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AUTHOR(S):

Kado, Yuya; Goto, Takuya; Hagiwara, Rika

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Thermodynamics of the O_2/O^{2-} redox couple in molten LiCl-KCl-Li_2O systems

Yuya Kado, Takuya Goto*, Rika Hagiwara

Department of Fundamental Energy Science, Graduate School of Energy Science,

Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

*Phone: +81-774-65-6676 Fax : no Fax

Email: tgoto@mail.doshisha.ac.jp

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Abstract

Activity coefficients of oxide ion were determined by the measurements of the standard formal potential of O_2/O^{2-} in molten LiCl-KCl mixtures; LiCl:KCl = 58.5:41.5 (eutectic), 65:35, 70:30, 75:25 mol% at 673 to 803 K. The activity coefficient decreases with the increase of the LiCl content in the melt; 18.7 ± 1.5, 7.7 ± 1.0, 4.1 ± 0.4 and 1.6 ± 0.1, respectively, at 773 K in each melt. The result is explained by the attractive force between Li^+ and O^{2-} which is stronger than that between K^+ and O^{2-}.

Keywords: boron-doped diamond electrode; oxygen evolution; activity coefficient

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1. Introduction

Oxide ion in the electrolytes is known as a strong Lewis base. It affects the passivation phenomena of metals [1] and plays an important role in acid-base reactions [2,3]. In order to understand chemical and electrochemical behavior of oxide ion, it is indispensible to measure the thermodynamic quantities of oxide ion such as chemical potentials in molten chlorides. Some researchers previously reported on the oxygen electrode reaction in molten chlorides [3-7], however, these results did not coincide with each other, which was attributed to the fact that an ideally polarizable electrode (IPE) under oxygen atmosphere at high temperatures was not available.

On the other hand, in our previous study, a boron-doped diamond (BDD) electrode was found to act as an oxygen gas evolution electrode in molten chloride systems below 773 K [8-10].

$$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^- \qquad (1)$$

In addition, thermodynamic investigations on the oxygen electrode reaction revealed that the BDD electrode acts as an IPE under oxygen atmosphere in a LiCl-KCl eutectic melt containing oxide ion [11]. The standard formal potential of O_2/O^{2-}, $E^{0'}_{O_2/O^{2-}}$, defined by eq. 2 is $2.995(\pm0.001)-7.38(\pm0.14)\times10^{-4}\ T$ vs. Li^+/Li in the temperature range of 673 to 803 K.

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

Here, $E^{0}_{O_2/O^{2-}}$ is the standard potential of O_2/O^{2-}, R; the gas constant, T; absolute temperature, F; the Faraday constant, γ_{O_2}; the fugacity coefficient of O_2 and $\gamma_{O^{2-}}$; the activity coefficient of the O^{2-}. In the present study, further investigations on the oxygen electrode reaction were carried out in various compositions of LiCl-KCl mixtures. The relationship between the standard formal potential of O_2/O^{2-} and the melt compositions was evaluated and activity coefficients of oxide ion were determined from the obtained data.

2. Experimental

Reagent-grade LiCl (Aldrich-APL 99.99 %) and KCl (Aldrich-APL 99.99 %) were mixed to prepare each composition (LiCl:KCl = 58.5:41.5, 65:35, 70:30, 75:25 mol%) and used for the melts in a high purity alumina crucibles (SSA-S, NIKKATO) after vacuum drying at 573 K for 24 hours. Li_2O (Aldrich. 97 %) was used as an oxide ion source which was directly added into the melts after vacuum drying at 453 K for 24 hours. All the experiments were performed in a glove box with a gas-refining instrument (MIWA, MS3-H60SN) under dried and deoxygenated atmosphere. The concentration of water and oxygen gas in the atmosphere were always monitored and

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kept less than 1 ppm. A BDD electrode (Sumitomo Electric Industries, Ltd., thickness: 20 μm, substrate: silicon, doped boron: 500-3000 ppm) was used as a working electrode. The Ag^{+}/Ag reference electrode was prepared by immersing a silver wire (Japan Metal Service, 99.99 %) was in the melt containing 0.5 mol% AgCl (Wako Pure Chemical Co. Ltd., 99.5 %) in a Pyrex glass tube with a thin bottom. The potential of the reference electrode was standardized against the potential of Li^{+}/Li. Electrochemical measurements were performed with the aid of an electrochemical measurement system (Hokuto Denko Corp., HZ-5000).

