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Visualization of TiO_2 reduction behavior in molten salt electrolysis

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Abstract:

An in-situ observation technique of the TiO_2 interfacial behavior in molten LiCl-KCl electrolysis was developed. The variation of the thin TiO_2 electrode surface were tracked through the high-speed digital microscopy synchronized with the electrochemical measurement. Two characteristic interfacial behaviors were discovered: physical breakage of the titanium oxide and Li(*l*) spreading on electrode surface. These electrochemically induced interfacial behaviors affect the current-time curves due to the heterogeneity of the titanium oxide film shape.

Keywords:

Molten salt electrolysis; Titanium oxide; High-speed microscopy; LiCl-KCl; Liquid Li;

In the refining industries of the oxide-stable metallic elements, the electrolysis of the molten chloride is indispensable. Thus, and efficient electrolysis has been developed, for example, for use in the Kroll process for titanium production. In the Kroll process, TiO_2 is first converted to $TiCl_4$ by Cl_2 gas. Then, liquid Mg reduces the $TiCl_4$ such that high-purity metallic sponge Ti is obtained. The liquid Mg and gaseous Cl_2 are regenerated by electrolysis of the byproduct $MgCl_2$ and recycled.

In order to avoid some complicated steps in the Kroll process, the direct electrochemical decomposition of TiO_2 in molten $CaCl_2$ has been proposed. In the FFC Cambridge process, the oxide anion cathodically transfers from the solid TiO_2 pellet to the anode in a molten salt bath.[1] Because the Ti-O binary system contains many suboxides, oxygen in the higher oxide is removed to form a lower oxide upon receiving an electrical charge from the cathode.

Another promising method, the OS process, has been proposed, in which the oxide anion transfer in $CaCl_2$ is better utilized because as much as 20 mol% CaO that acts as an electrolyte can dissolve into the molten $CaCl_2$ at 1173 K[2-5]. The electrochemically deposited, liquid Ca at the cathode also dissolves into the molten $CaCl_2$, and the dissolved Ca works effectively to reduce the titanium oxide powder. Similarly, LiCl and its binary chloride systems can dissolve oxygen anions at lower temperatures,[6-8] and KCl is sometimes added to lower the

62 temperature further.[9] Electrochemically deposited liquid Li in
63 molten LiCl-KCl has been observed to form droplets on an
64 attached cathode.[10] Despite its importance, there is only limited
65 knowledge about the dynamic reducing behavior of TiO_2 by liquid
66 Li. Recently, black, film-like, colloidal Li (in the form of a metal
67 fog) was observed on an electrodeposited thin Li metal in molten
68 LiCl-KCl.[11] The detailed behavior of reducing TiO_2 ,however,
69 has yet to be clarified.

70 A detailed understanding of the dynamic behavior of TiO_2
71 reduction is necessary to control and optimize the electrolysis.
72 Besides improving the FFC and OS processes, such knowledge
73 can be applied immediately to the current molten salt electrolysis
74 processes and would bring a large energy savings due to
75 increased thermal efficiency in the metal-refining industries.
76 Cyclic voltammograms (CVs) of the oxide electrode in high-
77 temperature molten salts display unique features that the
78 reduction current including multi-interfacial transient dynamic
79 behavior [12]. Data on the reduction rate, current efficiency, and
80 energy consumption during the electroreduction of oxides under
81 potentiostatic conditions were recorded, and these experimental
82 findings form the basis of the optimization of the
83 electroreduction method [13, 14]. For an in-depth discussion, we
84 developed an in-situ observation technique to observe the TiO_2
85 interfacial behavior in molten LiCl-KCl electrolysis by tracking
86 the thin fine TiO_2 electrode surface obtained by the high-speed

digital microscopy synchronized with the electrochemical measurement in this study.

