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Dissolution behavior of lithium oxide in molten LiCl-KCl systems

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Abstract

The solubility of lithium oxide was measured in molten LiCl-KCl containing 58.5, 75, 90 and 100 mol% LiCl in the temperature range from 673 to 923 K. The melt with higher content of LiCl has higher solubility of Li₂O. The neat LiCl has highest solubility of Li₂O and it is 12.0 ± 0.2 mol% at 923 K. The estimated standard formal potential of O₂/O²⁻ increases linearly as the temperature decrease and the increase of the mole fraction of LiCl.

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 purpose³. In addition to the electrode materials, high solubility of oxides in the melts is essential for fast electrochemical reduction of metal oxides with high efficiency⁴. Molten LiCl and CaCl₂ are strong candidates of the melts that satisfy the above requirement. Because of their high solubilities of oxides^{2,5}, reduction of metal oxides has been achieved chemically and/or electrochemically in these melts^{2,6}. However, high melting temperatures of LiCl and CaCl₂ are disadvantageous for the process. Lower temperature operation has advantages such as lower corrosive and thermal damages to the

vessels and electrode materials. Thus molten salts that have high solubility of oxides at lower temperatures are indispensable for the reduction processes of metal oxides although few reports are so far available on this subject. In this study, the temperature dependence of solubilities was investigated in molten LiCl-KCl systems with an electrochemical method. The compositions of LiCl-KCl melts were selected referring the reported binary phase diagram⁷.

Experimental Section

A glassy carbon rod (Tokai Carbon) was used as an anode material for cyclic voltammetry when it was used as an anode. The cathode materials were also glassy carbon rods at temperatures higher than 823 K while aluminum plates (99.2 %, Nilako Corp.) were used at lower than 823 K. The reference electrode was 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 Co. Ltd.) 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 as a current collector was immersed in melted 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 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, 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 the experiments were conducted in a globe 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 less than 1 ppm.

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

Results and discussion

Temperature dependence of the solubility of lithium oxide in molten LiCl-KCl

Figure 1 shows the cyclic voltammogram in the positive potential region obtained in an eutectic LiCl-KCl (58.5 : 41.5) melt containing various amounts of Li₂O 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 dioxide⁸.



The peak currents corresponding to CO₂ evolution plotted against the amount of Li₂O added in the melt are shown in Figure 2. The current increased almost linearly as the increase of the amount of Li₂O added and finally showed a constant value when the melt was saturated with Li₂O. As a result, the solubility of Li₂O in eutectic LiCl-KCl at 773 K is

determined to be 1.12 mol%. Intersecting point of the two lines shown in the figure was chosen as 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 neat LiCl , LiCl-KCl mixtures; $\text{LiCl} : \text{KCl} = 90 : 10$ 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 by the equation (2) using the mole fraction of lithium ion, X_{Li^+} , and that of oxide ion, $X_{\text{O}^{2-}}$. The solubility of Li_2O increases with the elevation of the temperature of the melt and the increase of the mole fraction of LiCl in the melt.

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

Thermodynamical study on the standard formal potential of O_2/O^{2-}

The standard formal potential of O_2/O^{2-} , $E_{O_2/O^{2-}}^0$, was calculated and estimated from the results obtained from the measurement of the solubility. Oxygen electrode reaction and the Nernstian equation in molten salts are described as follows;



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

where R ; the gas constant, F ; the Faraday constant, f_{O_2} ; the fugacity of O_2 , $a_{O^{2-}}$; the activity of O^{2-} , $E_{O_2/O^{2-}}^0$; the standard potential of O_2/O^{2-} . Equation (4) is described as below using the fugacity coefficient of O_2 , γ_{O_2} , the activity coefficient of O^{2-} anion, $\gamma_{O^{2-}}$, and the pressure of O_2 , P_{O_2} .