3. Results and discussion

3.1. Standard formal potential of O_2/O^{2-}

The standard formal potential of O_2/O^{2-} was measured by our method using the BDD electrode in LiCl-KCl mixtures; LiCl:KCl = 65:35, 70:30 and 75:25 mol% containing 0.5 mol% Li_2O as shown in Fig. 1. The result in the eutectic melt is also included as a reference [11]. In each melt, the standard formal potential of O_2/O^{2-} decreases almost linearly with the elevation of temperature. The temperature dependences of the standard formal potentials are summarized in Table 1**.** In addition, it

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is found that the potential is more positive in the melt which has a larger content of LiCl. Here, these potentials are referenced to the standard potential of the Li^+/Li redox couple regarding the activity of Li^+ as follows. The potential of Li^+/Li is expressed as;

$$E_{Li^+/Li} = E^0_{Li^+/Li} + \frac{RT}{F} \ln a_{Li^+} \quad (3)$$

where $E^0_{Li^+/Li}$ is the standard potential of Li^+/Li and a_{Li^+} is the activity of Li^+. Since $E_{Li^+/Li}$ was defined to be zero in each melt, $E^0_{Li^+/Li}$ is expressed as follows.

$$E^0_{Li^+/Li} = -\frac{RT}{F} \ln(\gamma_{Li^+} X_{Li^+}) \quad (4)$$

Here, γ_{Li^+} is the activity coefficient and X_{Li^+} is the cation fraction of Li^+ in the melt. The standard potential of Li^+/Li is calculated using the following relation between the activity coefficient of Li^+ and the cation fraction in molten LiCl-KCl [12].

$$RT \ln \gamma_{Li^+} = -13390(1 - X_{Li^+})^2 \quad (5)$$

Thus, the standard formal potential of O_2/O^{2-}, $E^{0'}_{O_2/O^{2-}}$, against the potential of Li^+/Li in each melt obtained in the present study is calculated to be the normalized value against the standard potential of Li^+/Li, $E^0_{Li^+/Li}$, from eq. 6 .

$$E^{0'}_{O_2/O^{2-}}(\text{vs. } E^0_{Li^+/Li}) = E^{0'}_{O_2/O^{2-}} - E^0_{Li^+/Li} \quad (6)$$

3.2. Change of free energy, entropy, enthalpy

The standard free energy change for the reaction (7) is given by eq. 8 [11].

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$$2\mathrm{Li}\ (\mathrm{l}) + \frac{1}{2}\mathrm{O}_2(\mathrm{g}) = 2\mathrm{Li}^+ + \mathrm{O}^{2-} \qquad (7)$$

$$\Delta G^{0'}(7) = -2F(E^{0'}_{\mathrm{O_2/O^{2-}}} - E^{0}_{\mathrm{Li^+/Li}}) \qquad (8)$$

The free energy change almost linearly increases with the elevation of temperature as shown in Fig. 2. In addition, it decreases with the increase of the LiCl content in the melt**;** – 456.4 ± 0.5, – 462.1 ± 0.8, – 466.1 ± 0.6 and – 472.1 ± 0.5, respectively, at 773 K in each melt, indicating the reaction (7) is more favorable to proceed to the right direction in the melt with a larger content of LiCl.

