

Electrochemical behavior of oxide ion in a LiCl-NaCl-CaCl₂ eutectic melt

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Abstract

The solubility of lithium oxide was determined to be 5.2 mol% in a LiCl-NaCl-CaCl₂ eutectic melt (52.3: 13.5: 34.2 mol%, m.p. 713 K) at 773 K. The electrochemical window of the melt, 3.4 V was determined by cyclic voltammetry at 773 K. The reaction at the anode limit was confirmed to as Cl₂ gas evolution. The reaction at the cathode limit was found to be a liquid Li-Na-Ca alloy formation identified by XPS and ICP analyses of the deposits.

Oxygen gas evolution occurred without dissolution of anode material according to the reaction; $\text{O}^{2-} \rightarrow 1/2\text{O}_2 + 2\text{e}^-$, when a boron-doped diamond electrode was anodically polarized at more positive potentials than 3.0 V vs. Li⁺,Na⁺,Ca²⁺/Li-Na-Ca in a LiCl-NaCl-CaCl₂ melt containing Li₂O at 773 K.

Keywords: Inert anodes; Boron-doped diamond; Oxygen gas evolution

1. Introduction

Electrochemical reduction of metal oxides (MO_x) in molten salts is widely used for metal refining and nuclear fuel reprocessing. Direct electrochemical reduction using metal oxides as cathodes [1,2] and pyrochemical reduction using alkali or alkali earth metals such as Li or Ca for reducing agents [3,4] are investigated. In those processes, oxide ion is generated as a by-product in the electrolytes and smooth removal of oxide ion is essential for developing the processes. However such a removal process of oxide ion has not been established. Carbon is traditionally used as a consumable anode in order to remove oxide ion in the electrolytes, though the use of carbon anodes in the electrochemical reduction of metal oxides in high-temperature molten salts evolves carbon monoxide and/or dioxide, and causes the dispersion of carbon particles into the melts. Inert anodes have therefore been considered for the electrochemical refining process for a long time. In our previous study, a boron-doped diamond (BDD) electrode was found to be an inert anode in a molten $\text{LiCl-KCl-Li}_2\text{O}$ system at 723 K [5]. However it has not been investigated in the other molten chlorides systems. Therefore it is important to study the behavior of a BDD electrode in various molten salts containing oxide ion.

In addition, high solubility of oxides in the electrolytes is also important for

electrochemical reduction of metal oxides. Molten LiCl or CaCl₂ is an attractive solvent that have high solubility of oxides [4,6]. Because of this property, reduction of metal oxides has been achieved by chemical and/or electrochemical reactions in molten LiCl or CaCl₂ [2]. The drawback of these melts is the high operation temperature (923 K and 1123 K). Lowering operation temperature gives many advantages such as smaller corrosive damage to the vessel, smaller thermal damage to the electrode materials and lower energy consumption. A new melt is thus desirable to perform reduction processes at lower temperatures with oxides solubility comparable to that of LiCl or CaCl₂. As a candidate for a new system, a LiCl-NaCl-CaCl₂ melt containing LiCl and CaCl₂ was selected, expecting dissolution of large amount of oxides. From the background, a removal process of oxide ion using a BDD electrode was evaluated in this melt. In advance of that, the electrochemical window of LiCl-NaCl-CaCl₂ and the solubility of oxides have been measured.

2. Experimental

A molybdenum plate (Nilaco Corp., 99.95 %) and a glassy carbon rod (Tokai carbon) were used as electrode materials for cyclic voltammetry. A molybdenum plate electrode was used for electrodeposition of alkali metal and/or alkali earth metal when

the electrochemical window was measured. A boron-doped diamond (BDD) electrode (Sumitomo Electric Industries, Ltd., thickness: 20 μm , Substrate: Si) was used as a working electrode when oxygen gas evolution was examined. The counter electrode was made of a glassy carbon rod when it was used for an anode and an aluminum plate (Nilaco Corp., 99.2 %) was also employed for a cathode. The reference electrode was Ag^+/Ag electrode. A silver wire (Japan Metal Service, 99.99 %) was immersed in the LiCl-NaCl-CaCl_2 eutectic melt containing 0.5 mol% AgCl (Wako Pure Chemical Co. Ltd., 99.5 %) in a Pyrex glass tube or a mullite tube. The potential of the reference electrode was standardized against the $\text{Li}^+, \text{Na}^+, \text{Ca}^{2+}/\text{Li-Na-Ca}$.

