



Title	Visualization of TiO ₂ Reduction Behavior in Molten Salt Electrolysis
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1 Visualization of TiO₂ reduction behavior
2 in molten salt electrolysis

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2 2 Abstract:

2 3 An in-situ observation technique of the TiO_2 interfacial behavior
2 4 in molten LiCl-KCl electrolysis was developed. The variation of
2 5 the thin TiO_2 electrode surface were tracked through the high-
2 6 speed digital microscopy synchronized with the electrochemical
2 7 measurement. Two characteristic interfacial behaviors were
2 8 discovered: physical breakage of the titanium oxide and $\text{Li}(l)$
2 9 spreading on electrode surface. These electrochemically induced
3 0 interfacial behaviors affect the current-time curves due to the
3 1 heterogeneity of the titanium oxide film shape.

3 2

3 3 *Keywords:*

3 4 Molten salt electrolysis; Titanium oxide; High-speed
3 5 microscopy; LiCl-KCl; Liquid Li;

3 6

3 7 In the refining industries of the oxide-stable metallic
3 8 elements, the electrolysis of the molten chloride is indispensable.
3 9 Thus, an efficient electrolysis has been developed, for example,
4 0 for use in the Kroll process for titanium production. In the Kroll
4 1 process, TiO_2 is first converted to TiCl_4 by Cl_2 gas. Then, liquid
4 2 Mg reduces the TiCl_4 such that high-purity metallic sponge Ti is
4 3 obtained. The liquid Mg and gaseous Cl_2 are regenerated by
4 4 electrolysis of the byproduct MgCl_2 and recycled.

4 5 In order to avoid some complicated steps in the Kroll process,
4 6 the direct electrochemical decomposition of TiO_2 in molten CaCl_2
4 7 has been proposed. In the FFC Cambridge process, the oxide
4 8 anion cathodically transfers from the solid TiO_2 pellet to the
4 9 anode in a molten salt bath.^[1] Because the Ti-O binary system
5 0 contains many suboxides, oxygen in the higher oxide is removed
5 1 to form a lower oxide upon receiving an electrical charge from
5 2 the cathode.

5 3 Another promising method, the OS process, has been proposed,
5 4 in which the oxide anion transfer in CaCl_2 is better utilized
5 5 because as much as 20 mol% CaO that acts as an electrolyte can
5 6 dissolve into the molten CaCl_2 at 1173 K^[2-5]. The
5 7 electrochemically deposited, liquid Ca at the cathode also
5 8 dissolves into the molten CaCl_2 , and the dissolved Ca works
5 9 effectively to reduce the titanium oxide powder. Similarly, LiCl
6 0 and its binary chloride systems can dissolve oxygen anions at
6 1 lower temperatures,^[6-8] and KCl is sometimes added to lower the

6 2 temperature further.^[9] Electrochemically deposited liquid Li in
6 3 molten LiCl-KCl has been observed to form droplets on an
6 4 attached cathode.^[10] Despite its importance, there is only limited
6 5 knowledge about the dynamic reducing behavior of TiO₂ by liquid
6 6 Li. Recently, black, film-like, colloidal Li (in the form of a metal
6 7 fog) was observed on an electrodeposited thin Li metal in molten
6 8 LiCl-KCl.^[11] The detailed behavior of reducing TiO₂, however,
6 9 has yet to be clarified.

7 0 A detailed understanding of the dynamic behavior of TiO₂
7 1 reduction is necessary to control and optimize the electrolysis.
7 2 Besides improving the FFC and OS processes, such knowledge
7 3 can be applied immediately to the current molten salt electrolysis
7 4 processes and would bring a large energy savings due to
7 5 increased thermal efficiency in the metal-refining industries.
7 6 Cyclic voltammograms (CVs) of the oxide electrode in high-
7 7 temperature molten salts display unique features that the
7 8 reduction current including multi-interfacial transient dynamic
7 9 behavior^[12]. Data on the reduction rate, current efficiency, and
8 0 energy consumption during the electroreduction of oxides under
8 1 potentiostatic conditions were recorded, and these experimental
8 2 findings form the basis of the optimization of the
8 3 electroreduction method^[13, 14]. For an in-depth discussion, we
8 4 developed an in-situ observation technique to observe the TiO₂
8 5 interfacial behavior in molten LiCl-KCl electrolysis by tracking
8 6 the thin fine TiO₂ electrode surface obtained by the high-speed

8 7 digital microscopy synchronized with the electrochemical
8 8 measurement in this study.

