

ELECTROCHEMICAL REDUCTION OF TITANIUM DIOXIDE THIN FILM IN LiCl-KCl-CaCl₂ EUTECTIC MELT

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The electrochemical reduction of a titanium dioxide (TiO₂) thin film was investigated in LiCl-KCl-CaCl₂ eutectic melt at 450°C. TiO₂ was reduced to Ti in the potential range from 0.2 to 1.0 V vs. Li/Li⁺, which is more positive than the Ca deposition potential (~0.1 V vs. Li/Li⁺). A cathodic reaction, which is presumably assigned to the insertion of Li⁺ into TiO₂, was observed at the potential more positive than the reduction of TiO₂ to Ti. It is suggested that the electrochemical reduction of TiO₂ to Ti is possible in LiCl-KCl-CaCl₂ eutectic melt at 450°C though the slow diffusivity of titanium and /or oxide species in titanium oxides may be disadvantageous for mass production of Ti metal.

INTRODUCTION

The direct electrochemical reduction of titanium dioxide (TiO₂) in calcium chloride (CaCl₂) molten salt can be a promising method for titanium metal production in place of the conventional Kroll method.¹⁻³ However, the electrode reaction of TiO₂ in CaCl₂ melt has not been elucidated in detail. In this preliminary study, the electrochemical reduction of TiO₂ was examined by use of a TiO₂ thin film formed on molybdenum substrates in order to observe the electrode reaction of TiO₂ minimizing the influence of the diffusion of oxygen in the solid electrode. LiCl-KCl-CaCl₂ eutectic melt was employed as the supporting electrolyte because the melting point of LiCl-KCl-CaCl₂ eutectic (~425°C) is lower than that of CaCl₂ (772°C). This melt has been successfully used for the electrochemical reduction of SiO₂ with a contacting electrode.⁴

EXPERIMENTAL

A mixture of LiCl, KCl and CaCl₂ (52 : 12 : 36 in mol%) was dried under vacuum at 200-300°C for more than 24 hours. A TiO₂ thin film was prepared by dipping molybdenum wire in 0.26 mol dm⁻³ tetra-n-butyl orthotitanate / 1-butanol solution, followed by drying at 60°C for 10 min and thermal decomposition at 450°C for ten minutes.⁵ The average thickness of the film was estimated to be ~0.1 μm from the weight gain. This process was repeated for four times to obtain a thick film. The TiO₂-coated Mo wire was used as a working electrode. Mo and Ti wires with or without oxidation in air at 450°C for 10 min were also used as working electrode. A carbon rod was used as a counter electrode. Pt wire was used as a quasi-reference electrode, of which the potential was regularly corrected against Li metal deposited on molybdenum wire. Electrochemical

measurements were carried out with a potentiogalvanostat (Hokuto Denko, HA-151) and a voltage scan generator (Bank Elektronik, VSG 72) using an air-tight glass cell filled with dry argon gas at 450°C.

RESULTS AND DISCUSSION

Cyclic voltammetry of a Mo electrode

The electrochemical study of LiCl-KCl-CaCl₂ eutectic melt has not been made in detail until now. Thus, the electrochemical behavior of this melt was examined with a pure Mo electrode since Mo does not form any alloy with Li and Ca.⁶ Figure 1 shows the transition of the potential observed during the galvanostatic cathodic reduction and open circuit on the Mo electrode. The most negative potential during the cathodic reduction can be assigned to the reduction potential of Li⁺. The potential was kept constant after stopping the reduction. However, the potential started to change to more positive side after a while probably due to the reaction of metallic lithium with Ca²⁺.



Thus, the potential of the Pt quasi-reference electrode was corrected against the constant open circuit potential observed just after the deposition of metallic lithium. All potentials in this paper are shown in this manner. Figure 2 shows the cyclic voltammogram of a Mo electrode in LiCl-KCl-CaCl₂ eutectic melt at 450°C. The molybdenum oxides on the Mo electrode were removed by cathodic reduction beforehand. The cathodic current observed in this cyclic voltammogram can be assigned to the reduction of Li⁺ and Ca²⁺ since the reduction potential of K⁺ is expected to be more negative than those of Li⁺ and Ca²⁺ in the same way as known for LiCl-KCl eutectic melt.⁷ The main cathodic peak can be ascribed to the reduction of Li⁺ since the mole fraction of Li⁺ is larger than Ca²⁺ in this melt. Thus, a shoulder superimposed on the main cathodic peak can be assigned to the reduction of Ca²⁺, of which the reduction potential is expected more positive than that of Li⁺. A sharp anodic current peak can be assigned to the anodic stripping of metallic Li. An anodic current peak at 0.50 V was always observed after the reduction of Ca²⁺ regardless of the reduction of Li⁺. Thus, this anodic current peak can be attributed to the stripping of metallic Ca. Since Ca and Li form some Ca-Li alloys,⁶ an anodic current peak at 0.14 V is probably due to the anodic decomposition of Ca-Li alloys.