Reagent-grade LiCl (Wako Pure Chemical Co. Ltd., 99.0 %, or Aldrich-APL 99.99 %), NaCl (Kojundo Chemical Co. Ltd., 99.9 %, or Aldrich-APL 99.99 %) and CaCl_2 (Kojundo Chemical Co. Ltd., 99.9 %, or Aldrich-APL 99.98 %) were used for the melt. The experimental temperature was 773 K. Li_2O (Aldrich, 97 %) was used as an oxide ion source which was directly added into the melt. All the experiments were conducted in **a glove box** filled with Ar gas. The eutectic composition was selected based on the reported ternary phase diagram [7].

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

obtained at the cathode limit was analyzed by ICP-AES (Seiko Instruments Inc., SPS4000) after the deposits were dissolved into distilled water and the pH was adjusted to 1.0 with an aqueous HNO_3 solution. The sampled gases during and after electrolysis were analyzed by an infrared spectrometer (BIORAD Ltd., FTS-155), oxygen gasometer (Panametric Japan Co. Ltd., OX-2). The BDD electrode before and after electrolysis was analyzed by X-ray diffraction (Rigaku, MultiFlex, and μ -Raman (Jobin-Yvon, Labram spectrometer).

3 . Results and discussion

3.1 Electrochemical window of LiCl-NaCl-CaCl_2

Figure 1 shows cyclic voltammograms obtained for LiCl-NaCl-CaCl_2 at 773 K. As working electrodes, a molybdenum plate was used in the negative potential region and a glassy carbon rod was used in the positive potential region. In the negative potential region (Fig. 1(a)), a sharp increase of a cathodic current and the corresponding anodic current are observed at about -2.3 V (vs. Ag^+/Ag). These currents are attributed to the deposition of M ($\text{M} = \text{Li}, \text{Na}$ and/or Ca) and the dissolution of the deposits, respectively. The potential, -2.3 V, at which the current became zero after the potential sweep was reversed to anodic direction, was defined as the cathode limit potential.

In the positive potential region of the cyclic voltammogram (Fig. 1(b)), the anodic current increased from about 1.2 V. When potentiostatic electrolysis was conducted at this potential, gas evolution was observed on the anode. Since the gas was confirmed to be elemental chlorine by a gas detector tube, it was concluded that the reaction at the anode limit is the oxidation of chlorine ion to form chlorine gas.



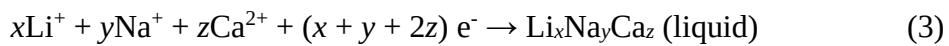
After the potential sweep was reversed to cathodic direction, the current constantly decreased and became zero at 1.1 V. This potential was defined as the anode limit potential. The electrochemical window was determined to be 3.4 V at 773 K. Standard formal potentials of cathode limits, $E_{\text{cathode}}^{0'}$, vs. Cl_2/Cl^- of LiCl , NaCl and CaCl_2 are -3.62, -3.65 and -3.54 V, respectively. They are calculated from the standard Gibbs energy of formation, ΔG_f^0 , of each compound [8] according to the equation:

$$E_{\text{cathode}}^{0'} = \frac{\Delta G_f^0 + RT \ln(X_{\text{M}^{n+}})}{nF} \quad (2)$$

where R ; the gas constant, T ; the absolute temperature, $X_{\text{M}^{n+}}$; the mole fraction of the M^{n+} cation, n ; the number of electrons, F ; the Faraday constant. This calculation indicates that the potential of the cathode limit determined in this study is more positive than that theoretically determined. This result suggests that the reaction at the cathode

limit reaction is the formation of alloy containing Li, Na and Ca.

In order to elucidate the reaction at the cathode limit, potentiostatic electrolysis was performed at -2.3 V (vs. Ag^+/Ag) at 773 K for 50 minutes using molybdenum plate as a working electrode. The deposits obtained were first polished by a file in an Ar glove box to remove adherent salts. Then, the deposits with metallic luster were dissolved into water and analyzed by ICP-AES. The analysis revealed 31.9 at% Li, 1.6 at% Na and 66.5 at% Ca. According to the XPS results (Fig. 2), the deposits include metallic Li, Na and Ca. Also it is revealed by a titration method that the amount of the salts in the deposit is negligibly small. From these results, it is confirmed that the reaction at the cathode limit of the LiCl-NaCl-CaCl_2 eutectic melt is the formation of Li-Na-Ca alloy. The alloy is considered to be in the liquid state at 773 K according to the observation of the shape of the deposits as well as the phase diagram of the Li-Na-Ca system shown in Fig. 3 [9].



