

Electrochemical Reduction of Titanium Dioxide Thin Film in LiCl-KCl-CaCl₂ Eutectic Melt

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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 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 melt (~425°C) is lower than that of CaCl₂. This melt has been successfully used for the electrochemical reduction of SiO₂ with a contacting electrode.⁴

Experimental

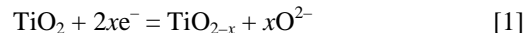
TiO₂ thin film was prepared by dipping molybdenum wire in 0.26 mol dm⁻³ tetra-n-butyl orthotitanate / 1-butanol solution, followed by drying at 60°C and thermal decomposition at 450°C.⁵ The average thickness of the film was estimated to be ~0.1 μm from the weight gain. A mixture of LiCl, KCl and CaCl₂ (52 : 12 : 36 in mol%) was dried under vacuum at 200-300°C for more than 24 hours. The TiO₂-coated Mo wire was used as a sample electrode. Carbon rod was used as a counter electrode. Mo 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 using an air-tight glass cell filled with dry argon gas at 450°C.

Results and Discussion

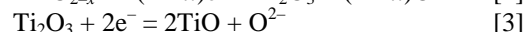
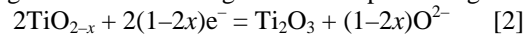
Figure 1 shows the cyclic voltammograms of a pure Mo electrode in LiCl-KCl-CaCl₂ eutectic melt with the cathodic switching potentials changed. There exist two major cathodic current peaks, C1 and C2, which can be assigned to the reduction of Ca²⁺ and Li⁺, respectively, since the reduction potential of Ca²⁺ is expected to be more positive than that of Li⁺. In addition, the cathodic peak current for Li⁺ reduction should be larger than that for Ca²⁺ reduction since the concentration of Li⁺ is higher than that of Ca²⁺ in this melt and Li⁺ would diffuse faster than Ca²⁺. The anodic peaks, A1 and A2, are assignable to the oxidation of metallic Ca and Li, respectively. There is another anodic peak, A2', which may be related to the Ca-Li alloy.

Figure 2 shows the cyclic voltammograms of TiO₂-coated Mo electrodes in the same melt. In this figure, each voltammogram was recorded only once for an individual TiO₂-coated electrode. A broad anodic current around 2.0 V can be ascribed to the oxidation of metallic Ti since the anodic dissolution of a Ti electrode was observed near this potential in a separate experiment. Thus, the reduction of TiO₂ seems to occur at the potential more positive than that of Ca²⁺ in LiCl-KCl-CaCl₂ eutectic

melt, as reported for CaCl₂ melt.^{1,3} There exist several cathodic peaks, which can be classified into three major potential regions. The first region around 1.5 V can be assigned to the reduction of TiO₂ to some non-stoichiometric TiO_{2-x} (x = 0.1 ~ 0.25) known as Magneli phases.



In the second region around 1.0 V, there are two major cathodic peaks, which were separated more clearly after the 2nd cycle. These peaks are probably attributed to the following reactions according to the Ti-O phase diagram.



The third region at the potential more negative than 0.6 V is expected to be the reduction of TiO to □-Ti since the oxidation of □-Ti occurred only after undergoing the cathodic reaction in the third region.

Acknowledgements

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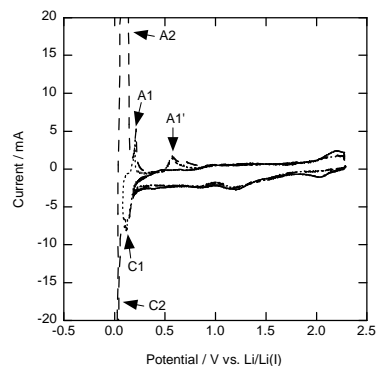


Fig. 1 Cyclic voltammograms of a Mo electrode in LiCl-KCl-CaCl₂ eutectic melt at 450°C. Scan rate : 50 mV s⁻¹.

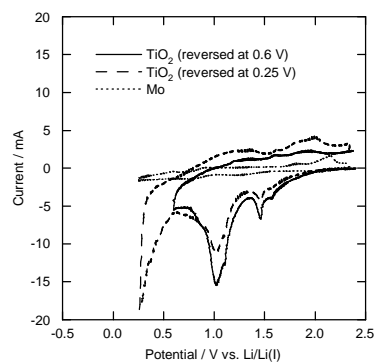


Fig. 2 Cyclic voltammograms of TiO₂-coated Mo electrodes in LiCl-KCl-CaCl₂ eutectic melt at 450°C. Scan rate : 50 mV s⁻¹.