A schematic diagram of the experimental apparatus is depicted in a reference.[10, 15] A vertical quartz glass vessel with a barrel-vaulted (semicylindrical) shape, 100 mm in diameter and 250 mm in height, (Kondo Science, Inc.) was employed. The flat side of the vessel enabled in-situ observations. An electric resistance furnace (SiC heater) with a flat quartz window was designed to observe the phenomena within the vessel under controlled temperature. A metal halide light (Photron Co., Ltd., HVC-SL, maximum light flux: 12,500 lm) was used as an auxiliary light source.

Changes in the electrode interface were recorded at a rate of 500 fps (0.002 s intervals) with the image size of 640 × 480 pixels using a high-speed digital camera (Ditect Co., Ltd., HAS-D71, monochrome). With a long-distance zoom lens (VS Technology Co. Ltd., VSZ-10100, working distance: 95 mm), the minimum field of view is 666 μm × 500 μm and the maximum resolution of 1.04 μm was obtained. The electrode surface morphology was tracked in each captured image by image processing software (Photron Co., Ltd., PFV Viewer). Reagent-grade LiCl (Wako Pure Chemical Co. Ltd., >99.0%) and KCl (Wako, >99.5%) were used for preparing the melt.

The eutectic mixture of LiCl–KCl (59:41 mol%, melting point = 625 K (352 ºC)) was packed in a borosilicate glass crucible with a flat side was settled in the vessel and was dried in vacuum at 573 K (300 ºC) for more than 12 h. Then it was heated up to 673 K (400 ºC, the constant

112 experimental temperature) and maintained for 5 h to remove residual
113 water. All experiments were conducted in an Ar atmosphere
114 (>99.9995%). The melt temperature was measured with a K-type
115 thermocouple with a glass sheath.

116 After the mixed salt was melted, the suspended electrodes were
117 immersed into the melt. Three types of working electrode were
118 prepared from Ti rod (Nilaco Corp., ϕ 1.5 mm, 99.5%). First was as
119 received, second and third were heat-treated for 1 h under 1073 and
120 1173 K, respectively. **Figure 1 (a)** shows the appearances of prepared
121 titanium oxide electrodes. On the surface of the heat-treated electrodes,
122 a white oxide film formed on each. The scanning electron microscope
123 (SEM) image shown in Fig. 1(b) clearly showed the formation of oxide
124 film on the surface of the electrode, and the X-ray diffraction (XRD)
125 pattern of the fabricated electrode (Fig. 1 (c)) identified the oxide film
126 as mainly TiO_2. The average thicknesses of the oxide films obtained
127 from the SEM images increased with the heat-treatment temperature,
128 namely 0.0, 2.0 and 7.3 μm; thus, the three samples were named T0.0,
129 T2.0 and T7.3. The immersion depth of the working electrode was fixed
130 at 40 mm and the other part of the electrodes was insulated using
131 protective Al_2O_3 tube as shown in Fig. 1 (a). The counter electrode was
132 a graphite rod (Toyo Carbon Corp., ϕ 10 mm). An Ag^+/Ag reference
133 electrode was employed. This electrode, consisted of a silver wire (ϕ
134 1.0 mm, 99.99%, Nilaco), a LiCl-KCl eutectic melt containing 0.5
135 mol% AgCl (Wako, 99.5%) and a borosilicate tube, and the silver wire
136 was immersed in the eutectic melt within the tube. Electrochemical

measurements were performed using an automatic polarization system (Hokuto Denko Corp., HZ-5000). The inter-electrode voltage and microscope images were synchronized with an error less than 4 μs by using an analogue signal synchronous system (Ditect Co., Ltd., DI-SYNC 29N).