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

Consequently $E_{O_2/O^{2-}}^0$ is given by the equation:

$$E_{O_2/O^{2-}}^0 = E_{O_2/O^{2-}}^0 + \frac{RT}{2F} \ln \frac{P_{O_2}^{1/2}}{X_{O^{2-}}}, \quad (6)$$

where $E_{\text{O}_2/\text{O}^{2-}}^{0'}$ is the standard formal potential of O_2/O^{2-} , which is given by the following equation.

$$E_{\text{O}_2/\text{O}^{2-}}^{0'} = E_{\text{O}_2/\text{O}^{2-}}^0 + \frac{RT}{2F} \ln \frac{\gamma_{\text{O}_2}^{1/2}}{\gamma_{\text{O}^{2-}}} \quad (7)$$

Now, when a LiCl-KCl melt is saturated with Li_2O , a solution equilibrium shown in the equation (8) is achieved and the standard free energy change of the reaction (8), $\Delta G^0(8)$, can be calculated using the activity of the Li^+ cation, a_{Li^+} .



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

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

$$\Delta G^{0'}(8) = \Delta G^0(8) - RT \ln (\gamma_{\text{Li}^+}^2 \cdot \gamma_{\text{O}^{2-}}), \quad (10)$$

where γ_{Li^+} is the activity coefficient of Li^+ cation⁹. Thus $\Delta G^{0'}(8)$ is given by the following equation using the mole fraction of Li^+ cation.

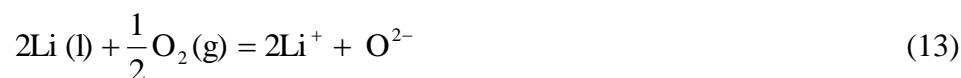
$$\Delta G^{0'}(8) = RT \ln (X_{\text{Li}^+}^2 \cdot X_{\text{O}^{2-}}) \quad (11)$$

This is the similar concept with the standard formal potential in the equation (7). Also the

standard formal free energy of the following reaction, $\Delta G^{0'}$ (12), is available the reported thermodynamical data¹⁰.



Then the free energy of the reaction shown in the equation (13), $\Delta G^{0'}$ (13), is calculated using $\Delta G^{0'}$ (8) and $\Delta G^{0'}$ (12).



$$\Delta G^{0'} (13) = \Delta G^{0'} (12) - \Delta G^{0'} (8) \quad (14)$$

$\Delta G^{0'}$ (13) is therefore obtained from experimental data of $\Delta G^{0'}$ (8). In addition, the standard formal entropy of formation, $\Delta S^{0'}$ (13), and the standard formal enthalpy of formation, $\Delta H^{0'}$ (13) is calculated according to the equations (15) and (16).

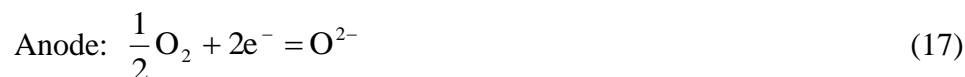
$$\Delta S^{0'} (12) = - \left(\frac{\partial \Delta G^{0'} (12)}{\partial T} \right)_p \quad (15)$$

$$\Delta H^{0'} (12) = \Delta G^{0'} (12) + T\Delta S^{0'} (12) \quad (16)$$

The obtained formal thermodynamic quantities are shown in Table 2. The error values are

the 95 % confidence intervals. Table 2 shows that $\Delta H^{0'}$ (13) is almost constant in all the systems. However, $\Delta S^{0'}$ (13) obtained in the neat LiCl is remarkably different from that in the melt containing KCl, which is attributed to the difference of the structure of oxide ion in the melts.

The equation (13) is divided into the following two half equations.