The equilibrium potential of the codeposition of Li, Na and Ca to form Li-Na-Ca alloy is expected to be more positive than that of Li, Na and Ca metals due to the lower activity than unity of each element in the alloy.

3.2 Solubility of oxides

The solubility of oxides in a LiCl-NaCl-CaCl₂ eutectic melt (52.3: 13.5: 34.2 mol%) at 773 K was measured by an electrochemical method. Lithium oxide (Li₂O) was used as an oxide ion source. When cyclic voltammetry was conducted using a glassy carbon electrode as an anode, the anodic current was observed at around 2.5 V (Fig.4). The current is due to the evolution of carbon monoxide or dioxide by gas analysis. The currents were also observed in the potential range of 3.0 to 3.5 V, however, the origins have not been known yet. The current corresponding to CO or CO₂ evolution increased as the amount of dissolved Li₂O increased and then it became constant when the melt was saturated with Li₂O. The solubility was determined to be 5.2 mol% at 773 K. From this result, a LiCl-NaCl-CaCl₂ eutectic melt (52.3: 13.5: 34.2 mol%) is expected to be a good electrolyte for reduction of metal oxides because it has high solubility of oxides at relatively low temperatures.

3.3 Oxygen gas evolution on a boron-doped diamond (BDD) electrode

Figure 5 shows cyclic voltammograms of the BDD electrode before and after the addition of Li₂O into the LiCl-NaCl-CaCl₂ melt. Before the addition of Li₂O, anodic currents were observed at around 3.6 V corresponding to the evolution of chlorine gas at

the anode limit of a LiCl-NaCl-CaCl₂ melt. After the addition of Li₂O, the new anodic current was observed at around 3.0 V. This current is attributed to the oxidation of oxide ion to form oxygen gas from the previous study of a LiCl-KCl eutectic melt [5]. In order to confirm the gas evolution in the potential range of 3.0 to 3.6 V, potentiostatic electrolysis was performed, and the sampled gas was analyzed by means of an oxygen gasometer and an infrared spectrometer. Figure 6 shows the variation of current densities and the concentration of oxygen gas against time when the potentiostatic electrolysis at 3.2 V was conducted. The concentration of oxygen gas increases almost linearly with the electrolysis time, indicating that oxygen gas evolution continuously occurs during the electrolysis. The IR spectrum of the sampled gas showed no gaseous species such as CO, CO₂ and O₃, as shown in Fig. 7. This result indicates that oxide ion is oxidized to form only O₂ gas on the BDD electrode:



The quantity of oxygen gas formed by thermal decomposition of Li₂O is negligibly small compared to that generated during electrolysis because the concentration of oxygen was less than 1 ppm over the Li₂O-containing melt before electrolysis. Moreover, the XRD patterns and μ -Raman spectra of the BDD electrode surface before and after potentiostatic electrolysis are almost identical as shown in Figs. 8 and 9. These

results indicate that the structure of diamond is not changed by the electrolysis and a BDD electrode is stable under the present condition. However, the stability of the electrode against a longer time electrolysis has not been guaranteed yet. The origins of anodic currents observed in the potential range of 3.2 to 3.6 V are attributed to oxygen evolution. It is considered from analogy with the behavior of oxygen-terminated diamond electrodes in aqueous solutions [10] that adsorption and termination of oxygen on the BDD electrode surface generate electrochemically passive sites for oxygen evolution and result in the increase of overpotential for oxygen evolution. This phenomenon is attributed to the difference of the electrode surface state by the quantities of doped boron. They will be investigated further in the near future.

Comparing the result in a LiCl-KCl eutectic melt at 723 K [5], the current density is so small that oxygen gas is hard to evolve in the present system. One of the conceivable reasons is the wetting phenomenon on the BDD electrode. The change of the surface wettability in LiCl-NaCl-CaCl₂ causes the adsorption of oxygen. Therefore, it is considered that electrochemically active sites decreases and the reaction of oxygen gas evolution is decelerated in this system.

4. Conclusion

The solubility of Li_2O has been determined to be 5.2 mol% in a LiCl-NaCl-CaCl_2 melt (52.3 : 13.5 : 34.2 mol%) at 773 K. The electrochemical window has also been determined to be 3.4 V at 773 K when a glassy carbon electrode is used as an anode. The reaction at the anode limit has been confirmed as chlorine gas evolution and that at the cathode limit as the formation of Li-Na-Ca alloy. The composition of the alloy is determined: Li; 31.9, Na; 1.6 and Ca; 66.5 mol% at 773 K.

