Preparation of Plate-shaped Crystals of Li_2MnO_3 by Reaction at a Solid/LiCl-Flux/Air Interface in a Tilted Crucible

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Plate-shaped crystals of Li_2MnO_3, red-colored with glossy surface, were obtained over a tilted crucible by LiCl flux evaporation at 923 K for 5 days. The growth of the Li_2MnO_3 crystal plates proceeded at the interface of three phases, i.e. the LiCl flux, the precipitated powder, and the atmosphere on the tilted crucible. The moving solid-liquid-air interface due to the continuous evaporation of LiCl flux plays an important role in the growth of Li_2MnO_3 crystal plate.

Manganese oxide compounds with layered or tunnel structures have attracted attention because of their applications as selective adsorbents,[1-3] cathode materials for advanced lithium batteries.[4,5] Since monoclinic Li_2MnO_3 has a rock salt structure similar to layered $LiCoO_2$ and a higher lithium content per unit weight (17.1 mmol/g) than other manganese oxides, it has attracted attention as a high capacity material for lithium adsorption or for a lithium rechargeable battery. In addition, Li_2MnO_3 is a promising precursor for the preparation of cathode materials.[6,7]

A single crystal of lithium manganese oxide is attractive from both the fundamental and applicable standpoints. It is suitable as a model compound for studying the solid-state diffusion of Li^+, and it is also expected to be a good precursor for cathode materials with high energy density and stability. A flux synthesis is a promising method for the preparation of well-crystallized oxide materials. Strobel et al. have first synthesized large crystals of Li_2MnO_3 from a LiCl flux and refined its structure.[8,9] Crystal growth in the flux method progresses in the melt by the dissolution-recrystallization mechanism. Therefore, the crystal growth of Li_2MnO_3 may progress mainly at the step of slow cooling, owing to the decrease of the solubility of manganese.

We are interested in a solid/flux/air interface as a reaction field for the preparation of new functional materials. The present paper describes a novel method to prepare plate-shaped Li_2MnO_3 crystals in the moving solid/LiCl-flux/air interface which is formed by the continuous evaporation of LiCl melts in a titled crucible. It has been well known that crystal growth on an interface progresses most readily because of a heterogeneous nucleation.[10] Generally, crystallization at the interface is not preferred in the flux synthesis, since it causes the impurity of crystals or prevents the formation of large crystal. However, the present results show that the solid/LiCl-flux/air interface is an attractive and effective field for the preparation of plate-like crystal. The crucible with large bottom space was used in order to increase the active interface area. In addition, we proposed to slant the crucible for continuous crystallization in the moving solid/LiCl-flux/air interface. A tilted crucible formed a solid/liquid/air interface of three phases, the LiCl flux, the precipitated powder, and the atmosphere, where Li_2MnO_3 crystal plates could be grown. The moving solid/liquid/air interface due to the continuous evaporation of LiCl flux encouraged crystal growth in the direction in which the interface moves.

A mixture of anhydrous LiCl (12.0 g) and γ-MnOOH (1.5 g) was placed uniformly in a high purity rectangular alumina crucible with a size of 80 mm(L) x 80 mm(D) x 40 mm(H). The crucible was set at a slant in an atmosphere-controlled electric furnace. The slope (β) of the crucible was set mainly at 8^o for preparation of large crystal plates. The crucible was heated to 923 K to melt the LiCl while introducing air at a flow rate of 400 cm^3/min. LiCl flux was evaporated slowly at 923 K and was completely evaporated by heating for 5 days. The crystal plates were formed on the surface of the tilted crucible during the heating. The crystal plate obtained was immersed in distilled water, filtered, washed and dried at 348 K. Lithium and manganese contents of the Li_2MnO_3 crystal plates were determined by inductively coupled plasma (ICP) spectroscopy after dissolving it in a mixed solution of HCl and H_2O_2. X-Ray diffraction (XRD) analysis and scanning electron microscope (SEM) observation were carried out conventionally with a Rigaku type RINT1200 X-ray diffractometer and Hitachi type S-2460N electron microscope, respectively.