Therefore the standard free energy of the equation (13) is given by the equation:

$$\Delta G^0 (13) = -2F(E_{\text{O}_2/\text{O}^{2-}}^0 - E_{\text{Li}^+/\text{Li}}^0), \quad (19)$$

where $E_{\text{Li}^+/\text{Li}}^0$ is the standard potential of Li⁺/Li. However, those values cannot be measured experimentally. Here standard formal free energy, $\Delta G^{0'}$ (13), is expressed by the equation (20)⁹.

$$\Delta G^{0'} (13) = \Delta G^0 (13) - RT \ln \frac{\gamma_{\text{O}_2}^{1/2}}{\gamma_{\text{O}^{2-}} \cdot \gamma_{\text{Li}^+}^2} \quad (20)$$

Thus $\Delta G^{0'}$ (13) is given by the equation:

$$\Delta G^{0'}(12) = -2F(E_{\text{O}_2/\text{O}^{2-}}^{0'} - E_{\text{Li}^+/\text{Li}}^{0'}), \quad (21)$$

where $E_{\text{Li}^+/\text{Li}}^{0'}$ is the standard formal potential of Li^+/Li , which is given by the following equation.

$$\begin{aligned} E_{\text{Li}^+/\text{Li}}^{0'} &= E_{\text{Li}^+/\text{Li}} - \frac{RT}{F} \ln X_{\text{Li}^+} \\ &= -\frac{RT}{F} \ln X_{\text{Li}^+} \end{aligned} \quad (22)$$

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

Consequently, the standard formal potential of O_2/O^{2-} , $E_{\text{O}_2/\text{O}^{2-}}^{0'}$ (vs. Li^+/Li), is obtained using the equations (11), (14), (21) and (22). Here the solubility of Li_2O was used as the mole fraction of oxide ion, $X_{\text{O}^{2-}}$. 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 the decrease of temperature and the increase of the mole fraction of LiCl in the melt.

Conclusion

The solubilities of Li_2O in molten LiCl-KCl systems were determined in the

temperature range of 673 to 923 K. The melt with higher content of LiCl in molten LiCl-KCl systems has higher solubility of Li_2O . The neat LiCl has highest solubility of Li_2O and it is 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 linearly increases with the decrease of the temperature and the increase of the mole fraction of LiCl in the melt.

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Table 1 Temperature dependence of the solubility products of Li_2O in molten LiCl-KCl

systems.

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

* The error values are the 95 % confidence intervals.

Table 2 Thermodynamic data for the reaction (13) : $2\text{Li}(\text{l}) + 1/2\text{O}_2(\text{g}) \rightarrow 2\text{Li}^+ + \text{O}^{2-}$.

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

* The error values are the 95 % confidence intervals.

Table 3 Standard formal potential of O_2/O^{2-} in molten LiCl-KCl systems.

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

* The error values are the 95 % confidence intervals.