8 9 A schematic diagram of the experimental apparatus is depicted in a
9 0 reference.^[10, 15] A vertical quartz glass vessel with a barrel-vaulted
9 1 (semicylindrical) shape, 100 mm in diameter and 250 mm in height,
9 2 (Kondo Science, Inc.) was employed. The flat side of the vessel enabled
9 3 in-situ observations. An electric resistance furnace (SiC heater) with a
9 4 flat quartz window was designed to observe the phenomena within the
9 5 vessel under controlled temperature. A metal halide light (Photron Co.,
9 6 Ltd., HVC-SL, maximum light flux: 12,500 lm) was used as an
9 7 auxiliary light source.

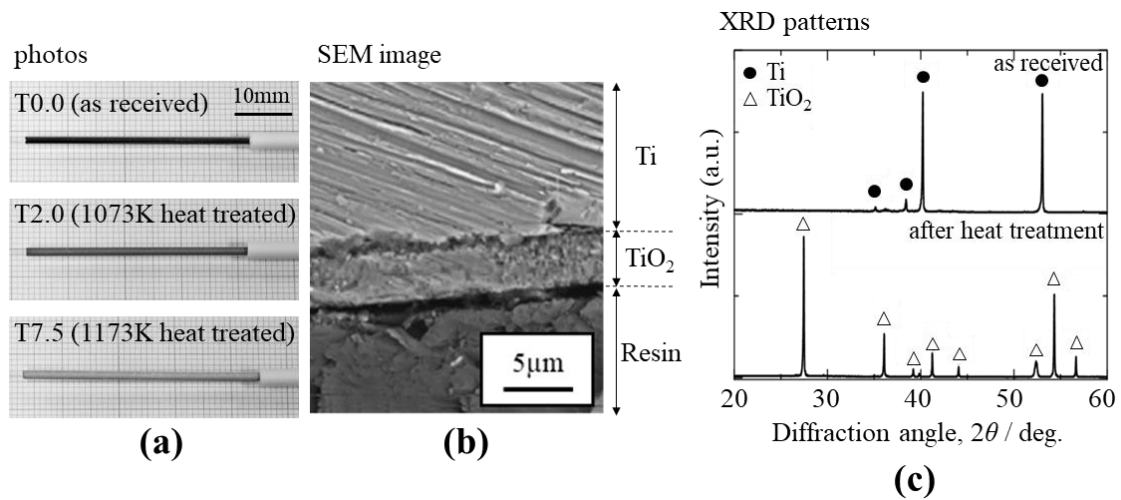
9 8 Changes in the electrode interface were recorded at a rate of 500
9 9 fps (0.002 s intervals) with the image size of 640 × 480 pixels using a
1 0 0 high-speed digital camera (Ditect Co., Ltd., HAS-D71, monochrome).
1 0 1 With a long-distance zoom lens (VS Technology Co. Ltd., VSZ-10100,
1 0 2 working distance: 95 mm), the minimum field of view is 666 μm × 500
1 0 3 μm and the maximum resolution of 1.04 μm was obtained. The electrode
1 0 4 surface morphology was tracked in each captured image by image
1 0 5 processing software (Photron Co., Ltd., PFV Viewer). Reagent-grade
1 0 6 LiCl (Wako Pure Chemical Co. Ltd., >99.0%) and KCl (Wako, >99.5%)
1 0 7 were used for preparing the melt.

