal potential of O_2/O^{2-}, $E^{0'}_{O_2/O^{2-}}$ (vs Li^+/Li) is obtained by using eqs 12, 15, 22, and 23. Here the solubility of Li_2O was used as the mole fraction of the oxide ion, $X_{O^{2-}}$. The result obtained in each LiCl−KCl melt is shown in Table 3 and Figure 5. The standard formal potential of O_2/O^{2-} increases with a decrease in temperature and an increase in the mole fraction of LiCl in the melt.

Conclusions

The solubilities of Li_2O in molten LiCl−KCl systems were determined in the temperature range of (673 to 923) K. The melt with a higher content of LiCl in molten LiCl−KCl systems has a higher solubility of Li_2O. The pure LiCl has the highest solubility of Li_2O, (12.0 ± 0.2) mol % at 923 K.

The standard formal potential of O_2/O^{2-} evaluated from the results in the present study increases linearly with a decrease in temperature and an increase in the mole fraction of LiCl in the melt.

Supporting Information Available:

Data for Figures 3, 4, and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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