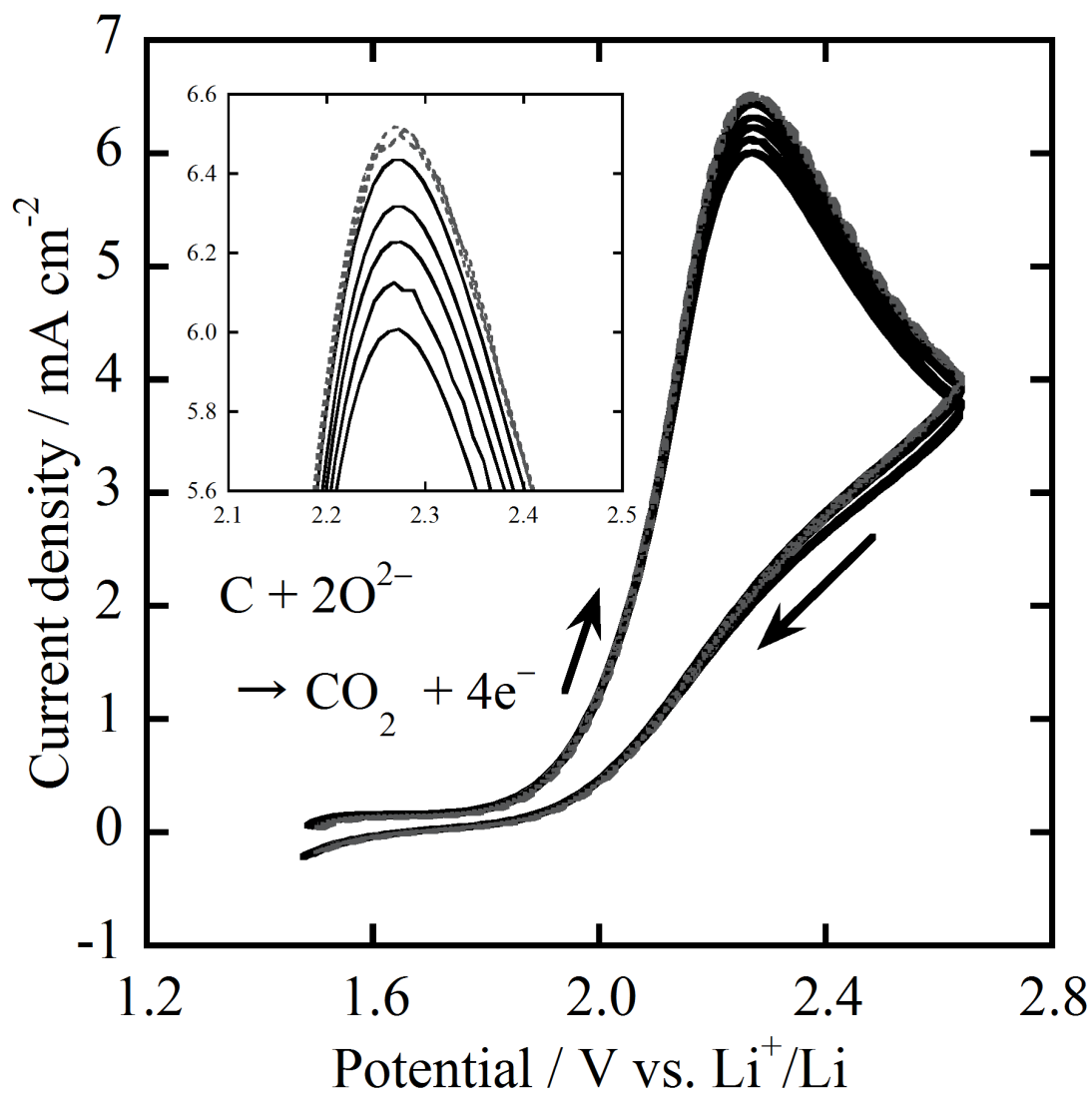


Figure 1 Cyclic voltammograms of a glassy carbon rod in eutectic LiCl-KCl (58.5: 41.5) with the addition of Li₂O (Solid line; 0.975, 1.000, 1.025, 1.050, 1.100 mol%, Dotted line; 1.150, 1.200, 1.225 mol%) at 773 K. Scan rate is 0.2 V s⁻¹. The inset is the close-up drawing around the current density peaks.