1 0 8 The eutectic mixture of LiCl–KCl (59:41 mol%, melting point = 625
1 0 9 K (352 °C)) was packed in a borosilicate glass crucible with a flat side
1 1 0 was settled in the vessel and was dried in vacuum at 573 K (300 °C)
1 1 1 for more than 12 h. Then it was heated up to 673 K (400 °C, the constant

1 1 2 experimental temperature) and maintained for 5 h to remove residual
1 1 3 water. All experiments were conducted in an Ar atmosphere
1 1 4 (>99.9995%). The melt temperature was measured with a K-type
1 1 5 thermocouple with a glass sheath.

1 1 6 After the mixed salt was melted, the suspended electrodes were
1 1 7 immersed into the melt. Three types of working electrode were
1 1 8 prepared from Ti rod (Nilaco Corp., ϕ 1.5 mm, 99.5%). First was as
1 1 9 received, second and third were heat-treated for 1 h under 1073 and
1 2 0 1173 K, respectively. **Figure 1 (a)** shows the appearances of prepared
1 2 1 titanium oxide electrodes. On the surface of the heat-treated electrodes,
1 2 2 a white oxide film formed on each. The scanning electron microscope
1 2 3 (SEM) image shown in Fig. 1(b) clearly showed the formation of oxide
1 2 4 film on the surface of the electrode, and the X-ray diffraction (XRD)
1 2 5 pattern of the fabricated electrode (Fig. 1 (c)) identified the oxide film
1 2 6 as mainly TiO_2 . The average thicknesses of the oxide films obtained
1 2 7 from the SEM images increased with the heat-treatment temperature,
1 2 8 namely 0.0, 2.0 and 7.3 μm ; thus, the three samples were named T0.0,
1 2 9 T2.0 and T7.3. The immersion depth of the working electrode was fixed
1 3 0 at 40 mm and the other part of the electrodes was insulated using
1 3 1 protective Al_2O_3 tube as shown in Fig. 1 (a). The counter electrode was
1 3 2 a graphite rod (Toyo Carbon Corp., ϕ 10 mm). An Ag^+/Ag reference
1 3 3 electrode was employed. This electrode, consisted of a silver wire (ϕ
1 3 4 1.0 mm, 99.99%, Nilaco), a LiCl-KCl eutectic melt containing 0.5
1 3 5 mol% AgCl (Wako, 99.5%) and a borosilicate tube, and the silver wire
1 3 6 was immersed in the eutectic melt within the tube. Electrochemical

1 3 7 measurements were performed using an automatic polarization system
 1 3 8 (Hokuto Denko Corp., HZ-5000). The inter-electrode voltage and
 1 3 9 microscope images were synchronized with an error less than 4 μ s by
 1 4 0 using an analogue signal synchronous system (Ditect Co., Ltd., DI-
 1 4 1 SYNC 29N).

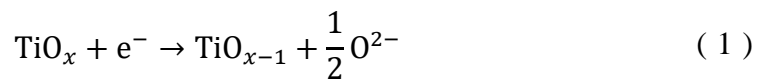


1 4 2 Fig. 1 Titanium oxide electrode previously prepared by heat treatment under air environment. (a):
 1 4 3 Photos of the three, different-thickness titanium oxide electrodes. (b): Scanning electron microscope
 1 4 4 (SEM) image of the T2.0 electrode cross-section. (c): X-ray diffraction (XRD) pattern of electrodes
 1 4 5 before and after heat treatment.

