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Short communication

Mechanism of Li-doping into $Li_4Ti_5O_{12}$ negative active material for Li-ion cells by new chemical method

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Abstract

$Li_{4+X}Ti_5O_{12}$ ($X > 0$) negative active material has been successfully synthesized by a new chemical method for Li-doping with the catalytic function of naphthalene in Li-organic complex solution of butylmethylether (BME) or dimethoxyethane (DME) solvent. The Li-doping reaction rate constant in BME was found to be greater than that of the case of DME and its value was 5.10 and $2.78 \times 10^{-4}\ S^{-1/2}$, respectively, by the calculation from the slope of distinct straight line in the relationship between $\ln(1/1 - Y)$ and $\sqrt{t}$, where Y is molar fraction of Li-doping materials of $Li_7Ti_5O_{12}$.

Keywords: $Li_{4+X}Ti_5O_{12}$ ($X > 0$); $Li_4Ti_5O_{12}$; Chemical method; Li-organic complex solution; Naphthalene; Li-ion cells

1. Introduction

Lithium titanium oxide such as $Li_4Ti_5O_{12}$, TiO_2, and $LiTi_2O_4$ has been extensively studied as negative active material for Li-ion cells [1–9]. The $Li_4Ti_5O_{12}$ negative active material, which has theoretical capacity of 175 mAh g^{-1} with potential plateau at around 1.55 V versus Li/Li$^+$, has been recently focused to realize Li-ion cells with excellent cycle performance because of its small volume change in the charge and discharge process with very small initial irreversible capacity [10–12]. $Li_{4+X}Ti_5O_{12}$ ($X > 0$) in the charged state of the $Li_4Ti_5O_{12}$ will be capable for the combination of non-lithiated positive active material such as NiOOH [13,14], FeOOH [15,16], and MnO_2 [17,18], which are expected to be promising candidate as an alternative to current $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ for high capacity and low cost materials. The new synthesis method of $Li_{4+X}Ti_5O_{12}$ ($X > 0$) was, therefore, strongly demanded for the realization of new Li-ion system with above-mentioned non-lithiated positive active materials. We have successfully synthesized the $Li_{4+X}Ti_5O_{12}$ ($X > 0$) by a new chemical method with immersion of $Li_4Ti_5O_{12}$ starting material at room temperature into Li-organic complex solution obtained by dissolving metallic Li and naphthalene in BME or DME solvent. In this report, the newly developed chemical method will be described with the detailed mechanism of Li-doping process according to the consideration on the chemical reaction rate by the measurement of electrochemical properties of the electrode together with results of X-ray diffraction analysis.

2. Experimental

The $Li_4Ti_5O_{12}$ negative electrode was prepared as follows. First, the commercially available $Li_4Ti_5O_{12}$ active material powder, acetylene black as an electro-conductive material, and poly-vinylidene fluoride as a binder were mixed in the mass ratios of 80:5:15 with *N*-methyl-2-pyrrolidone solvent to prepare a slurry. The slurry was loaded in a foamed Ni substrate with area of 2 cm^2 as a current collector to prevent from pealing off the active material in Li-doping process. The loading mass amount of active material was controlled to 18 mg cm^{-2} in any electrode after drying at 150 °C for 5 h

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in a vacuum. The $Li_4Ti_5O_{12}$ electrode was then immersed at room temperature with different time into Li-organic complex solution of 10 cm^3, which was obtained by dissolving metallic Li together with naphthalene into BME or DME solvent. The metallic Li packed with porous polyethylene film was used to prevent the contact of Li with the test electrode during Li-doping process. The electrode after this process was finally rinsed with dimethyl carbonate to remove the remained solution. The immersing and washing processes of electrode were conducted in an argon-filled grove box.

