Novel Spinel Oxide $Li_{4/3}Ti_{5/3}O_4$ as Electrochemical Insertion Materials for Rechargeable Lithium Batteries

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We firstly claim that the unique performance of $Li_{4/3}Ti_{5/3}O_4$ as electrochemical materials in terms of a flat potential and an infinitesimal structural change is caused by a cation ordering of Li^+ and Ti^{4+} at 16d sites in the spinel superstructure.

Rechargeable lithium batteries are very attractive as one of advanced type batteries, so that many researchers have investigated them from various view points. The development of cathode materials is one of serious problems to realize high rechargeability and large capacity of such a battery. Therefore, many kinds of cathode materials have been proposed using inorganic and organic compounds. Specially, transition metal oxides have been extensively investigated as the most promising candidates among various cathode materials. Recently, some transition metal oxides, such as $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$, have been investigated and applied to commercial lithium batteries.[1-9] On the other hand, some of transition metal oxides have been utilized to anode materials of rechargeable lithium batteries. $Li_{4/3}Ti_{5/3}O_4$ has been studied as an anode material to find a very unique electrochemical and structural characteristics.[10-16] However, its insertion electrochemistry has not been clarified, yet. This compound is a cubic spinel structure which space group is assigned to Fd3m. Usually, two different sites in spinel structure are occupied by more than two kinds of metal ions. In the case of $Li_{4/3}Ti_{5/3}O_4$, tetrahedral sites are occupied by Li^+ ions and octahedral sites are occupied by both Li^+ and Ti^{4+} ions. If Li^+ ions and Ti^{4+} ions are arranged in octahedral sites according to a regular cation ordering, its crystal structure is different from a disordered normal spinel. Such an atomic arrangement may influence the insertion (or extraction) electrochemistry for spinel oxides. In this study, we found a relationship between a unique solid state electrochemical characteristics and a regular atomic arrangement.

$Li_{4/3}Ti_{5/3}O_4$ was prepared by heating a mixture of anatase type TiO_2 and LiOH with a molar ratio of 5:4 at 750 °C for 24 h. The crystal structure of the prepared $Li_{4/3}Ti_{5/3}O_4$ was analyzed by an x-ray diffraction method with Cu kα line. Figure 1 shows the X-ray diffraction pattern of $Li_{4/3}Ti_{5/3}O_4$. Peaks observed in 2θ range from 100° to 10° were in good agreement with those for $Li_{4/3}Ti_{5/3}O_4$ having a spinel structure. The x-ray diffraction pattern was well understood by a spinel type crystal structure having Fd3m space group. From this result, it is concluded that the crystal structure of $Li_{4/3}Ti_{5/3}O_4$ prepared in this study is a cubic spinel. A similar x-ray diffraction pattern has been reported in some references.[9, 11] However, the x-ray diffraction patterns in 2θ range less than 10° have never been reported. In this study, we analyzed the x-ray diffraction pattern in such low 2θ range, as shown in Figure 1 (b). Two clear peaks were observed in 2θ range from 10° to 3° and their mirror indexes were assigned to (1/2 1/2 1/2) and (1/3 1/3 1/3), respectively. These peaks indicate that a regular atomic arrangement over a unit cell is present in $Li_{4/3}Ti_{5/3}O_4$ prepared in this study. Another peak appeared at around 3.5°, but its intensity was so weak that an certainty was included in the determination of

this mirror index. Therefore, the exact superstructure existing in $Li_{4/3}Ti_{5/3}O_4$ could not be determined only from this x-ray diffraction pattern. But, from the chemical composition of this compound, it might be expected that Li^+ ions and Ti^{4+} ions in 16d sites has a regular atomic arrangement. These peaks observed in the low 2θ angle range have never been reported before. This report firstly suggests that $Li_{4/3}Ti_{5/3}O_4$ may have a superstructure.

This material has interstitial sites for Li^+ ions, which are 16c sites. When the electrochemical reduction of $Li_{4/3}Ti_{5/3}O_4$ takes place in nonaqueous media, Li^+ ions are inserted into these 16c sites. When 16d sites are occupied by Li^+ ions and Ti^{4+} ions without any regular arrangement, all 16c sites are equivalent with each other. However, the $Li_{4/3}Ti_{5/3}O_4$ prepared in this study has a regular atomic arrangement, so that 16c sites are distinguished by the kind of cation at 16d sites. It can be easily considered that 16c sites neighboring to 16d sites occupied by Li^+ ions are more preferable for the occupation by Li^+ ions inserted during an electrochemical reduction of $Li_{4/3}Ti_{5/3}O_4$. If Li^+ and Ti^{4+} occupied 16d sites in the regular atomic arrangement according to chemical composition of $Li_{8a}[(Li_{1/3}Ti_{5/3})_{16d}(\square)_{16c}]O_4$, a half of 16c sites are neighboring sites to the 16d site occupied by only Ti^{4+} ion. This regular atomic arrangement may a provide different discharge and charge characteristics from disordered materials.