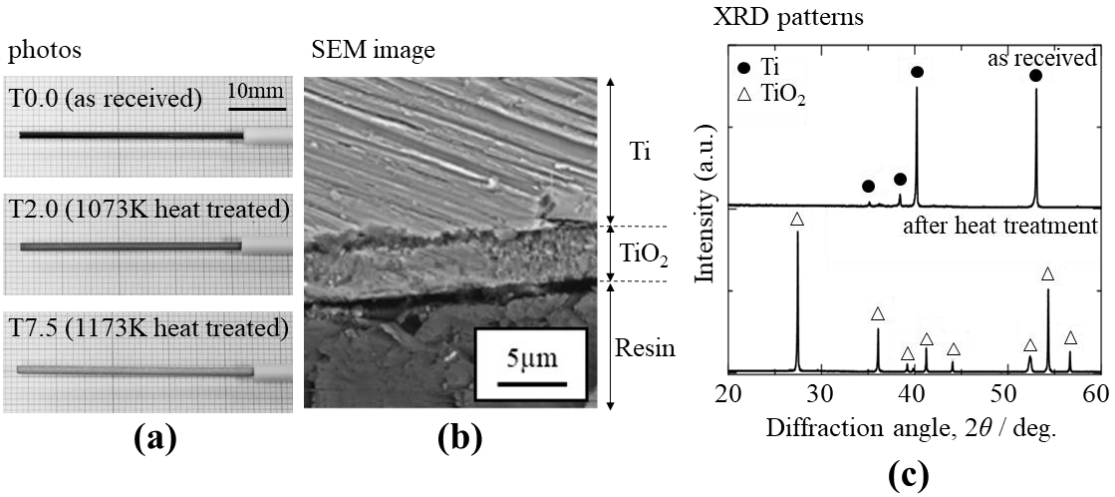


Fig. 1 Titanium oxide electrode previously prepared by heat treatment under air environment. (a): Photos of the three, different-thickness titanium oxide electrodes. (b): Scanning electron microscope (SEM) image of the T2.0 electrode cross-section. (c): X-ray diffraction (XRD) pattern of electrodes before and after heat treatment.

Figure 2 shows the cyclic voltammogram (CV, scan rate: 10 mV / s) obtained by the T7.5 working electrode. Sharp increases in the cathodic and corresponding anodic currents compared to the Ag/Ag^+ reference electrode were observed at about E = −2.4 V. These two current changes are thought to be due to the deposition of Li(*l*) and the dissolution of the deposits, respectively.[16] The cathodic current at E = −0.7 to −1.0 V is the reported reduction potential of the

titanium ion: $Ti^{4+} + e^- \rightarrow Ti^{3+}$ (E = −0.9 V); $Ti^{3+} + e^- \rightarrow Ti^{2+}$ (E = −1.0 V).[17] Although the solubility of Li_2O was estimated to be 0.31 mol% in LiCl-KCl eutectic melt at 673 K (400 ºC) [8], because of the negligible solubility of TiO_2, the direct electrochemical reduction of the TiO_2 following the mechanism of the FFC process described in Eq. 1.