The standard formal entropy change, $\Delta S^{0'}(7)$, and the standard formal enthalpy change, $\Delta H^{0'}(7)$, are also calculated according to eqs. 9 and 10.

$$\Delta S^{0'}(7) = -\left(\frac{\partial \Delta G^{0'}(7)}{\partial T}\right)_p \qquad (9)$$

$$\Delta H^{0'}(7) = \Delta G^{0'}(7) + T\Delta S^{0'}(7) \qquad (10)$$

The obtained standard formal entropy and enthalpy are summarized in Table 2. $\Delta S^{0'}(7)$ and $\Delta H^{0'}(7)$ are practically constant in these temperature ranges. These values are plotted against the cation fraction of Li^+ in Figs. 3 and 4. $\Delta S^{0'}(7)$ increases and $\Delta H^{0'}(7)$ decreases with the increase of the cation fraction of Li^+. $\Delta S^{0'}(7)$ and $\Delta H^{0'}(7)$ in a LiCl single salt ($X_{\mathrm{Li^+}} = 1$) are estimated to be –115 ± 6 J K^{-1} mol^{-1} and –584.8 ± 0.1 kJ mol^{-1}, respectively by the extrapolation of the obtained data. The standard formal free energy change and the standard formal potential of O_2/O^{2-} are given by eqs. 11 and

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12.

$$\Delta G^{0'}(7) = 116(\pm 6) \times 10^{-3} T - 584.8(\pm 0.1) / \text{kJ mol}^{-1} \quad (11)$$

$$E^{0'}_{O_2/O^{2-}} = 3.031(\pm 0.001) - 5.96(\pm 0.31) \times 10^{-4} T / \text{V vs. } Li^+/Li \quad (12)$$

At 923 K, which is the typical temperature for the reduction of uranium oxides in a LiCl single salt, they are respectively –477.7 ± 5.4 kJ mol^{-1} and –2.474 ± 0.028 V vs. Li^+/Li. From this result, the EMF for the electrochemical reduction of uranium oxides expressed by the reaction (13) is calculated to be 0.13 ± 0.03 V vs. Li^+/Li in a LiCl melt containing 0.52 mol% Li_2O.

$$UO_2\,(s) + 4e^- = U\,(s) + 2O^{2-} \quad (13)$$

This value is estimated from the standard formal potential of O_2/O^{2-} obtained in the present study and the standard potential of U^{4+}/U calculated from the standard Gibbs free energy of formation of solid UO_2 for the reaction (15) [13], corresponding to the potential of the redox couple of O_2/O^{2-} estimated from the polarization curve in the previous report by Sakamura et al. [14].

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

$$U\,(s) + O_2\,(g) = UO_2\,(s) \quad (15)$$

3.3. Activity coefficients of oxide ion

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The obtained formal thermodynamic quantities are compared with the literature data for formation of liquid Li_2O from liquid Li and gaseous O_2 [13,15].

$$2\mathrm{Li}\ (\mathrm{l}) + \frac{1}{2}\mathrm{O_2}(\mathrm{g}) = \mathrm{Li_2O}\ (\mathrm{l}) \tag{16}$$

$$2\mathrm{Li}\ (\mathrm{l}) + \frac{1}{2}\mathrm{O_2}(\mathrm{g}) = 2\mathrm{Li}^+ + \mathrm{O}^{2-} \tag{7}$$

When the standard state is defined to be pure Li_2O liquid, the standard free energy of formation of Li_2O (l), $\Delta G_f^0(\text{liquid } \mathrm{Li_2O})$, corresponds to the standard free energy change of the reaction (7), ΔG^0 (7). Therefore, the difference between $\Delta G_f^0(\text{liquid } \mathrm{Li_2O})$ and $\Delta G^{0'}(7)$ is expressed by the activity coefficient of O_2, γ_{O_2}, and O^{2-}, $\gamma_{O^{2-}}$, using the relation given by eq. 18.

$$\Delta G(7) = \Delta G^0(7) + RT \ln \frac{\gamma_{O_2}^{1/2}}{\gamma_{O^{2-}}} + RT \ln \frac{P_{O_2}^{1/2}}{X_{O^{2-}}} \tag{17}$$

$$\Delta G^0(7) = \Delta G^{0'}(7) + RT \ln \frac{\gamma_{O_2}^{1/2}}{\gamma_{O^{2-}}} \tag{18}$$