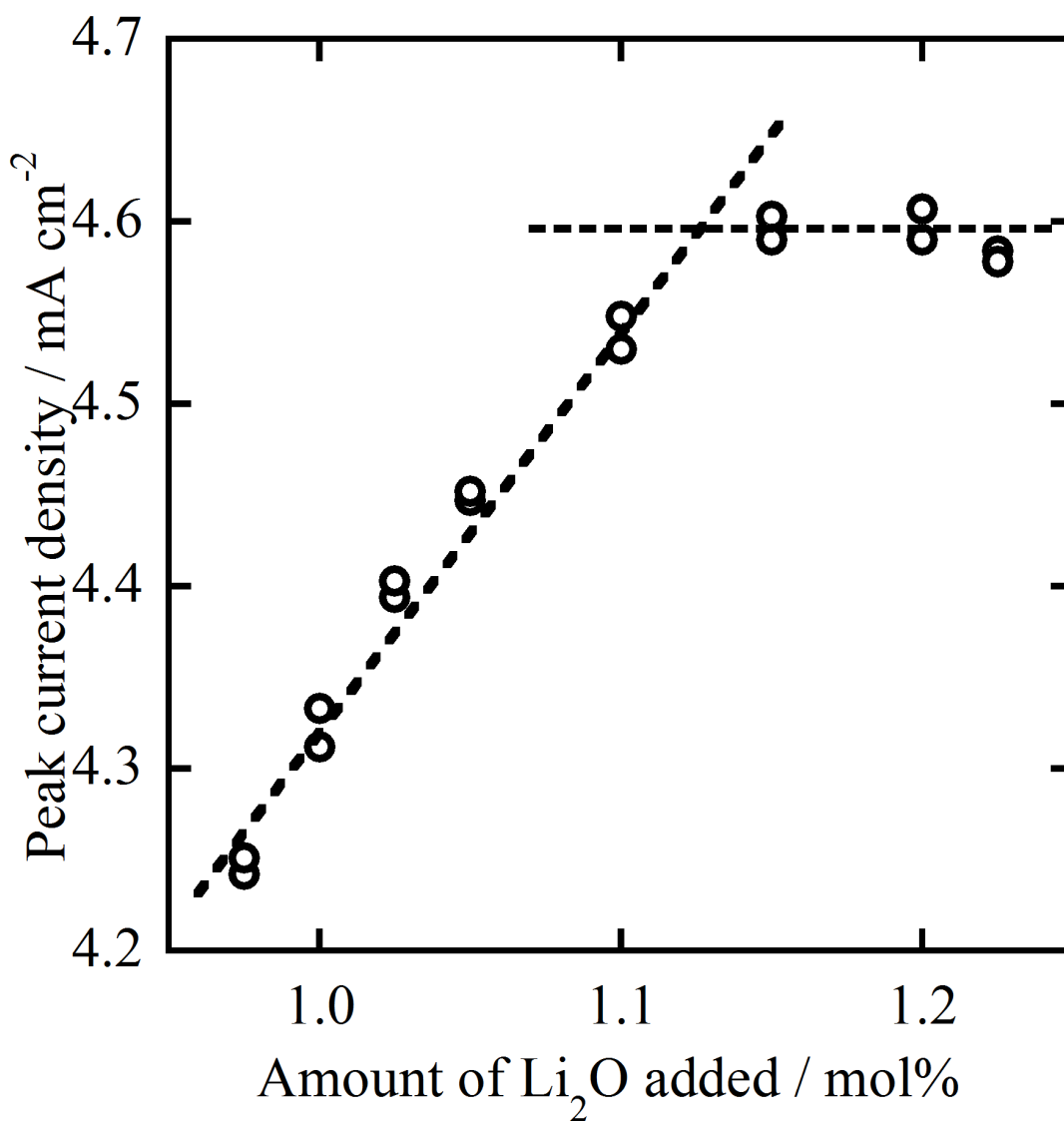


Figure 2 The peak currents against the amount of Li₂O added in the melt determined from cyclic voltammograms of a glassy carbon electrode in eutectic LiCl-KCl (58.5: 41.5) at 773

K.