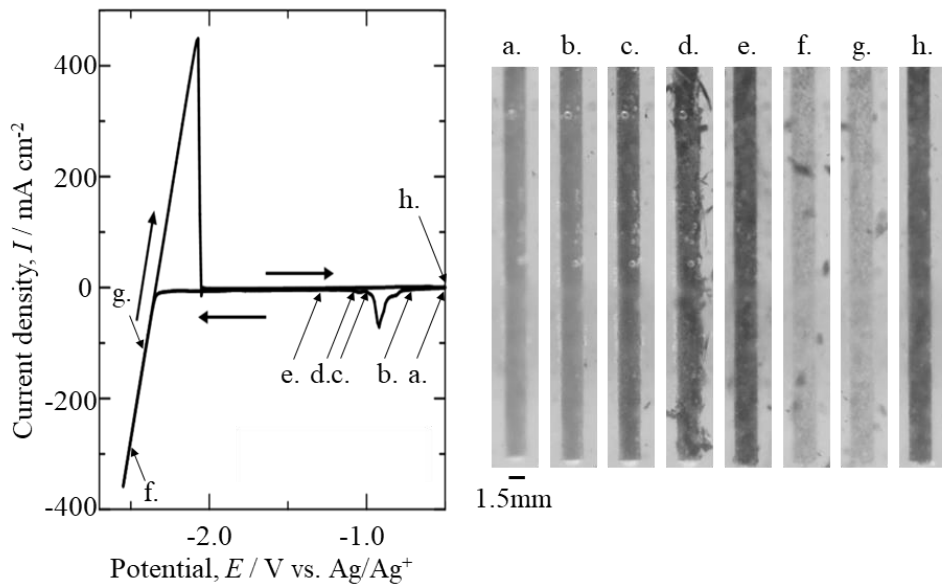
1 4 6

1 4 7 **Figure 2** shows the cyclic voltammogram (CV, scan rate: 10 mV /
 1 4 8 s) obtained by the T7.5 working electrode. Sharp increases in the
 1 4 9 cathodic and corresponding anodic currents compared to the Ag/Ag⁺
 1 5 0 reference electrode were observed at about $E = -2.4$ V. These two
 1 5 1 current changes are thought to be due to the deposition of Li(*l*) and
 1 5 2 the dissolution of the deposits, respectively.^[16] The cathodic current
 1 5 3 at $E = -0.7$ to -1.0 V is the reported reduction potential of the

1 5 4 titanium ion: $\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+}$ ($E = -0.9 \text{ V}$); $\text{Ti}^{3+} + \text{e}^- \rightarrow \text{Ti}^{2+}$ ($E =$
 1 5 5 -1.0 V).^[17] Although the solubility of Li_2O was estimated to be 0.31
 1 5 6 mol% in LiCl-KCl eutectic melt at 673 K (400 °C) ^[8], because of the
 1 5 7 negligible solubility of TiO_2 , the direct electrochemical reduction of
 1 5 8 the TiO_2 following the mechanism of the FFC process described in
 1 5 9 Eq. 1.



1 6 0



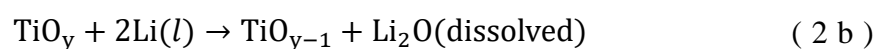
1 6 1 Fig. 2. Cyclic voltammogram and corresponding photographs of T7.5 titanium oxide electrode in
 1 6 2 LiCl-KCl . Images were taken at a: -0.50V, b: -0.70V, c: -1.00V, d: -1.10V, e: -1.30V, f: -2.50V, g: -
 1 6 3 2.45V, h: -0.50V.

1 6 4

1 6 5 With the progress of potential, the appearance of the TiO_2
 1 6 6 electrode changed from white to black as shown in the photos in Fig.
 1 6 7 2a-c. Fig. 2d showed the breakage of the black surface, and small

1 6 8 pieces broke apart from the electrode. At this moment, the current
1 6 9 density became approximately zero, and thus the reactivity of the
1 7 0 electrode surface was lost due to mechanical disconnection. In the
1 7 1 initial stage of potential progression, the deformation of the titanium
1 7 2 oxide occurred due to the volume change with the electrochemical
1 7 3 reduction. Next, the deformed part of the surface was partially peeled
1 7 4 off from the electrode and dispersed into the melt. In Fig. 2f-g, no
1 7 5 metal fog was observed in the Li(*l*) electrodeposition while only silver
1 7 6 white precipitate was observed. According to a previous study ^[10],
1 7 7 when an inactive Mo electrode was used as the working electrode, a
1 7 8 blue metal fog was generated, and the amount of the fog generation
1 7 9 decreased as the amount of oxide ions increased. The metal fog is also
1 8 0 related to the amount of Li(*l*) and the time of the dissolution; however,
1 8 1 it was likely that the oxide ions already existed in the vicinity of the
1 8 2 working electrode due to the titanium oxide reduction.