The Li_2MnO_3 crystal plates, red-colored with a glossy surface, were formed over the tilted crucible. The yield of the plate with a size greater than 0.1×0.1 mm^2 exceeded 20 wt% of the total product of lithium manganese oxide. The SEM photograph of a typical plate shows that it has a multilateral form with a thickness of about 30 μm (Figure 1 top). The lithium and manganese contents of the Li_2MnO_3 crystal plates were 17.4 and 8.6 mmol/g, respectively. The chemical formula was calculated as $Li_{2.0}MnO_{3.0}$ on the basis of the chemical analysis result, which is consistent with the theoretical formula for Li_2MnO_3. XRD pattern of the Li_2MnO_3 crystal plate was obtained by pasting it on a glass holder (Figure 1 bottom). Only three peaks were observed at 2θ = 18.7, 37.9, and 58.3 degrees. The peaks correspond to the (*0 0 i*) (*i* = 1, 2, 3) reflections of Li_2MnO_3 crystal, indicating that the present Li_2MnO_3 plate forms a layered structure.[9] This shows that the Li_2MnO_3 has a high degree of crystal orientation with its c axis along the plane of the Li_2MnO_3 plate. Li_2MnO_3 has a rock salt structure with a close-packed oxygen anion array in which layers of Li atoms and layers of the mixture of Li and Mn atoms (Li:Mn = 2:1) alternate with one another along the c axis direction.[12] Since the plane of the plate is orthogonal with the c axis, the Li and (Li + Mn) layers are arranged parallel to the plane of the plate.

The process of plate formation was studied through the observation of particles obtained by heating for 4 hours and 3 days. Only a black-colored powder was obtained after 4-hour heating, and XRD analysis indicates that the crystal system is identical to that of spinel-type $LiMn^{III}Mn^{IV}O_4$ with a small portion of Mn_2O_3. This shows that spinel type $LiMn^{III}Mn^{IV}O_4$ is

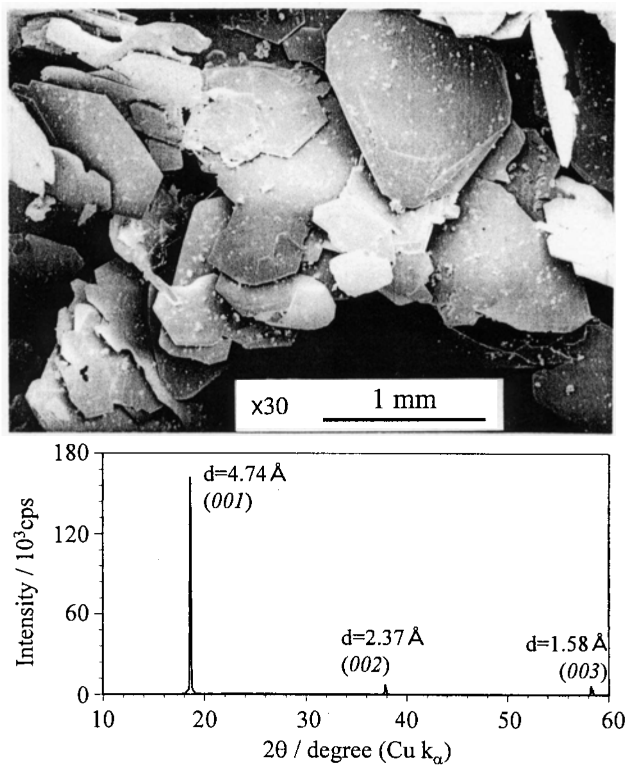

Figure 1. SEM photograph (top) and XRD pattern (bottom) of the Li_2MnO_3 crystal plates.