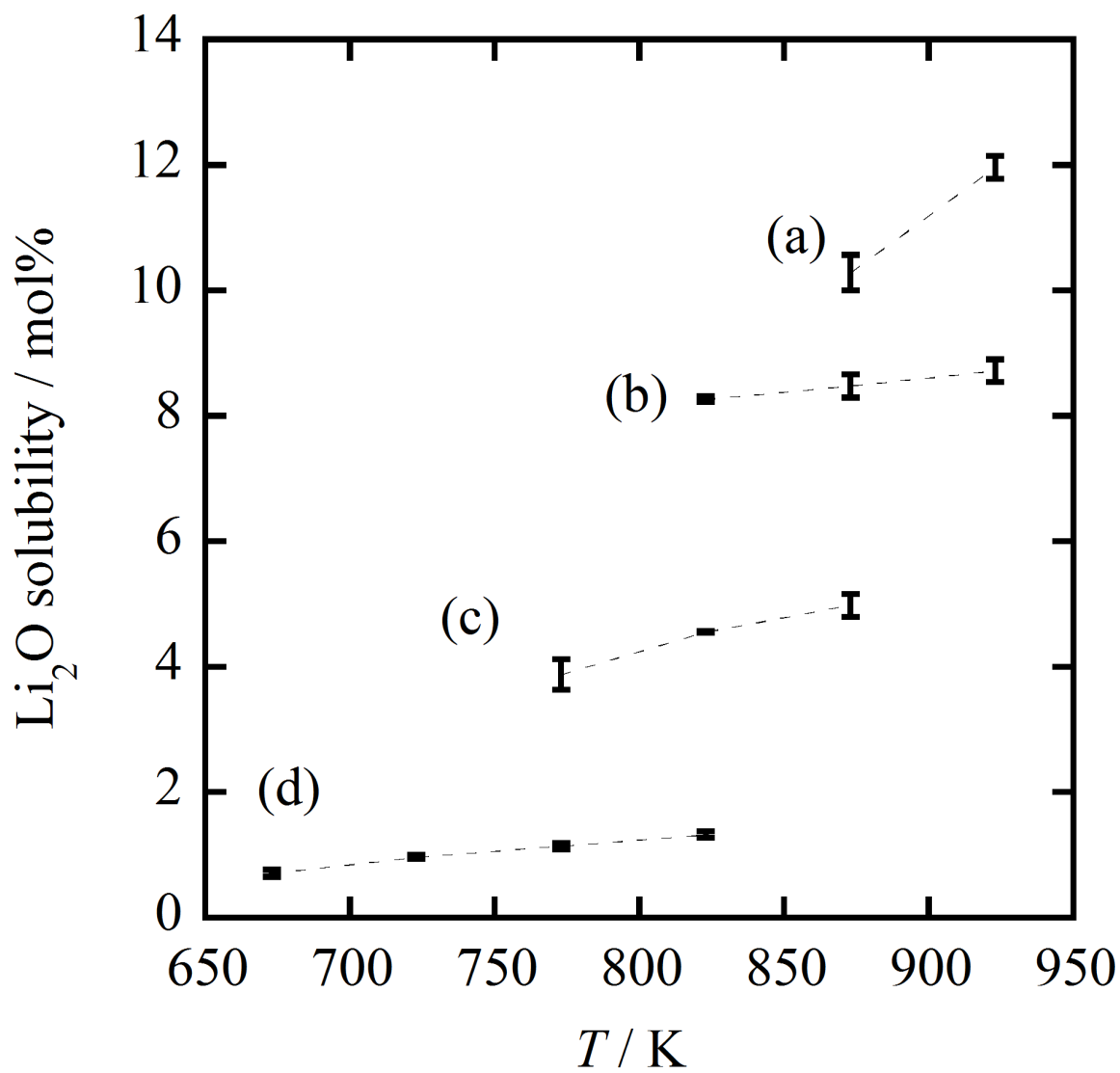


Figure 3 Solubilities of Li_2O in molten LiCl - KCl systems [$\text{LiCl} : \text{KCl} =$ (a) 100 : 0, (b) 90 :

10, (c) 75 : 25, (d) 58.5 : 41.5].