Here, activity coefficient of oxygen gas can be regarded as unity because only oxygen gas is used as a gas phase and it does not depend on oxygen pressures [11]. Therefore $\gamma_{O^{2-}}$ in the dilute O^{2-} region is estimated as shown in Fig. 5. The activity coefficient decreases with the increase of the LiCl content in the melt and depends more strongly on the melt composition than on the temperature. It is considered that the attractive force between Li^+ and O^{2-} ion is stronger than that between K^+ and O^{2-} affecting the

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acitivity of oxide ions in the melt. In a LiCl melt which is a typical system for the reduction of uranium oxides, the activity coefficient of O^{2-} is estimated to be 0.07 ± 0.05. The result is explained by the repulsive force between O^{2-} and Cl^{-} which is weaker than that between the two O^{2-}.

4. Conclusion

Standard formal potentials of O_2/O^{2-} were measured using the BDD electrode as an IPE and activity coefficients of oxide ion were determined in molten LiCl-KCl mixtures; LiCl:KCl = 58.5:41.5 (eutectic), 65:35, 70:30 and 75:25 mol% containing 0.5 mol% Li_2O at 673 to 803 K. The standard formal potential of O_2/O^{2-} is more positive in the melt which has a larger content of LiCl and the activity coefficient of oxide ion decreases with the increase of the LiCl content in the melt. From these results, in a LiCl melt at 923 K which is a typical system for the reduction of uranium oxides, the standard formal potential and the activity coefficient are estimated by extrapolation to be $E^{0'}_{O_2/O^{2-}}$ = – 2.474 ± 0.028 V vs. Li^+/Li and 0.07 ± 0.05, respectively. Thus, this study has given available data for thermodynamic consideration on chemical and electrochemical processes involving oxygen gas and/or oxide ion such as reduction

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processes of metal oxides in molten LiCl-KCl systems.

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Table 1 The standard formal potential of O_2/O^{2-} against the standard potential of Li^+/Li in molten LiCl-KCl mixtures; LiCl:KCl = 58.5:41.5 (eutectic), 65:35, 70:30 and 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95% confidence intervals.)

Table 2 Thermodynamic data (a) obtained in this study and (b) calculated data from the solubility of Li_2O for the reaction (7): $2Li + 1/2O_2 = 2Li^+ + O^{2-}$ (The error values denote the 95 % confidence intervals.)

Fig. 1 Temperature dependence of the standard formal potential of O_2/O^{2-} vs. the standard formal potential of Li^+/Li in molten LiCl-KCl mixtures; LiCl:KCl = (a) 58.5:41.5 (eutectic), (b) 65:35, (c) 70:30 (d) 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95% confidence intervals.)

Fig. 2 Temperature dependence of the standard free energy change for the reaction (7): $2Li + 1/2O_2 = 2Li^+ + O^{2-}$ in molten LiCl-KCl mixtures; LiCl:KCl = (a) 58.5:41.5 (eutectic), (b) 65:35, (c) 70:30 (d) 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95 % confidence intervals.)

Fig. 3 Relationship between the cation fraction of Li^+ and the standard formal entropy

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change for the reaction (7): $2Li + 1/2O_2 = 2Li^+ + O^{2-}$ in molten LiCl-KCl mixtures; LiCl:KCl = 58.5:41.5 (eutectic), 65:35, 70:30 and 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95 % confidence intervals.)

Fig. 4 Relationship between the cation fraction of Li^+ and the standard formal enthalpy change for the reaction (6): $2Li + 1/2O_2 = 2Li^+ + O^{2-}$ in molten LiCl-KCl mixtures; LiCl:KCl = 58.5:41.5 (eutectic), 65:35, 70:30 and 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95 % confidence intervals.

Fig. 5 Activity coefficients of O^{2-} ion in molten LiCl-KCl mixtures; LiCl:KCl = 58.5:41.5 (eutectic), 65:35, 70:30 and 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95 % confidence intervals.)