$$TiO_x + e^- \rightarrow TiO_{x-1} + \frac{1}{2}O^{2-} \quad (1)$$

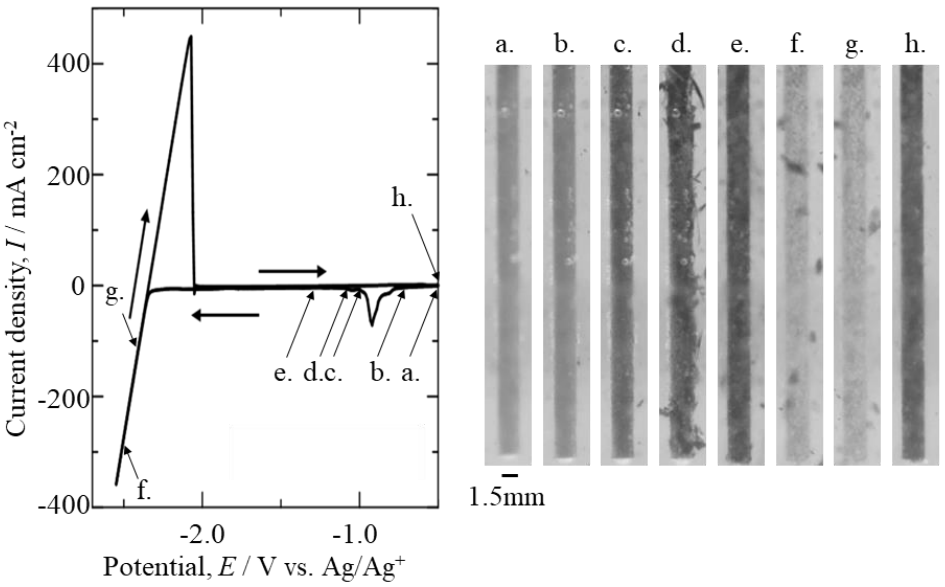


Fig. 2. Cyclic voltammogram and corresponding photographs of T7.5 titanium oxide electrode in LiCl-KCl. Images were taken at a: -0.50V, b: -0.70V, c: -1.00V, d: -1.10V, e:-1.30V, f:-2.50V, g: -2.45V, h: -0.50V.

With the progress of potential, the appearance of the TiO_2 electrode changed from white to black as shown in the photos in Fig. 2a-c. Fig. 2d showed the breakage of the black surface, and small

pieces broke apart from the electrode. At this moment, the current density became approximately zero, and thus the reactivity of the electrode surface was lost due to mechanical disconnection. In the initial stage of potential progression, the deformation of the titanium oxide occurred due to the volume change with the electrochemical reduction. Next, the deformed part of the surface was partially peeled off from the electrode and dispersed into the melt. In Fig. 2f-g, no metal fog was observed in the Li(l) electrodeposition while only silver white precipitate was observed. According to a previous study [10], when an inactive Mo electrode was used as the working electrode, a blue metal fog was generated, and the amount of the fog generation decreased as the amount of oxide ions increased. The metal fog is also related to the amount of Li(l) and the time of the dissolution; however, it was likely that the oxide ions already existed in the vicinity of the working electrode due to the titanium oxide reduction.

The ratio of the electric charges passing through the anode to one through the cathode, (q_a/q_c), in the region of E < -2.0V gave a momentary coulombic efficiency of $q_a/q_c = 0.871$. This showed that the precipitation of the Li(l) advanced the cathodic reaction of the Ti oxide by the OS process mechanism as described by Eq. 2:

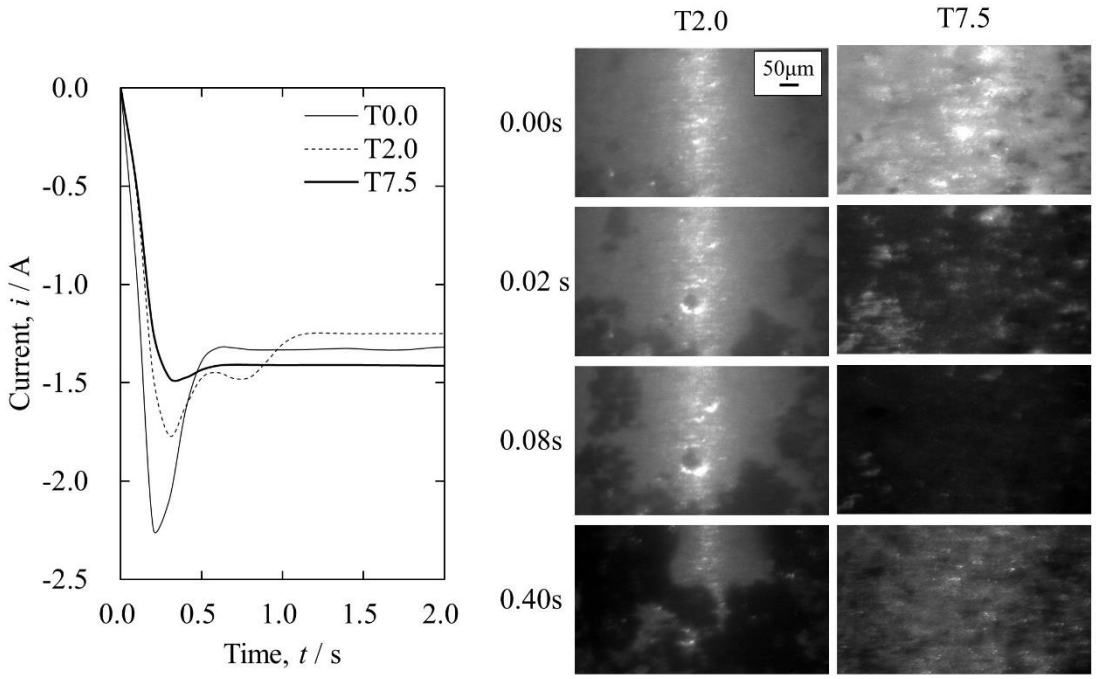
$$Li^+ + e^- \rightarrow Li(l) \quad (2a)$$