Li^+ ion concentration in the Li-organic complex solution was determined by inductively coupled plasma analysis using Thermo Tarrell Ash IRIS/AP. The crystalline structure of product sample was identified by X-ray diffraction (XRD) with Cu Kα radiation using Rigaku RINT 2400 after covered with polypropylene film to prevent the evolved oxidation reaction with air. The open-circuit potential and charge–discharge characteristics of test electrodes treated by using the Li-organic complex solution containing 0.25 mol dm^{-3} naphthalene were investigated by using a three-terminal test cell with metallic Li foil as counter and reference electrodes in the electrolyte of ethylene carbonate and diethyl carbonate mixed solution containing 1.0 mol dm^{-3} $LiClO_4$. The open-circuit potential of test electrode was measured after 30 h rest after the cell fabrication and its discharge test was then conducted. The electrode was discharged to 3.0 V versus Li/Li^+ at the current density of 0.028 A g^{-1}. The measurement of $Li_4Ti_5O_{12}$ electrode with no Li-doping was charged down to 1.0 V versus Li/Li^+ at the beginning and then discharged to 3.0 V versus Li/Li^+ at the same current density of 0.028 A g^{-1}.

3. Results and discussion

Li^+ ion concentration in the Li-organic complex solution was investigated using different solvents as a function of amount of naphthalene. The change in Li^+ ion saturated concentration of the Li-organic complex solution with BME and DME solvents is shown in Fig. 1. The value of Li^+ ion concentration for BME is found to be drastically increased compared with the case of DME. The value of the former becomes to be saturated at around 0.2 mol dm^{-3} beyond 0.1 mol dm^{-3} naphthalene concentration, but for the latter case, the value tends to be increased gradually still beyond the naphthalene concentration of 0.5 mol dm^{-3} and its value is only 0.12 mol dm^{-3}. The reason of high value for BME is considered to be that Li^+ ion in BME solvent becomes to be more solvated because of its polarity with the asymmetric structure than that in DME with its symmetric structure. That is to say, Li^+ ion concentration is controllable by the selection of appropriate solvent and amount of naphthalene.

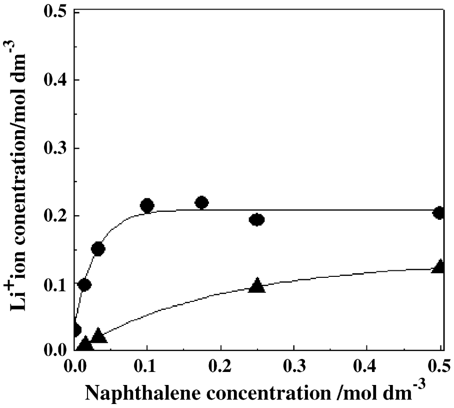

Fig. 1. Effect of naphthalene concentration on saturated Li^+ ion concentration of Li-organic complex solution with (●) BME or (▲) DME solvent.

The change in open-circuit potential of $Li_4Ti_5O_{12}$ electrode is shown in Fig. 2 as a function of immersion time in the Li-organic complex solution of BME or DME solvent. The open-circuit potential is found to be drastically decreased at the beginning of immersion for both cases. The potential in BME and DME was reached to the constant value of 0.20 and 0.38 V versus Li/Li^+ after 10 h immersion time, respectively. This result shows that the reduction reaction of Li-doping into $Li_4Ti_5O_{12}$ proceeds with the immersion time in Li-organic complex solution. The change of potential behavior by the different solvents is also considered to be due to the above-mentioned effect of Li^+ ion interaction with kinds of solvents.

XRD patterns of $Li_4Ti_5O_{12}$ electrodes with immersion time of 0.00, 0.17, and 3.00 h in the Li-organic complex solution of BME are shown in Fig. 3. The sharp peaks assigned to spinel $Li_4Ti_5O_{12}$ with a face-centered cubic lattice are clearly confirmed on the sample of electrode before Li-doping process. The peak position with immersion time is found to have no change, while the intensity is decreased slightly with its immersion time. This means that Li^+ ion is clearly doped into $Li_4Ti_5O_{12}$ with the immersion in Li-organic complex solution.