Oxygen gas evolution is observed during the electrolysis on a BDD electrode in a LiCl-NaCl-CaCl_2 melt containing Li_2O . The oxidation of oxide ion occurs at more positive potentials than 3.0 V (vs. $\text{Li}^+, \text{Na}^+, \text{Ca}^{2+}/\text{Li-Na-Ca}$) to produce oxygen gas.



The XRD patterns and μ -Raman spectra shows the same surface morphology of diamond before and after the potentiostatic electrolysis at 3.2 V in a LiCl-NaCl-CaCl_2 eutectic melt containing 2.0 mol % Li_2O at 773 K. The BDD electrode is stable under this electrolysis condition. However, it has also been indicated that the reaction of oxygen gas evolution is slower than that in molten LiCl-KCl systems because of the larger viscosity of the melt at the electrolysis temperature in the present study.

References

- [1] G. Z. Chen, D. J. Flay, T. W. Farthing, *Nature* **407**, 361 (2000).
- [2] Y. Sakamura, M. Kurata and T. Inoue, *J. Electrochem. Soc.*, **153**, D31 (2006).
- [3] R. O. Suzuki and K. Ono, Electrochemical Society Proceedings Volume 19, p. 810 (2002) .
- [4] T. Usami, M. Kurata, T. Inoue, H. E. Sims, S. A. Beetham, and J. A. Jenkins, *J.Nucl. Mater.*, **300**, 15 (2002).
- [5] T. Goto, Y. Araki and R. Hagiwara, *Electrochem. Solid-State Lett.*, **9**, D5 (2006).
- [6] E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagrams for Ceramists 1969 Supplements*, National Bureau of Standards, The American Ceramic Society, Inc. (1969).
- [7] G. A. Bukhalove and A. S. Arabadzhen, *Zh. Neorgan. Khim.*, **7** [9], 2230 (1962).
- [8] F*A*C*T, <http://www.crct.polymtl.ca/fact/index.php>.
- [9] Shengjun Zhang, Dongwon Shin and Zi-Kui Liu, *Calphad*, **27**, 2, 235 (2003).
- [10] I. Yagi, H. Notsu, T. Kondo, D. A. Tryk and A. Fujishima, *J. Electroanal. Chem.*, **473**, 173 (1999).

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Fig. 1 Cyclic voltammograms for (a) a Mo electrode in the negative potential region and (b) a glassy carbon electrode in the positive region in the LiCl-NaCl-CaCl₂ eutectic melt at 773 K. Scan rate is 0.1 V s⁻¹.

Fig. 2 Results of analysis by XPS for deposits formed on a molybdenum plate after potentiostatic electrolysis at -2.3 V vs. Ag⁺/Ag in the LiCl-NaCl-CaCl₂ eutectic melt at 773 K.

Fig. 3 Phase diagram of the Li-Na-Ca system [9].

Fig. 4 Cyclic voltammogram on a GC electrode after the addition of 2.0 mol% Li₂O in LiCl-NaCl-CaCl₂ at 773 K.

Fig. 5 Cyclic voltammograms on a BDD electrode before (a) and after (b) adding 2.0 mol% Li₂O in LiCl-NaCl-CaCl₂ at 773 K.

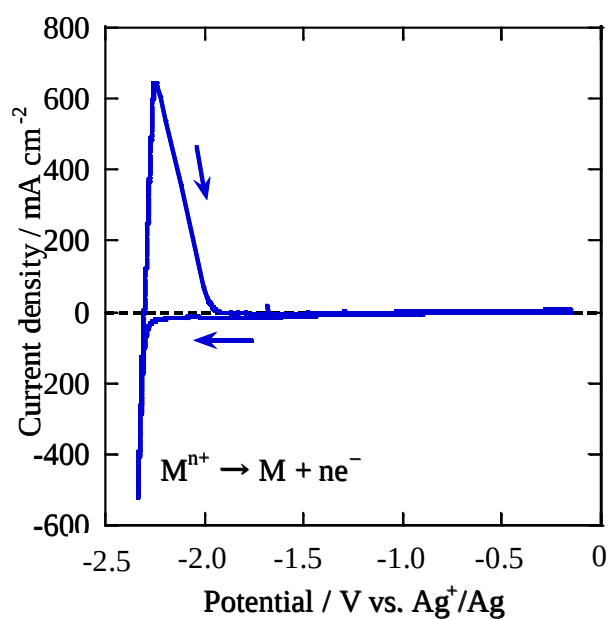
Fig. 6 Variation of current densities and the concentration of oxygen gas during potentiostatic electrolysis at 3.2 V on a BDD electrode in a LiCl-NaCl-CaCl₂ eutectic melt containing 2.0 mol % Li₂O at 773 K.