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$$E^{0'}_{O_2/O^2} = a - bT \text{ vs. } E^{0}_{Li^+/Li}$$

LiCl:KCl / mol%	Temperature / K	*a*	*b*
58.5:41.5(Ref. 11)	673 – 803	2.972 ± 0.001	7.84 ± 0.13
65:35	723 – 803	2.976 ± 0.001	7.52 ± 0.27
70:30	723 – 803	2.987 ± 0.001	7.38 ± 0.29
75:25	773 – 803	2.995 ± 0.001	7.10 ± 0.47

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LiCl:KCl	T / K	$\Delta S^{0'}(7)$ / J K^{-1} mol^{-1}	$\Delta H^{0'}(7)$ / kJ mol^{-1}
58.5:41.5	673 - 803	–151 ± 3	–573.5 ± 0.1
65:35	723 - 803	–145 ± 5	–574.2 ± 0.1
70:30	723 - 803	–142 ± 6	–576.4 ± 0.2
75:25	773 - 803	–137 ± 8	–578.0 ± 0.1

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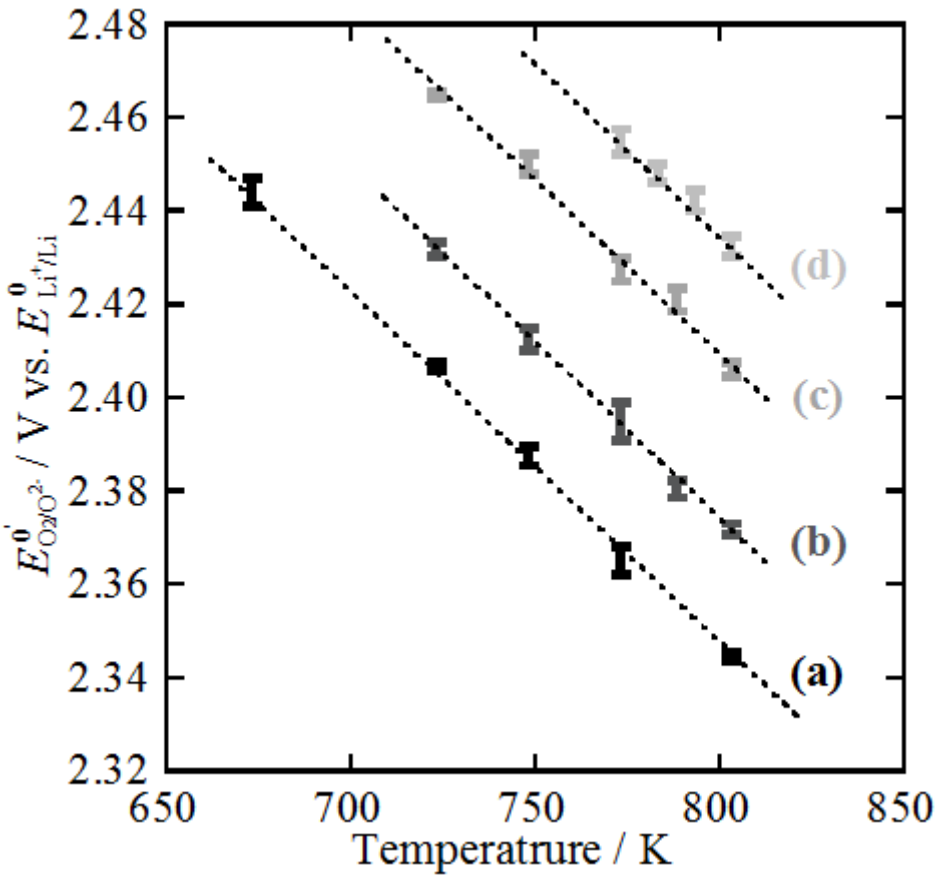

Fig. 1 Temperature dependence of the standard formal potential of O_2/O^{2-} vs. the standard formal potential of Li^+/Li in molten LiCl-KCl mixtures; LiCl:KCl = (a) 58.5:41.5 (eutectic), (b) 65:35, (c) 70:30 (d) 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95% confidence intervals.)