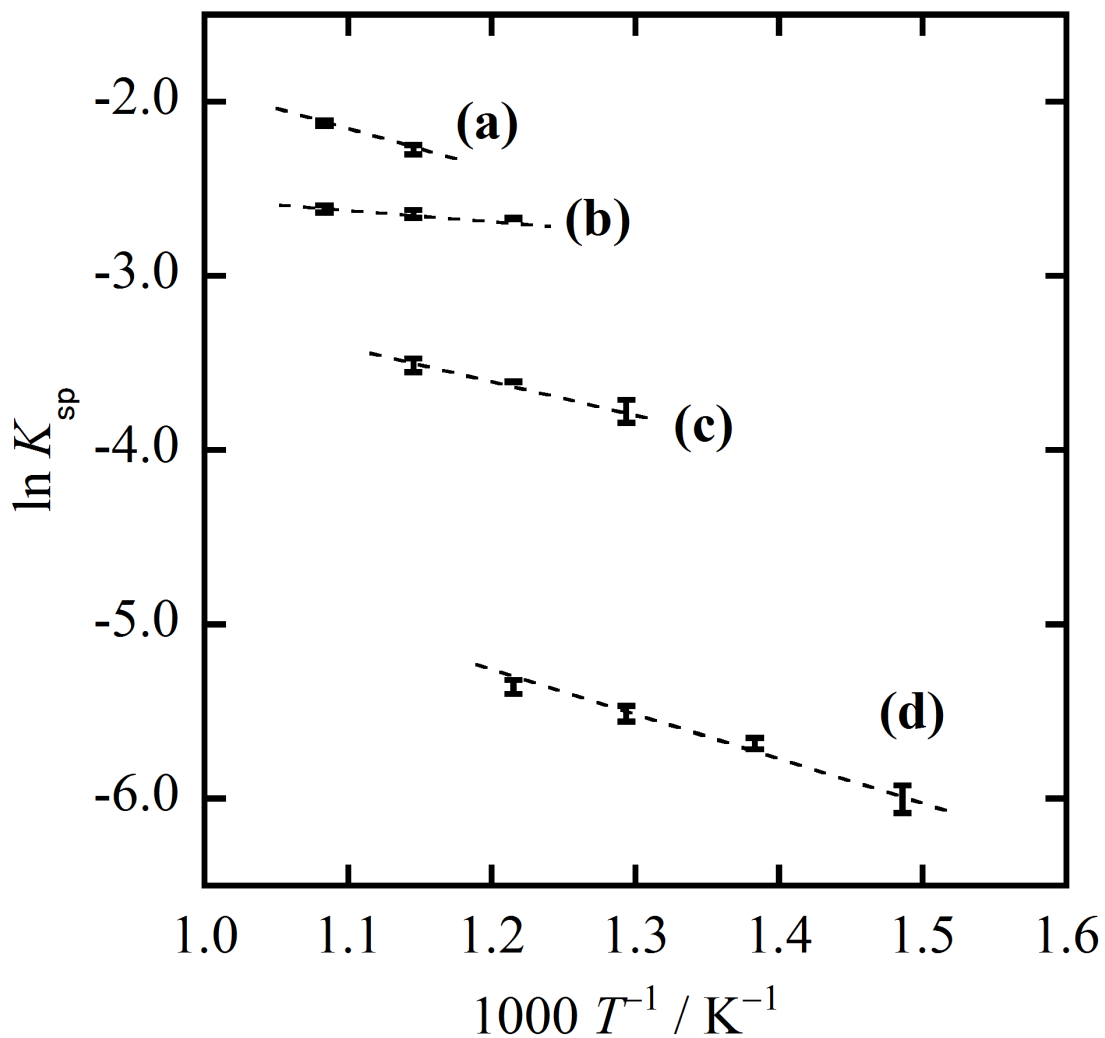


Figure 4 The relationship between temperature and the solubility products of Li_2O in molten LiCl-KCl systems [$\text{LiCl} : \text{KCl} =$ (a) 100 : 0, (b) 90 : 10, (c) 75 : 25, (d) 58.5 : 41.5].