Fig. 7 IR spectra of the generated gas during potentiostatic electrolysis at 3.2 V on a BDD electrode in a LiCl-NaCl-CaCl₂ eutectic melt containing 2.0 mol % Li₂O at 773 K.

Fig. 8 XRD patterns of a BDD electrode before (a) and after (b) potentiostatic electrolysis at 3.2 V in a LiCl-NaCl-CaCl₂ eutectic melt containing 2.0 mol % Li₂O at 773 K.

Fig. 9 μ -Raman spectra a BDD electrode before (a) and after (b) potentiostatic electrolysis at 3.2 V in a LiCl-NaCl-CaCl₂ eutectic melt containing 2.0 mol % Li₂O at 773 K.

(a)



(b)

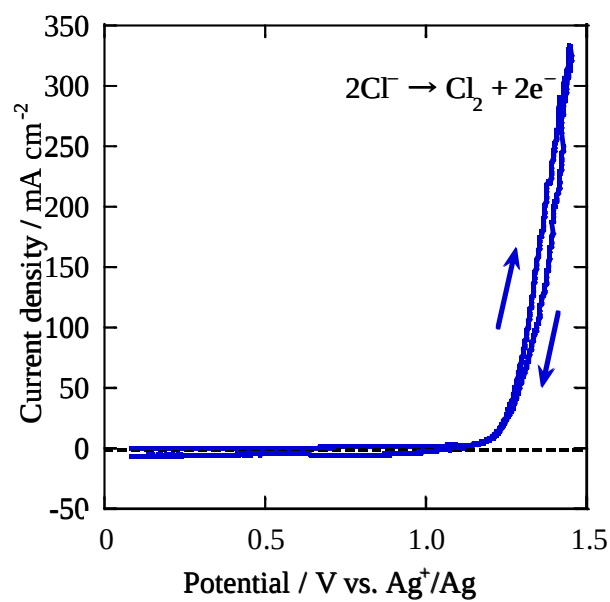
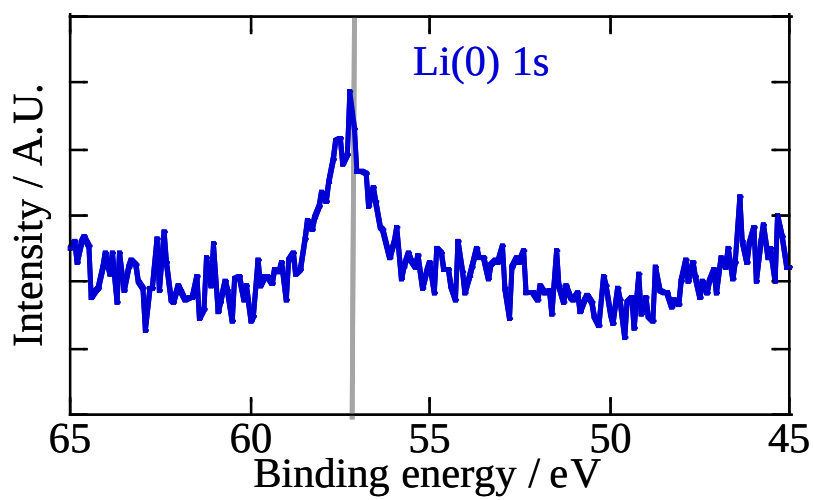


Fig. エラー! メイン文書しかありません。 Cyclic voltammograms for (a) a Mo electrode in the negative potential region and (b) a glassy carbon electrode in the positive region in the LiCl-NaCl-CaCl₂ eutectic melt at 773 K. Scan rate is 0.1 V s^{-1} .