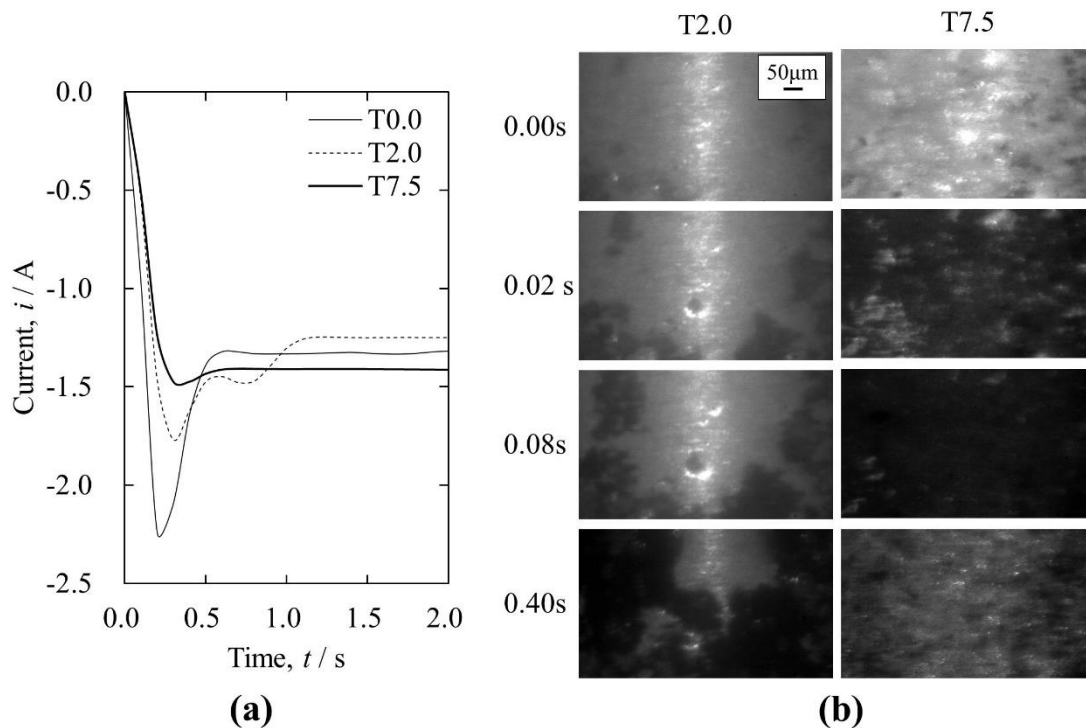
1 8 3 The ratio of the electric charges passing through the anode to
1 8 4 one through the cathode, (q_a/q_c), in the region of $E < -2.0V$ gave a
1 8 5 momentary coulombic efficiency of $q_a/q_c = 0.871$. This showed that the
1 8 6 precipitation of the Li(*l*) advanced the cathodic reaction of the Ti oxide
1 8 7 by the OS process mechanism as described by Eq. 2:



1 8 8 In the CV measurement, mechanical deformation of titanium oxide

1 8 9 occurs during the potential sweep, so it is difficult to know the
1 9 0 behavior of the TiO_2 electrode that corresponds to the $\text{Li}(l)$
1 9 1 electrodeposition potential.

1 9 2 **Figure 3** shows the behavior of the TiO_2 electrode surface obtained
1 9 3 by the high-speed observation during the chronoamperometry
1 9 4 measurement under -2.75 V for 2.000 s . (See also the electronic
1 9 5 supplementary video files for more detailed understanding. Each video
1 9 6 is 6 seconds long.)