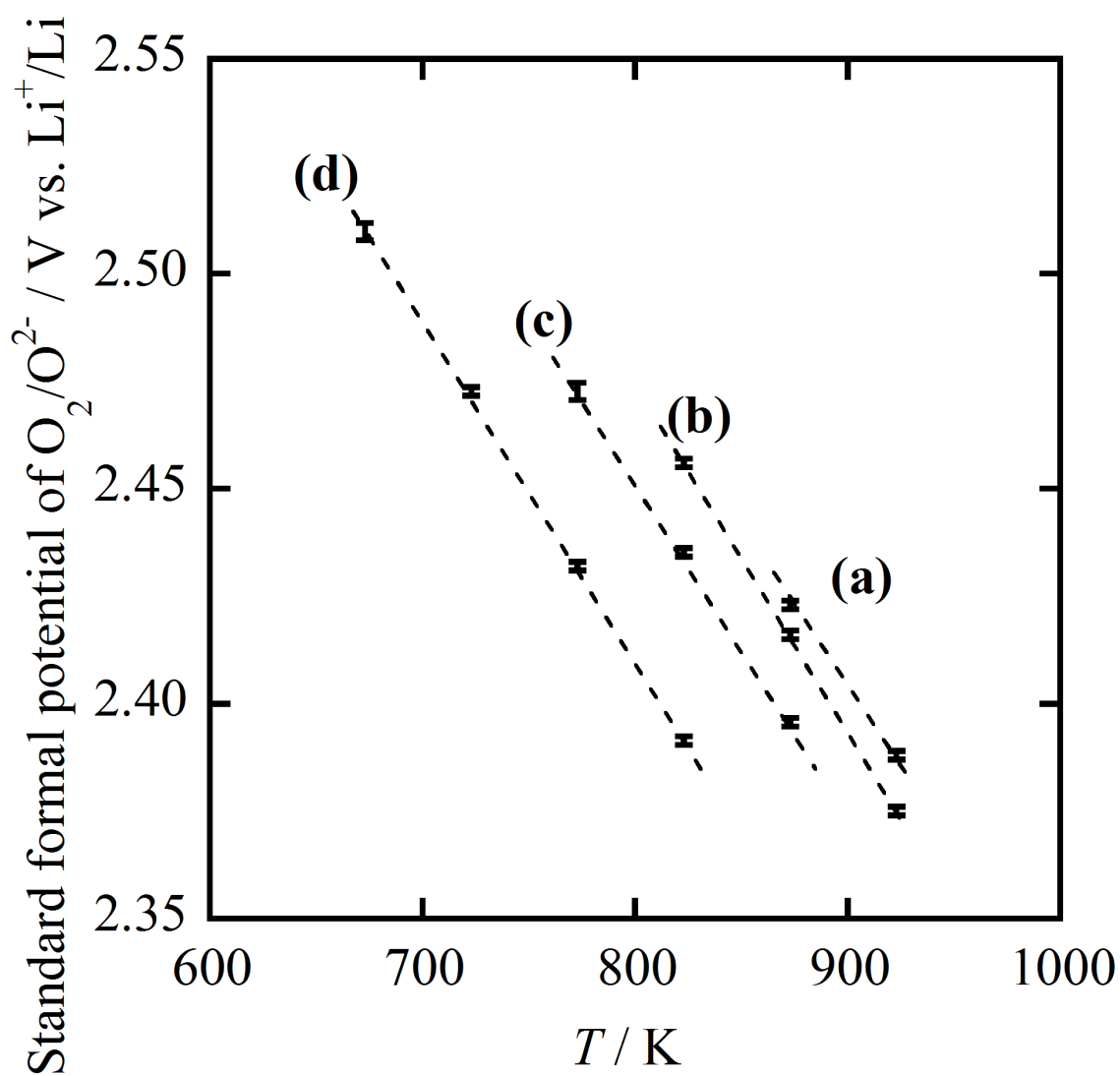


Figure 5 The standard formal potential of O_2/O_2^{2-} in molten LiCl-KCl systems [LiCl : KCl =

(a) 100 : 0, (b) 90 : 10, (c) 75 : 25, (d) 58.5 : 41.5].