$$TiO_y + 2Li(l) \rightarrow TiO_{y-1} + Li_2O(\text{dissolved}) \quad (2b)$$

In the CV measurement, mechanical deformation of titanium oxide

189 occurs during the potential sweep, so it is difficult to know the
190 behavior of the TiO_2 electrode that corresponds to the Li(*l*)
191 electrodeposition potential.

192 **Figure 3** shows the behavior of the TiO_2 electrode surface obtained
193 by the high-speed observation during the chronoamperometry
194 measurement under -2.75 V for 2.000s. (See also the electronic
195 supplementary video files for more detailed understanding. Each video
196 is 6 seconds long.)



197

198 Fig. 3. Electro-reduction behavior of T2.0 and T7.3 TiO_2 electrodes observed by chronoamperometry
199 (at E = -2.75 V). (a): current-time curves, (b): representative photographs of electrode.

200

201 After the initial increase, the current converged to the approximately
202 constant value in all samples. The initial peak current was the largest
203 at T0.0 and showed a tendency to decrease as the TiO_2 film thickness

increased. The surface of the T2.0 electrode changed from white to black immediately after the application of potential. This change proceeded non-uniformly and showed mottled pattern grown from black spots. The black part was the titanium oxide reduced by the mechanism of Eq. 1 (or perovskites like $LiTiO_2$ and $LiTi_2O_4$ [18]). After the electrolysis at a constant potential, the black-colored titanium oxide surface was also observed in the CV test.

In the case of the T7.5 electrode, the black surface rapidly developed, and it became uniform as electrochemical reduction progressed. After t = 0.08 s, the metallic droplets formed, and the metallic liquid spread onto the cathode surface. This phenomenon indicated that the reduction reaction of the TiO_x was progressing by the electrochemical deposition mechanism of Eq. 2a and 2b. After t = 2.0 s, all metallic droplets disappeared, and the black titanium oxide surface remained. To understand in detail the transient change in the TiO_x structure, our future work will involve the chemical analysis of the sample.

From the differences in behaviors of the T2.0 and T7.5 electrodes, the following conclusions can be drawn. For the initial TiO_2 with a high electric resistance, the reduction proceeds by the mechanism of Eq. 1 and the conductivity increases; this reaction should grow heterogeneously on the cathode surface. Therefore, after Li(l) generated in a region having a relatively high conductivity on the cathode surface, the reaction progresses by spreading over the surface of the electrode. The T7.5 sample has not only thicker but also more porous TiO_2 layer than the T2.0 film.[19,20] The reduction of film TiO_2

did not damage the electrolytic product because of the presence of the electrochemical reaction interface, i.e. highly conductive Li (*l*) and molten salt, on the oxide film. Thus, before electrolysis, the molten salt penetrates into the inside of the porous TiO_2, and the generated Li(*l*) droplet causes a lower electrical resistance. The reduction of titanium oxide on the surface progresses by Eq. 2 to wet Li(*l*) on the entire electrode surface.