Cyclic voltammetry of an oxidized Mo electrode – Reduction of molybdenum oxides

Since Mo was used as the substrate for TiO₂ thin film in this study, the electrochemical behavior of molybdenum oxides was also examined in brief. The surface of a Mo electrode was oxidized in air at 450°C for 10 min. Figure 3 shows the cyclic voltammogram of the oxidized Mo electrode in LiCl-KCl-CaCl₂ eutectic melt at 450°C. There are several cathodic current peaks, which can be assigned to the reduction of molybdenum oxides, such as MoO₃ and MoO₂.



The reversible potentials for eqs. 2 and 3 can be calculated as follows.

$$E_{\text{MoO}_3/\text{MoO}_2} = \frac{\Delta_{\text{MoO}_3}^0 - \Delta_{\text{MoO}_2}^0}{2F} - \frac{\Delta_{\text{O}^{2-}}^0}{2F} \quad [4]$$

$$E_{\text{MoO}_2/\text{Mo}} = \frac{\Delta_{\text{MoO}_2}^0 - \Delta_{\text{Mo}}^0}{4F} - \frac{\Delta_{\text{O}^{2-}}^0}{2F} \quad [5]$$

Using the thermodynamic data at 450°C (FactSage[®]), the difference in the reversible potentials between MoO₃/MoO₂ and MoO₂/Mo couples can be estimated to be ~0.60 V. Thus, the cathodic current peaks at ~1.45 V and ~1.05 V are probably ascribed to the reduction of MoO₃ and MoO₂, respectively.

Cyclic voltammetry of a TiO₂-coating – Reduction of titanium oxides

The reduction of titanium oxides formed by oxidation of titanium in air was examined for reference. Figure 4 shows the linear sweep voltammogram of a Ti electrode, of which the surface was oxidized in the air at 450°C for 10 min. The cathodic current increasing below 1 V can be related to the reduction of titanium oxides as reported in molten CaCl₂.³ After the potentiostatic cathodic reduction of the oxidized Ti electrode at 0.2 V for several minutes, the color of the immersed part of the electrode changed into the silvery color of Ti metal, indicating the titanium oxides are reduced into titanium metal in this potential region. The reduction of TiO₂ to Ti is presumed to proceed by the following steps.



The reversible potentials for eqs. 6, 7 and 8 are represented as follows.

$$E_{\text{TiO}_2/\text{Ti}_2\text{O}_3} = \frac{2\Delta_{\text{TiO}_2}^0 - \Delta_{\text{Ti}_2\text{O}_3}^0}{2F} - \frac{\Delta_{\text{O}^{2-}}^0}{2F} \quad [9]$$

$$E_{\text{Ti}_2\text{O}_3/\text{TiO}} = \frac{\Delta_{\text{Ti}_2\text{O}_3}^0 - 2\Delta_{\text{TiO}}^0}{2F} - \frac{\Delta_{\text{O}^{2-}}^0}{2F} \quad [10]$$

$$E_{\text{TiO}/\text{Ti}} = \frac{\Delta_{\text{TiO}}^0 - \Delta_{\text{Ti}}^0}{2F} - \frac{\Delta_{\text{O}^{2-}}^0}{2F} \quad [11]$$

When the reversible potential of eq. 11 is taken as a potential standard (i.e. assumed to be zero), the difference in the reversible potentials of eqs. 9 and 10 against eq. 11 are calculated to +0.842 and +0.529 V, respectively. Thus, the reduction of TiO₂ starts below 1 V in LiCl-KCl-CaCl₂ eutectic melt since Ti metal forms at ~0.2 V, as described above. In addition, the difference in the reversible potentials of eqs. 4 and 5 against eq. 11 can be

calculated to +1.893 and +1.27 V, respectively. These values are reasonably consistent with the results for molybdenum oxides.

Several cathodic current peaks were observed for a TiO₂ coated Mo electrode as shown in Fig. 5. The cathodic current peaks at ~1.45 (shoulder) and ~1.05 V can be ascribed to the reduction of molybdenum oxides as described above. The cathodic current peaks at ~1.55 and ~0.20 V can be related to the reduction of TiO₂. The cathodic current peak at ~1.55 V in Fig. 5 is possibly ascribed to the electrochemical insertion of Li⁺ into TiO₂.⁸



The existence of Ti was confirmed by the XPS analysis of the TiO₂-coating reduced in LiCl-KCl-CaCl₂ eutectic melt. Consequently, it is suggested that a Ti thin film can be formed by the electrochemical reduction of TiO₂ thin film in this melt.

CONCLUSION

In this preliminary study, it was demonstrated that the electrochemical reduction of TiO₂ is possible in LiCl-KCl-CaCl₂ eutectic, of which the melting point is much lower than that of CaCl₂. Furthermore, molybdenum oxides can be also reduced electrochemically in this melt. Thus, LiCl-KCl-CaCl₂ eutectic melt can be applicable for the de-oxidation of various metal oxides at lower temperature. However, the slow diffusivity of oxide ions in the solids at low temperature may be disadvantageous for industrial processes.