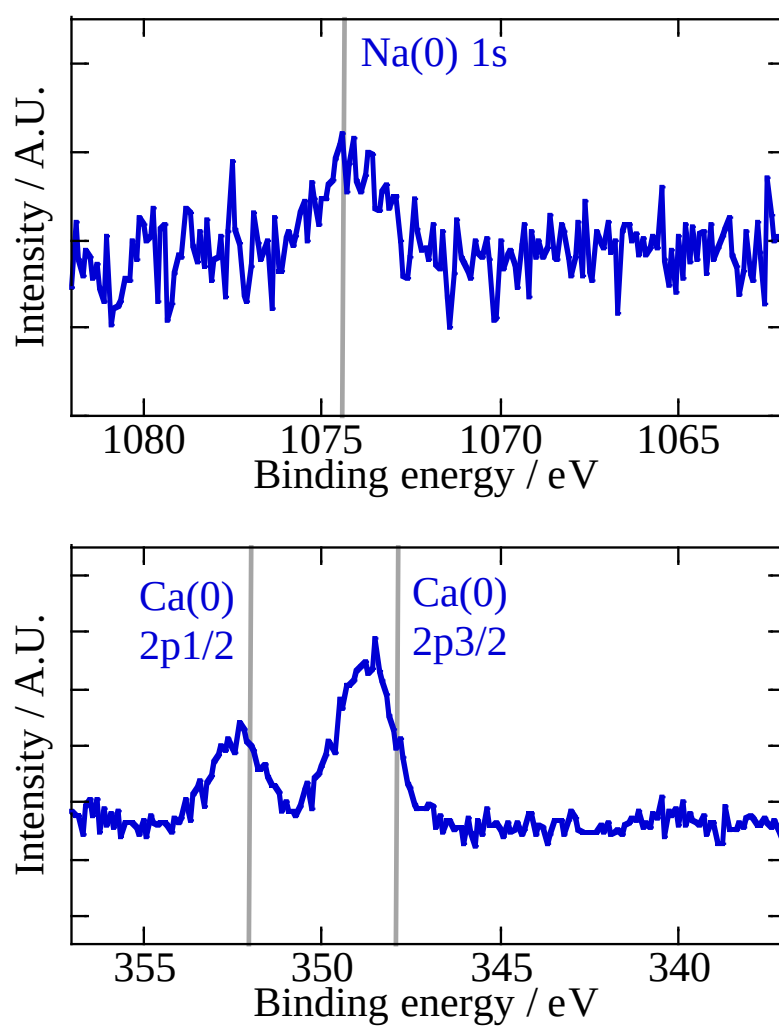


Fig. エラー! メイン文書しかありません。 Results of analysis by XPS for deposits formed on a molybdenum plate after potentiostatic electrolysis at -2.3 V vs. Ag^+/Ag in the LiCl-NaCl-CaCl_2 eutectic melt at 773 K.

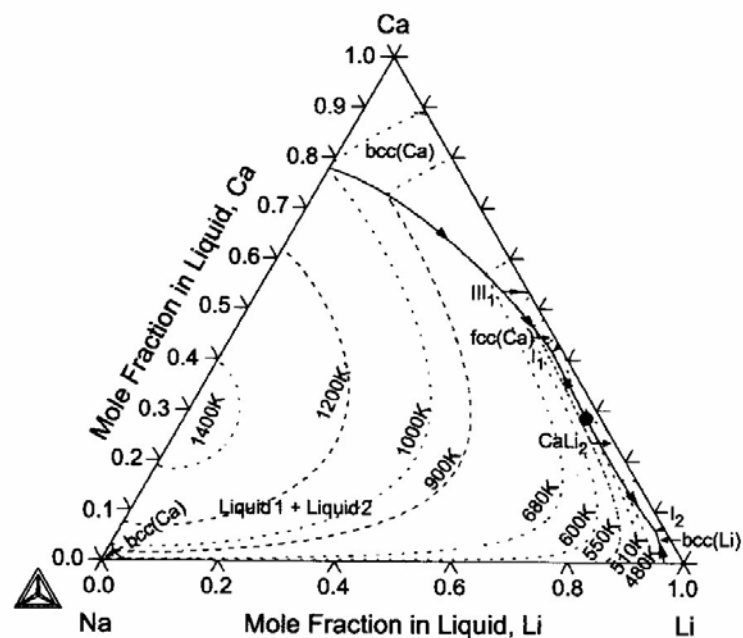


Fig. エラー! メイン文書しかありません。 Phase diagram of the Li-Na-Ca system [9].