Figure 4 shows the voltage behavior between WE and CE, *U*, and the observed T2.0-TiO_2 electrode surface under various potentials for 2.000 s. At *E* = -1.0 V, *V* became almost constant and showed a maximum at *t* = 0.08 s, but *V* at *E* = -1.5, -2.0, and -2.5 V showed unstable behaviors. As seen in the figure, the color of each electrode changed to black after the potential was applied. However, when TiO_x broke locally as shown in Fig. 2, the electrical conductivity of the electrode became non-uniform. This is the probable reason for voltage fluctuations. When *E* = -2.75 V, some shiny parts that appear to be Li(*l*) are found at *t* = 1.90 s. Here, Eq. 1 was the dominant reaction initially, but Eq. 2 was dominant on some parts of the electrode surface. Once Li(*l*) is formed, it becomes the current-carrying site and Eq. 2 proceeds further.

Summarizing, a system was constructed to visualize titanium oxide reduction based on molten salt electrolysis in order to better understand its representative interfacial behavior in this study. We focused on reducing TiO_2 in molten LiCl-KCl eutectic salt at 673 K. The observed characteristic interfacial behaviors include (1)

mechanical breakage of titanium oxide by the electrochemical reduction and dispersion of titanium oxide into the bath, (2) local electrochemical reductions at the conductive regions, due to surface nonuniformity, and (3) electrodeposited Li(*l*) wetting the titanium oxide during the reduction reaction. The results from both the cathode interfacial snapshots and the current-time curves suggest that it is important to increase the area of the reactive region between the titanium oxide and the molten salt for efficient reduction by electrodeposited Li(*l*) by avoiding a concentration of Li(*l*).

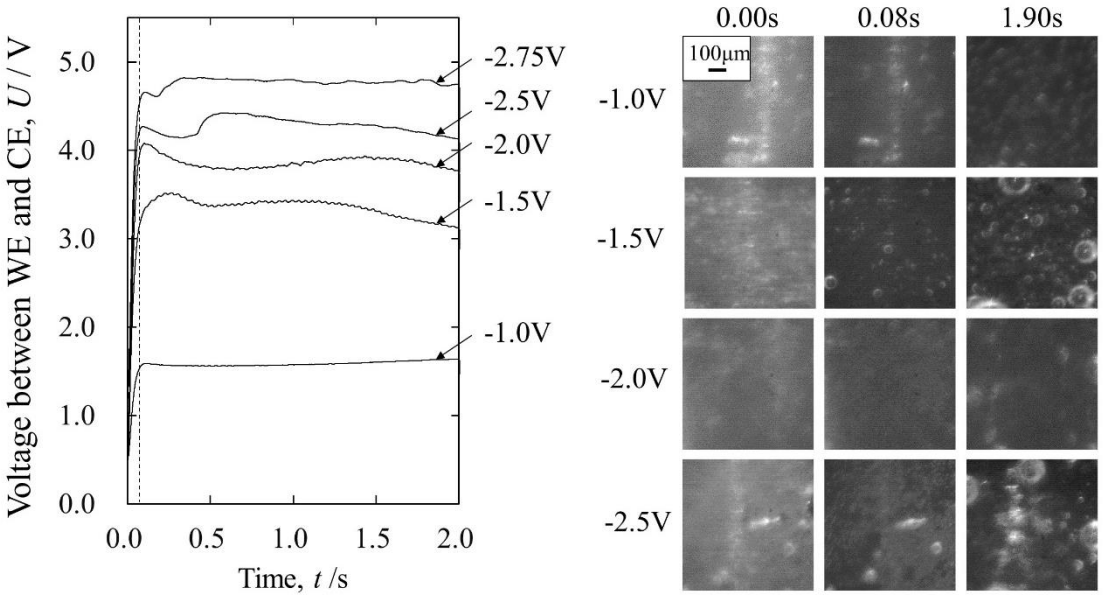


Fig. 4. Electro-reduction behavior of T2.0 TiO_2 electrodes observed by chronoamperometry (at various potentials). (a): voltage-time curves, (b): representative photographs of electrode.

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316 Captions List

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