1 9 7

1 9 8 Fig. 3. Electro-reduction behavior of T2.0 and T7.3 TiO_2 electrodes observed by chronoamperometry
1 9 9 (at $E = -2.75\text{ V}$). (a): current-time curves, (b): representative photographs of electrode.

2 0 0

2 0 1 After the initial increase, the current converged to the approximately
2 0 2 constant value in all samples. The initial peak current was the largest
2 0 3 at T0.0 and showed a tendency to decrease as the TiO_2 film thickness

2 0 4 increased. The surface of the T2.0 electrode changed from white to
2 0 5 black immediately after the application of potential. This change
2 0 6 proceeded non-uniformly and showed mottled pattern grown from black
2 0 7 spots. The black part was the titanium oxide reduced by the mechanism
2 0 8 of Eq. 1 (or perovskites like LiTiO_2 and LiTi_2O_4 ^[18]). After the
2 0 9 electrolysis at a constant potential, the black-colored titanium oxide
2 1 0 surface was also observed in the CV test.

2 1 1 In the case of the T7.5 electrode, the black surface rapidly developed,
2 1 2 and it became uniform as electrochemical reduction progressed. After
2 1 3 $t = 0.08$ s, the metallic droplets formed, and the metallic liquid spread
2 1 4 onto the cathode surface. This phenomenon indicated that the reduction
2 1 5 reaction of the TiO_x was progressing by the electrochemical deposition
2 1 6 mechanism of Eq. 2a and 2b. After $t = 2.0$ s, all metallic droplets
2 1 7 disappeared, and the black titanium oxide surface remained. To
2 1 8 understand in detail the transient change in the TiO_x structure, our
2 1 9 future work will involve the chemical analysis of the sample.

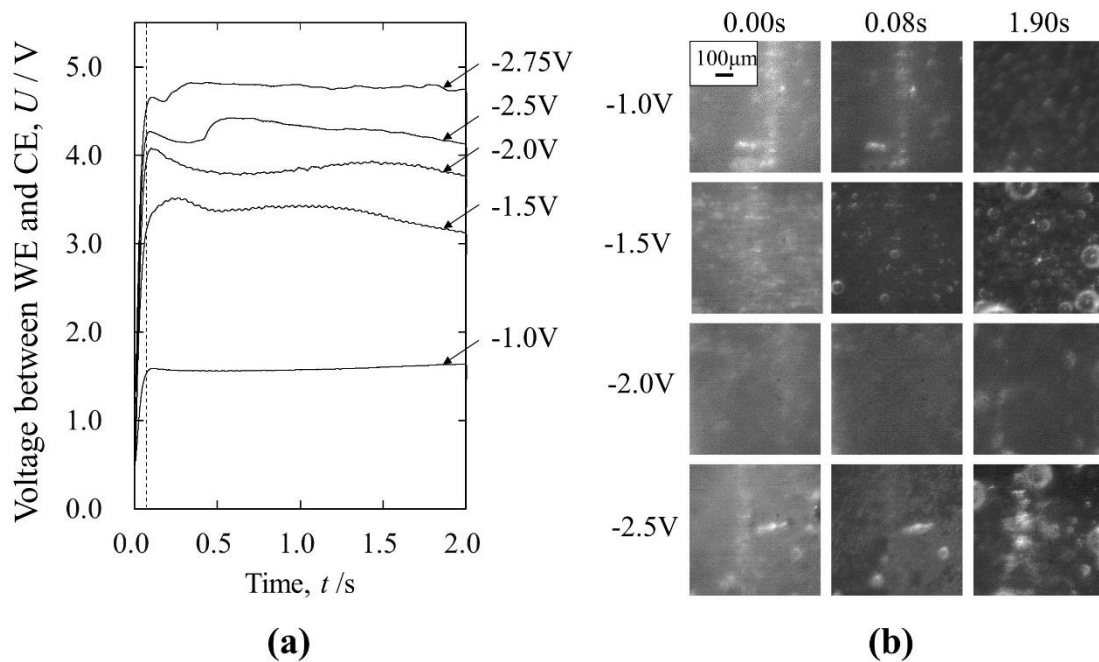
2 2 0 From the differences in behaviors of the T2.0 and T7.5 electrodes,
2 2 1 the following conclusions can be drawn. For the initial TiO_2 with a
2 2 2 high electric resistance, the reduction proceeds by the mechanism of
2 2 3 Eq. 1 and the conductivity increases; this reaction should grow
2 2 4 heterogeneously on the cathode surface. Therefore, after $\text{Li}(l)$
2 2 5 generated in a region having a relatively high conductivity on the
2 2 6 cathode surface, the reaction progresses by spreading over the surface
2 2 7 of the electrode. The T7.5 sample has not only thicker but also more
2 2 8 porous TiO_2 layer than the T2.0 film.^[19,20] The reduction of film TiO_2