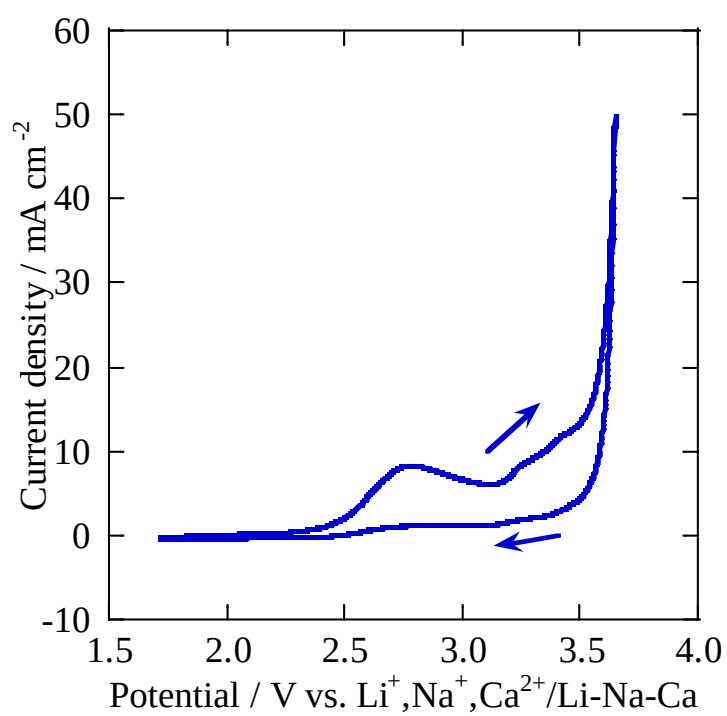


Fig. エラー! メイン文書しかありません。 Cyclic voltammogram on a GC electrode after

the addition of 2.0 mol% Li_2O in LiCl-NaCl-CaCl_2 at 773 K.

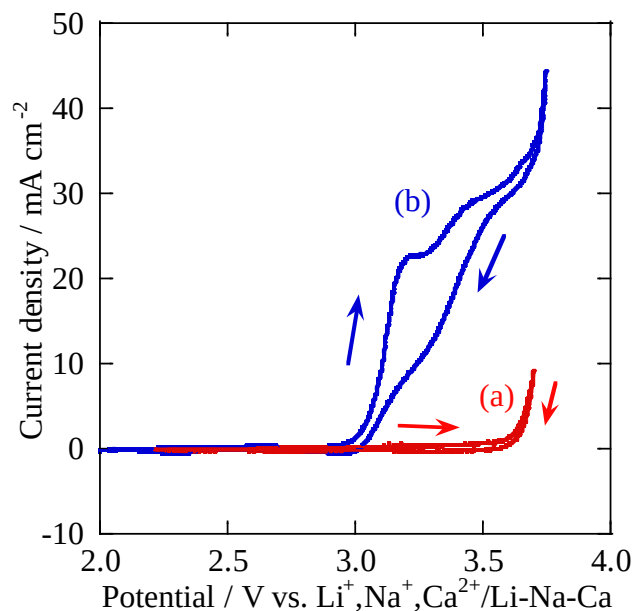


Fig. エラー! メイン文書しかありません。 Cyclic voltammograms on a BDD electrode before (a) and after (b) adding 2.0 mol% Li_2O in LiCl-NaCl-CaCl_2 at 773 K.

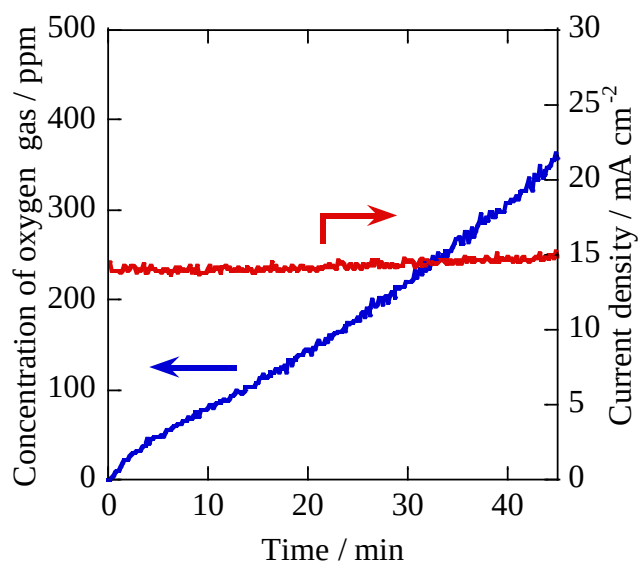


Fig. エラー! メイン文書しかありません。 Variation of current densities and the concentration of oxygen gas during potentiostatic electrolysis at 3.2 V on a BDD electrode in a LiCl-NaCl-CaCl_2 eutectic melt containing 2.0 mol % Li_2O at 773 K.