In order to see such an effect of a regular atomic arrangement of $Li_{4/3}Ti_{5/3}O_4$ on an electrochemical behavior, the following electrochemical reduction and oxidation cycle test was performed using a standard three electrodes cell. Propylene carbonate containing 1.0 mol dm^{-3} $LiClO_4$ was used as an electrolyte and
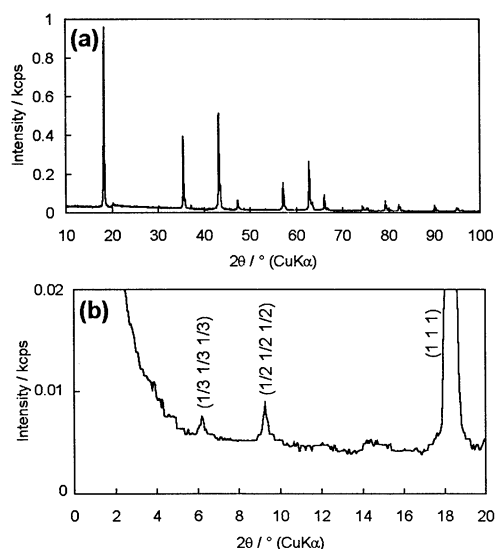
Figure 1. X-ray diffraction pattern of $Li_{4/3}Ti_{5/3}O_4$ prepared from TiO_2 and LiOH, mirror index are also shown in this figure, (a) in 2θ range from 100° to 10°, (b) in 2θ range from 10° to 0°, x-ray pattern was obtained using Cu Kα line with a graphite monochrometer.
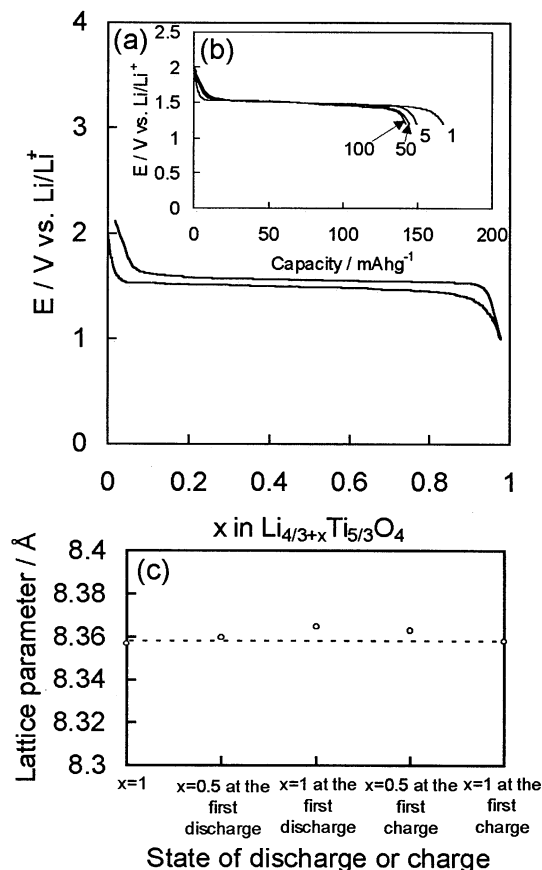
Figure 2. (a) : Discharge and charge curves of $Li_{4/3}Ti_{5/3}O_4$ prepared in this study in propylene carbonate containing 1.0 mol dm^{-3} $LiClO_4$ at 0.5 mA cm^{-2} at the 1st discharge and charge cycle. (b) : Discharge curves at 1st, 5th, 50th, and 100th cycles. (c) : lattice constant change during lithium insertion and extraction cycle. These were obtained from results of Rietveld analysis for x-ray diffraction patterns at various stages of discharge and charge cycle.

lithium metal was used as the counter and reference electrodes. This experiment was conducted in an argon dry atmosphere at ambient temperature. Figure 2 (a) shows the discharge and charge curves of $Li_{4/3}Ti_{5/3}O_4$ in propylene carbonate containing 1.0 mol dm^{-3} $LiClO_4$ at 0.5 mA cm^{-2}. The electrode potential changes were very flat and the difference in the electrode potential changes during the electrochemical reduction and oxidation cycle were very small. The capacity for the electrochemical reduction at the hundred cycle was slightly shorter than that at the first cycle, as shown in Figure 2 (b). From these results, it can be said that $Li_{4/3}Ti_{5/3}O_4$ prepared in this study exhibits a high rechargeability and a fast kinetics for the discharge and charge processes. In general, the structural change of cathode materials takes place during the discharge and charge cycles. In some cases, such a structural change causes a decrease of discharge capacity with cycles. The discharged or charged $Li_{4/3}Ti_{5/3}O_4$ samples were analyzed by an x-ray diffraction pattern. However, the x-ray diffraction pattern did not change during the discharge and charge cycle, significantly. Figure 2 (c) shows the lattice constant change during the discharge and charge cycle which was obtained from the x-ray diffraction patterns at various discharge and charge stages. This infinitesimal structural change is inconsistent with the flat potential changes at discharge and charge processes which are usually observed for a two-phase reaction.[3, 17-19] This may be due to a regular atomic arrangement. The insertion or extraction of lithium into/from host matrix in a regular manner

may show a different feature which is caused by an effect of a cation ordering on an entropy term of the ion insertion (or extraction) process.[20] If Li^+ ions insert in a classified site of a host matrix, the electrochemical behavior is influenced by the ordered Li^+ ions. Probably, this type of atomic arrangement may lead to an decrease in an entropy change of host matrix produced by an insertion of Li^+ ions. Since an electrode potential corresponds to a free energy change of a host matrix, such a entropy change may result in the apparently constant free energy during lithium insertion or extraction. Perhaps, the flat potential may be explained by the ordering effect of Li^+ ions. [20] The similar behavior has been reported in literature dealing with the intercalation of alkali metal ions into graphite structure.

Thus, $Li_{4/3}Ti_{5/3}O_4$ is very attractive as insertion materials for rechargeable lithium batteries. This is mainly related to a regular atomic arrangement which provides ideal insertion and extraction processes. If it is true, other spinel compounds having a superstructure would also exhibit a very interesting behavior.

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