Electrochemical Reduction of TiO_2 in Molten LiCl–Li_2O

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An investigation into the electrochemical reduction of TiO_2 to Ti in molten LiCl–Li_2O has been performed. Analysis of the time-dependent changes of a phase composition shows that the reduction proceeds through lithium-containing intermediates consisting of $LiTi_2O_4$ and $LiTiO_2$. The reduction of TiO_2 in molten LiCl–Li_2O allows a much lower reaction temperature compared to the conventional reduction process in molten $CaCl_2$.

Over the recent past, the development of an electrochemical reduction technique using molten salts has been pursued intensively, particularly for the reduction of TiO_2 to Ti.[1–8] In an electrochemical reduction of TiO_2, usually molten $CaCl_2$ at 850 °C is employed as the electrolyte. Also, there is a report for the electrochemical reduction of TiO_2 to Ti in LiCl–KCl–$CaCl_2$ eutectic melt at 450 °C though the slow diffusivity of oxide species in the solid phase at lower temperatures may be disadvantages for mass production of Ti metal.[8] As a part of research efforts for the treatment of spent nuclear fuel, the electrochemical reduction of uranium oxides in molten LiCl–Li_2O at 650 °C has been studied, and the reduction of U_3O_8 to U metal was achieved with a more than 99% conversion.[9] The molten LiCl–Li_2O system can be applied to the electrochemical reduction of TiO_2 since LiCl is stable over the voltage range for the electrochemical reduction of TiO_2 and has a high oxide ion solubility, which was measured as 8.8 wt % of Li_2O in LiCl at 650 °C.[10] The report for the electrochemical synthesis of lithium titanate showed that the constant voltage electrolysis (1.2–3.2 V) of TiO_2 in pure molten LiCl only resulted in the formation of lithium titanate compounds, even at 700 °C.[11] Here, we report on Ti production in molten LiCl–Li_2O, with the expectation of the promotion of TiO_2 reduction by in situ electrolysis of Li_2O. This study provides a valuable insight into the reaction mechanism and its dependency on the Li_2O in the system. The experimental approach consists of the investigation of partially reduced specimens and measurement of the Li_2O concentration during the reduction reaction.

The electrochemical experiments were performed in a vertical tubular stainless steel reactor with a magnesia crucible that served as the reaction vessel. The upper end of the reactor was equipped with feedthroughs for the electrode leads, gas inlet and outlet, and a thermocouple as well as a sampling port. The interior of the reactor was continuously purged with argon. In this experimental set-up, the TiO_2 powder (Showa, rutile, 99%, 5.0 g) kept in a porous magnesia holder was made the cathode in a electrolytic cell and charged into molten LiCl (Alpa, 99%)–Li_2O (Cerac, 99.5%) at 650 °C. The porous magnesia holder enables the molten salt to readily migrate through the cathode assembly. Electric contact to the cathode was through a stainless steel rod. Each experiment was performed with a computer-controlled potentiostat/galvanostat (Won-A-tech, WPG100), and a constant current (1.2 A) versus time was applied. Pt rods were used for an anode and a pseudo-reference electrode. In order to produce partially reduced titanium oxides, the electrochemical reduction was interrupted after different reaction times. The recovered samples were thoroughly rinsed with distilled water and then methanol to remove the residual salts, and vacuum drying was applied at around 25 °C. Phase composition of the various specimens was determined through X-ray powder diffraction (XRD). XRD patternes were collected on a Rigaku MiniFlex diffractometer with a monochromatic Cu Kα radiation ($\lambda = 0.15405$ nm), at a scan rate of 4 deg/min. Micrographic analysis was performed with a SEM system (Jeol, JXA 8600). During the electrochemical reduction experiments, the samples of the electrolyte were collected and titrated by using 0.1 M HCl and a phenolphthalein indicator to measure the Li_2O concentration in LiCl.

Figure 1 shows typical potential–time curves, which were recorded during the chronopontentiometry experiments. The operation voltage is lower than the thermodynamic decomposition potential of LiCl, -3.46 V but higher than the decomposition potential of Li_2O, -2.47 V. It should be emphasized that the nonconducting magnesia holder in the cathode assembly can confine the in situ generated Li inside the magnesia holder. In the earlier stages of the electrochemical reduction, the decrease of the Li_2O concentration was in accordance with Faraday's law of an electrolysis. On the other, the decrease rate of the Li_2O concentration was slowed in the later stages of the reaction.