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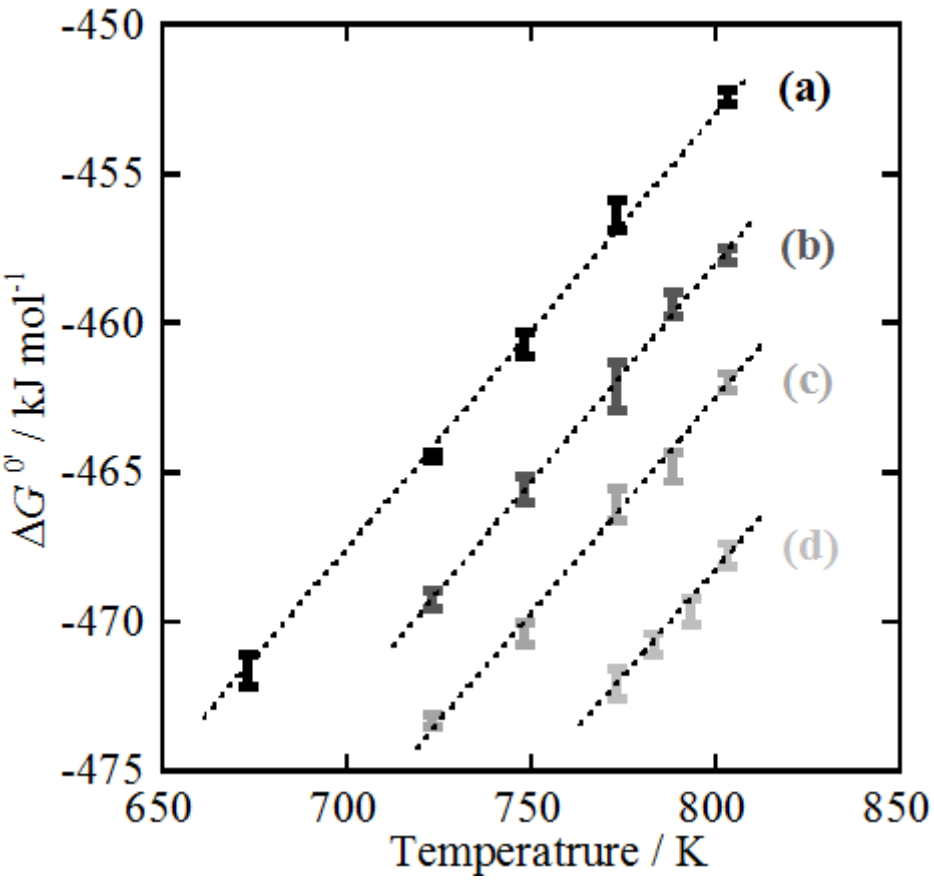

Fig. 2 Temperature dependence of the standard free energy change for the reaction (7): $2Li + 1/2O_2 = 2Li^+ + O^{2-}$ in molten LiCl-KCl mixtures; LiCl:KCl = (a) 58.5:41.5 (eutectic), (b) 65:35, (c) 70:30 (d) 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95 % confidence intervals.)