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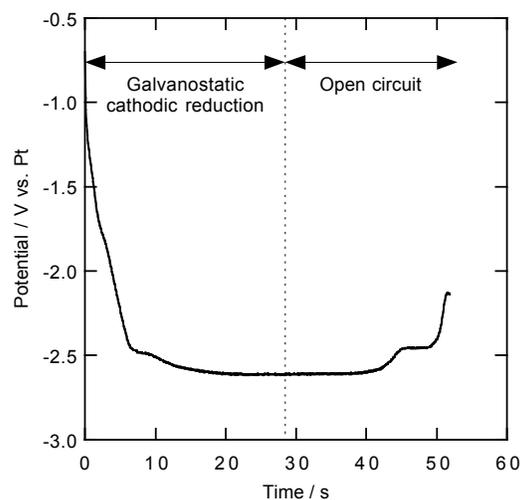


Fig. 1 Potential during the galvanostatic cathodic reduction and open circuit on a Mo electrode in molten LiCl-KCl-CaCl_2 at 450°C .

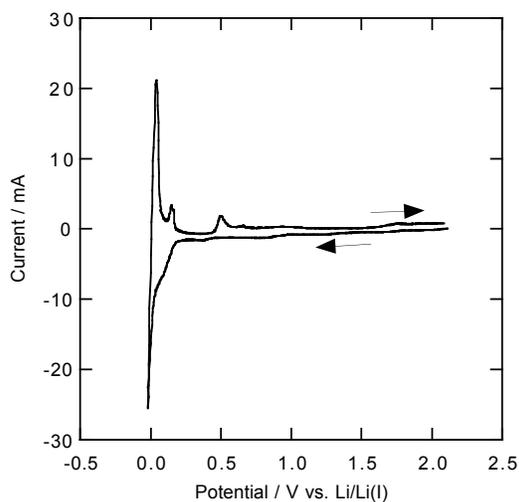


Fig. 2 Cyclic voltammogram of a Mo electrode in molten LiCl-KCl-CaCl_2 at 450°C . Scan rate = 50 mV s^{-1} .

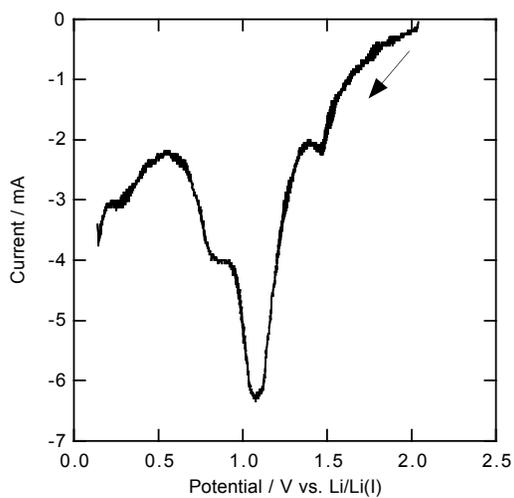


Fig. 3 Linear sweep voltammogram of an oxidized Mo electrode in molten LiCl-KCl-CaCl_2 at 450°C . Scan rate = 30 mV s^{-1} .

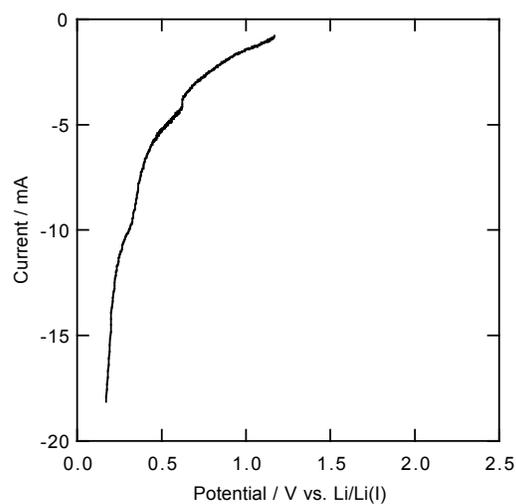


Fig. 4 Linear sweep voltammogram of an oxidized Ti electrode in molten LiCl-KCl-CaCl_2 at 450°C . Scan rate = 50 mV s^{-1} .

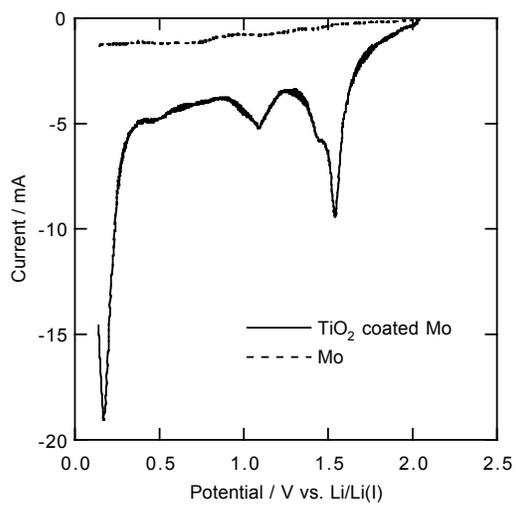


Fig. 5 Linear sweep voltammogram of a TiO₂ coated Mo electrode in molten LiCl-KCl-CaCl₂ at 450°C. Scan rate = 30 mV s⁻¹.