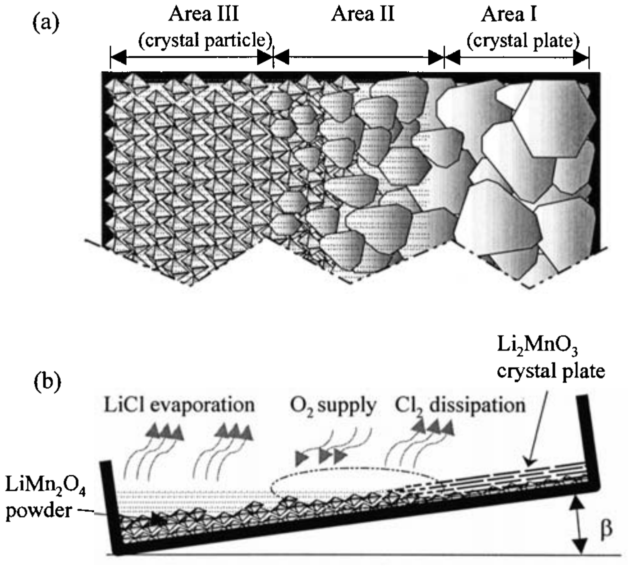

Figure 2. Schematic representation on the formation of the Li_2MnO_3 crystal plate in a tilted crucible heated at 923 K for 3 days.

formed in the initial reaction at 923K. The appearance of the crucible after 3-day heating is illustrated in Figure 2. Three different regions were observed clearly in the crucible. Larger crystal plates were formed at the upper part of the tilted crucible (Figure 2, Area I) in which the LiCl flux was evaporated completely. Only crystal particles of a black color were formed at the lower part of the tilted crucible (Figure 2, Area III), and they were covered by the remaining LiCl flux. The XRD analysis showed that the main component of the particles was spinel type $LiMn_2O_4$, with small portions of Li_2MnO_3. Area II in Figure 2 corresponds to the solid-liquid-air interface of the three phases, the LiCl flux, the precipitated powder, and the atmosphere. Crystal plates of a small size formed in this area. They can be ascribed to the particles in the middle of plate growth. The appearance of the tilted crucible suggested that the growth of the Li_2MnO_3 crystal plate progresses at the three-phases interface.

The chemical reactions which occurred in the LiCl flux can be written by the following two equations.

Initial stage:

$$8Mn^{III}OOH + 4LiCl + O_2 = 4LiMn^{III}Mn^{IV}O_4 + 4HCl + 2H_2O \quad (1)$$

Subsequent reaction:

$$2LiMn^{III}Mn^{IV}O_4 + 6LiCl + 2O_2 \;=\; 4Li_2MnO_3 + 3Cl_2 \quad (2)$$

We observed the evolution of HCl gas at the initial stage of reaction, and the evolution of Cl_2 gas in the subsequent reaction. Equation 2 progresses by the manganese dissolution of $LiMn_2O_4$ to the LiCl flux followed by recrystallization to Li_2MnO_3 accompanied by the oxidation of Mn(III). Strobel et al. have pointed out that the limited nucleation due to the very low oxide concentration in the flux as well as the slow oxygen diffusion of O^{2-} ions in the melts causes the formation of large Li_2MnO_3 crystals.[8] The present results show that the oxidation of chloride ions as well as the supply of oxygen is essential for the formation of Li_2MnO_3 plates.

The solid-flux-atmosphere interface is suitable for the crystallization of Li_2MnO_3, because the evaporation of LiCl flux is fast and the O_2 supply and Cl_2 dissipation are easy, as shown in Figure 2b. The high degree of supersaturation of manganese, due to the fast evaporation of the LiCl flux, facilitates the growth of the Li_2MnO_3 crystals at the interface, accompanied by the oxidation of Mn^{3+} to Mn^{4+} with atmospheric oxygen. In addition, the present interface has the ability to move continuously owing to the evaporation of LiCl flux. This may encourage the formation of Li_2MnO_3 plate along the surface of the crucible; the continuous evaporation may promote the crystal growth in the direction in which the interface moves.

In conclusion, flux evaporation in a tilted crucible is a unique method for the preparation of Li_2MnO_3 crystal plate. The moving solid-flux-atmosphere interface plays an important role in the formation of oxide plate.

References and Notes

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