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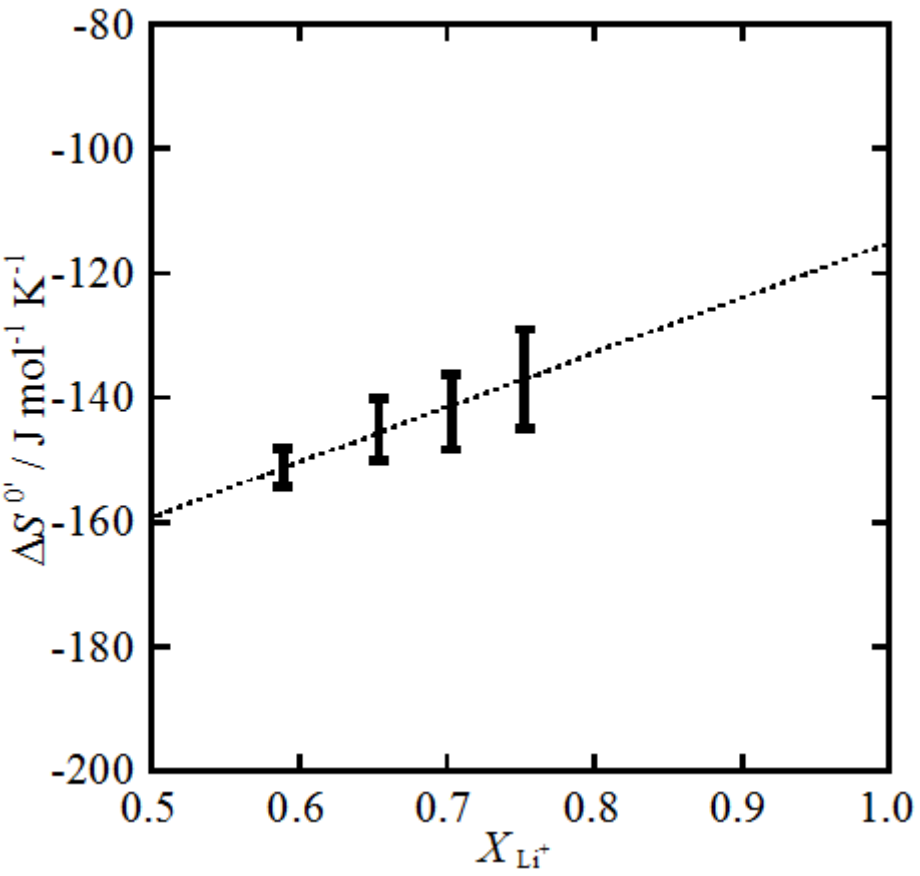

Fig. 3 Relationship between the cation fraction of Li^+ and the standard formal entropy change for the reaction (7): $2Li + 1/2O_2 = 2Li^+ + O^{2-}$ in molten LiCl-KCl mixtures; LiCl:KCl = 58.5:41.5 (eutectic), 65:35, 70:30 and 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95 % confidence intervals.)

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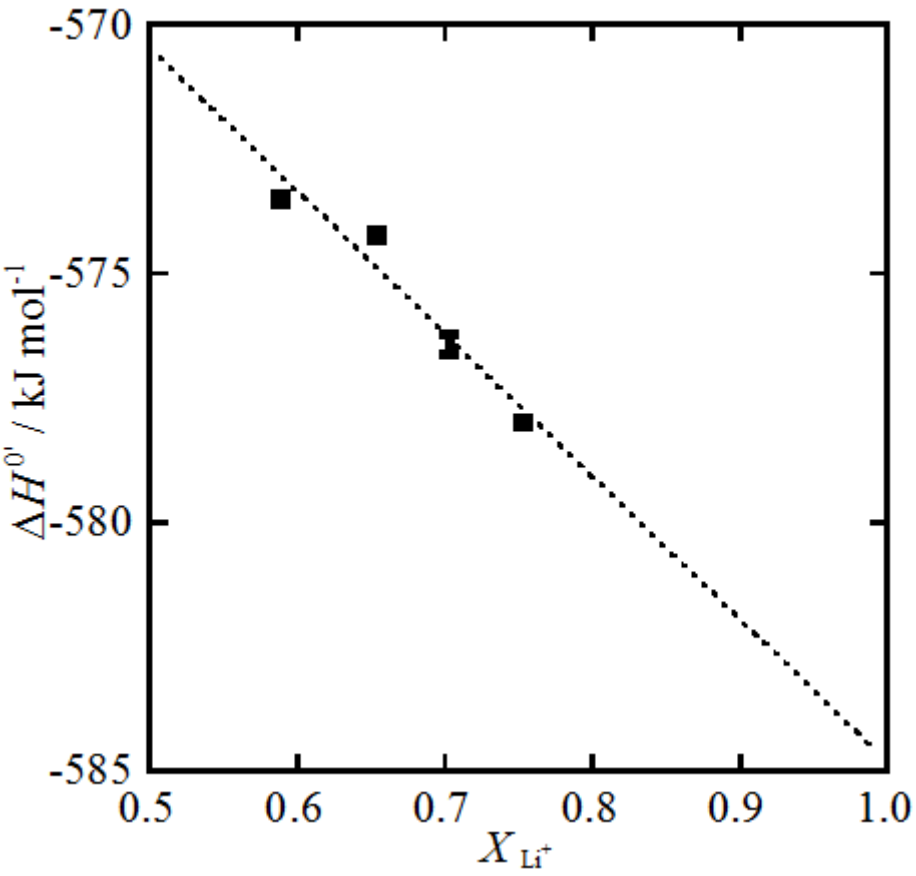