2 2 9 did not damage the electrolytic product because of the presence of the
2 3 0 electrochemical reaction interface, i.e. highly conductive Li (*l*) and
2 3 1 molten salt, on the oxide film. Thus, before electrolysis, the molten
2 3 2 salt penetrates into the inside of the porous TiO₂, and the generated
2 3 3 Li(*l*) droplet causes a lower electrical resistance. The reduction of
2 3 4 titanium oxide on the surface progresses by Eq. 2 to wet Li(*l*) on the
2 3 5 entire electrode surface.

2 3 6 Figure 4 shows the voltage behavior between WE and CE, U , and the
2 3 7 observed T2.0-TiO₂ electrode surface under various potentials for
2 3 8 2.000 s. At $E = -1.0$ V, V became almost constant and showed a
2 3 9 maximum at $t = 0.08$ s, but V at $E = -1.5$, -2.0 , and -2.5 V showed
2 4 0 unstable behaviors. As seen in the figure, the color of each electrode
2 4 1 changed to black after the potential was applied. However, when TiO_x
2 4 2 broke locally as shown in Fig. 2, the electrical conductivity of the
2 4 3 electrode became non-uniform. This is the probable reason for voltage
2 4 4 fluctuations. When $E = -2.75$ V, some shiny parts that appear to be Li(*l*)
2 4 5 are found at $t = 1.90$ s. Here, Eq. 1 was the dominant reaction initially,
2 4 6 but Eq. 2 was dominant on some parts of the electrode surface. Once
2 4 7 Li(*l*) is formed, it becomes the current-carrying site and Eq. 2 proceeds
2 4 8 further.

2 4 9 Summarizing, a system was constructed to visualize titanium oxide
2 5 0 reduction based on molten salt electrolysis in order to better
2 5 1 understand its representative interfacial behavior in this study. We
2 5 2 focused on reducing TiO₂ in molten LiCl-KCl eutectic salt at 673 K.
2 5 3 The observed characteristic interfacial behaviors include (1)

2 5 4 mechanical breakage of titanium oxide by the electrochemical
 2 5 5 reduction and dispersion of titanium oxide into the bath, (2) local
 2 5 6 electrochemical reductions at the conductive regions, due to surface
 2 5 7 nonuniformity, and (3) electrodeposited Li(*l*) wetting the titanium
 2 5 8 oxide during the reduction reaction. The results from both the cathode
 2 5 9 interfacial snapshots and the current-time curves suggest that it is
 2 6 0 important to increase the area of the reactive region between the
 2 6 1 titanium oxide and the molten salt for efficient reduction by
 2 6 2 electrodeposited Li(*l*) by avoiding a concentration of Li(*l*).



2 6 3
 2 6 4 Fig. 4. Electro-reduction behavior of T2.0 TiO₂ electrodes observed by chronoamperometry (at
 2 6 5 various potentials). (a): voltage-time curves, (b): representative photographs of electrode.

2 6 6

2 6 7

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2 7 2 of Technology.

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- 3 1 4
- 3 1 5

3 1 6 Captions List

3 1 7

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3 3 1

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