The samples for the XRD and SEM analyses were prepared by withdrawing the cathode from the electrolytic cell when the value of the electric charge that passed through the cell was about 10378 C, 22518 C, and 33552 C. Samples quenched after 10378 C of current passage were found to consist predominantly

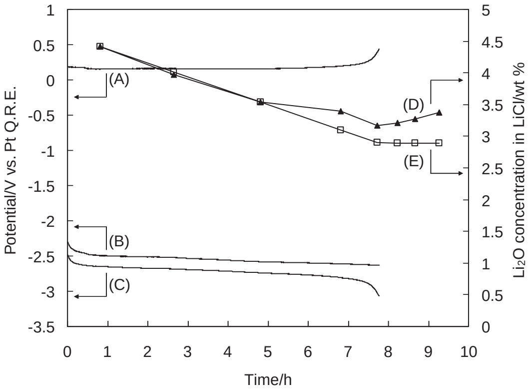

Figure 1. Variations of the anode (A), cathode (B), and cell (C) potential during a chronopotentiometry experiment in molten LiCl–Li_2O. The observed Li_2O concentration in LiCl was denoted by (D). (E) means the calculated Li_2O concentration in LiCl values according to supplied charge.

of $LiTiO_2$ and a small amount of $LiTi_2O_4$. Samples recovered after 22518 C of current passage were primarily composed of $LiTiO_2$. After about 33552 C of current passage, this value was about 139% of the theoretical electric charge necessary for reducing 5 g of TiO_2, the X-ray diffraction spectra obtained were those of Ti metal. The significant evolution of the hydrogen gas by hydration of this sample with the molten salt in water suggests that a large amount of Li accumulation occurs inside the magnesia holder.

The experimental results obtained in the present study provide strong evidence that the electrochemical reduction of TiO_2 to Ti metal in molten LiCl–Li_2O proceeds through lithium-containing intermediates, and we could propose the following mechanism. This electrochemical reaction commences with the formation of Li metal and then incorporation of Li metal into the titanium compounds with a change of the Ti oxidation states from +4 finally to +0. It should be noted that except for reaction (1), the other cathode reactions are chemically driven. And except for reaction (4), the cathode reactions do not involve the liberation of an oxide ion. From the proposed mechanism, the change of the Li_2O concentration during the electrochemical reduction reaction can be explained. While the formation of lithium titanates with Li metal was ongoing, the liberation of oxide ion from the cathode could not occur. Therefore, the decrease of the Li_2O concentration in molten LiCl was in accordance with Faraday's law of an electrolysis in the earlier stages of the electrochemical reduction. On the other, when the compound formation had ceased in the later stages of the electrochemical reduction, the generation of oxide ion through reaction (4) becomes the predominant process causing the slowing down of the decrease rate of the Li_2O concentration. After stopping a supply of the electric energy, the increase of the Li_2O concentration in a bulk electrolyte was observed suggesting the accumulation of oxide ions inside the magnesia holder. The anodic reaction is the generation of oxygen gas (reaction (5)). Under theses conditions, the overall reaction is the reduction of Ti^{4+} to Ti at the cathode and the evolution of oxygen gas at the anode.

$$Li^+ + e^- = Li \tag{1}$$

$$Li + 2TiO_2 = LiTi_2O_4 \tag{2}$$

$$LiTi_2O_4 + Li = 2LiTiO_2 \tag{3}$$

$$LiTiO_2 + 3Li = 4Li^+ + Ti + 2O^{2-} \tag{4}$$

$$1/2O_2 + 2e^- = O^{2-} \tag{5}$$

The samples analyzed by XRD were also subjected to SEM analysis (Figure 2). As is visible in Figure 2A, the particle size of the TiO_2 powder, the starting material, is around 0.2 µm and rather uniform. Figure 2B illustrates the microstructure of the sample which is composed of $LiTi_2O_4$ and $LiTiO_2$. Particles are coarse and heterogeneous with an average particle size above 0.2 µm. The $LiTiO_2$ shown in Figure 2C emerges in the form of sintered grains. Figure 2D shows the microstructure of the Ti metal. The grain of the particles reduces in size, and the overall appearance is similar to coral and a little similar to that of Figure 2C. At this point, it should be mentioned that only the major phases of the sample could be identified in the XRD analysis. Therefore, small amounts of Ti in the sample for Figure 2C might not be detected by XRD. The unique coral-like structure with the surfaces covered with Ti metal flakes (Figure 2D) is different from the Ti sponge produced by a direct electrochemical reduction in molten $CaCl$.[4]

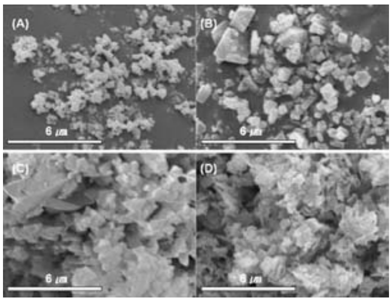

Figure 2. SEM image TiO_2 (A), the starting material, as well as those of samples collected after the value of the electric charge that passed through the cell was about 10378 C (B), 22518 C (C), and 33552 C (D).

In summary, we were able to reduce TiO_2 to Ti by using, for the first time, a molten LiCl–Li_2O electrolyte. Analysis of the reaction mechanism proved that the reaction advances through a chemically driven reduction by Li metal uptake inside the magnesia holder. This approach using in situ generation of Li can be applied to produce other metals from their respective oxides in molten LiCl–Li_2O.

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