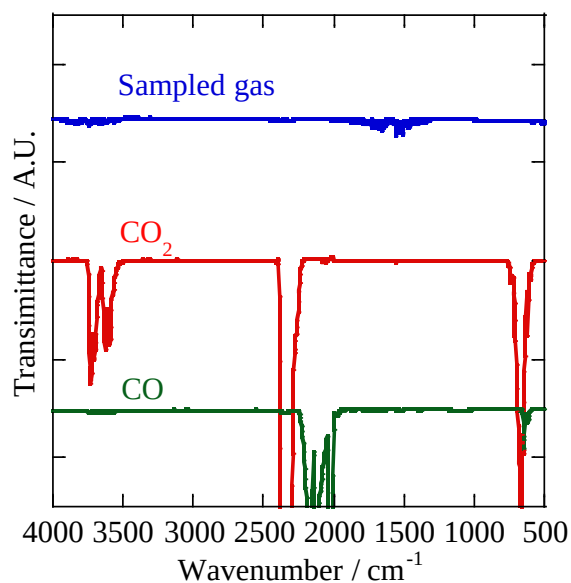


Fig. エラー! メイン文書しかありません。 IR spectra of the sampled gas during potentiostatic electrolysis at 3.2 V on a BDD electrode in a LiCl-NaCl-CaCl₂ eutectic melt containing 2.0 mol % Li₂O at 773 K.

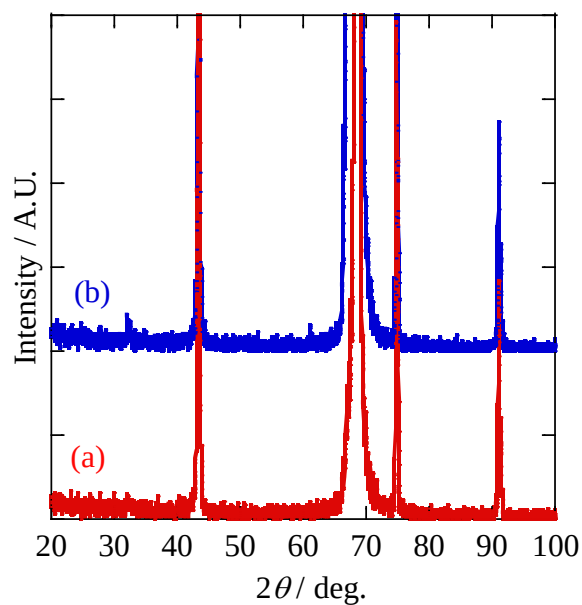


Fig. エラー! メイン文書しかありません。 XRD patterns of a BDD electrode before (a) and after (b) potentiostatic electrolysis at 3.2 V in a LiCl-NaCl-CaCl₂ eutectic melt containing 2.0 mol % Li₂O at 773 K.

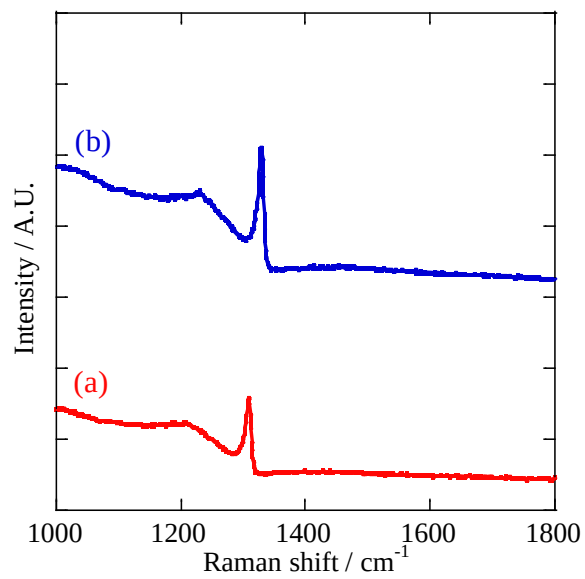


Fig. エラー! メイン文書しかありません。 μ -Raman spectra a BDD electrode before (a) and after (b) potentiostatic electrolysis at 3.2 V in a LiCl-NaCl-CaCl₂ eutectic melt containing 2.0 mol % Li₂O at 773 K.