Fig. 4 Relationship between the cation fraction of Li^+ and the standard formal enthalpy change for the reaction (7): $2Li + 1/2O_2 = 2Li^+ + O^{2-}$ in molten LiCl-KCl mixtures; LiCl:KCl = 58.5:41.5 (eutectic), 65:35, 70:30 and 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95 % confidence intervals.)

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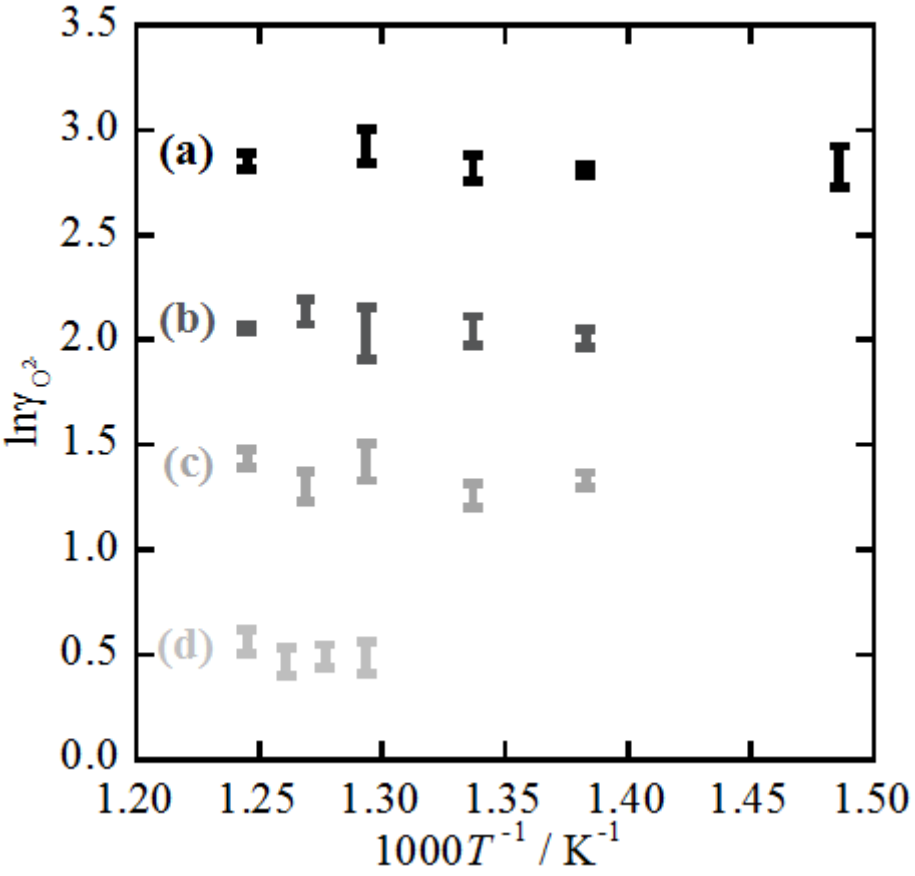

Fig. 5 Activity coefficients of O^{2-} ion in molten LiCl-KCl mixtures; LiCl:KCl = 58.5:41.5 (eutectic), 65:35, 70:30 and 75:25 mol% containing 0.5 mol% Li_2O. (The error values denote the 95 % confidence intervals.)