The charge and discharge characteristics of $Li_4Ti_5O_{12}$ electrode after Li-doping process are shown in Fig. 4. The electrode shows very flat potential plateau at around 1.55 V Li/Li^+. The corresponding reaction is expressed by one elec-

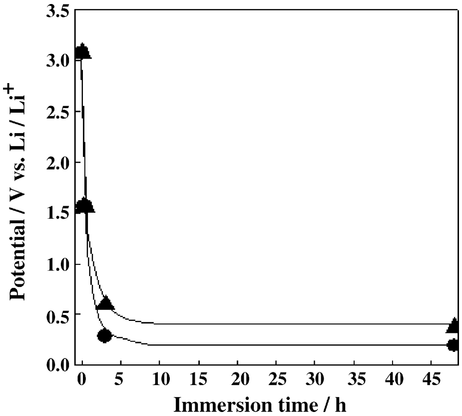

Fig. 2. Change in open-circuit potential of $Li_4Ti_5O_{12}$ electrode as a function of immersion time in Li-organic complex solution with (●) BME or (▲) DME solvent containing 0.25 mol dm^{-3} naphthalene.

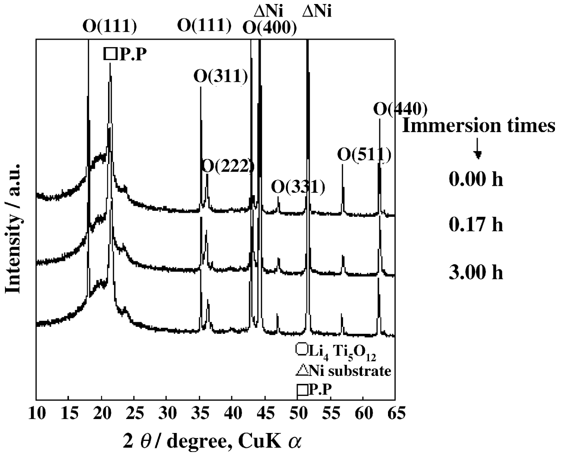

Fig. 3. XRD patterns of $Li_4Ti_5O_{12}$ electrode with different immersion times in Li-organic complex solution with BME solvent containing 0.25 mol dm^{-3} naphthalene.

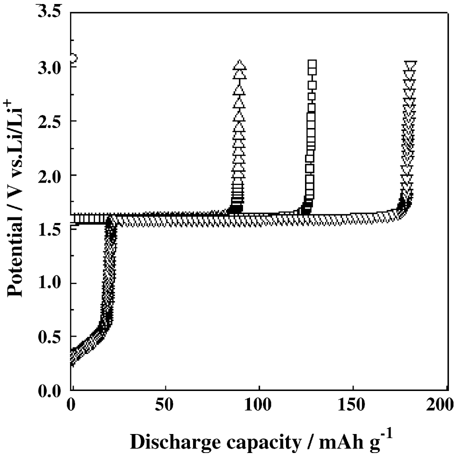

Fig. 5. Initial discharge characteristics of $Li_4Ti_5O_{12}$ electrode with immersion time of (◯) 0.00 h, (□) 0.17 h, (▽) 0.50 h, and (□) 3.00 h in Li-organic complex solution with BME solvent containing 0.25 mol dm^{-3} naphthalene.

tron change reaction according to the following equation described below [7]

$$1/3(Li_4Ti_5O_{12}) + Li^+ + e^- = 1/3(Li_7Ti_5O_{12}) \quad (1)$$

The value of charged electricity and discharge capacity was 155.7 and 154.1 mAh g^{-1}, respectively, resulting in very small irreversible capacity of 1.6 mAh g^{-1}. The discharge capacity of $Li_4Ti_5O_{12}$ electrode after Li-doping process with immersion time of 0.00, 0.17, 0.50, and 3.00 h in the different solvents of BME and DME are shown in Figs. 5 and 6, respectively. The discharge capacity in both cases is found to be increased with the immersion time and its potential plateau is appeared at around 1.55 V versus Li/Li^+. In addition, the electrodes after long time immersion of 3.00 h is also found to show the additional small capacity appeared the potential range between 0.0 and 1.0 V versus Li/Li^+ by the discharge reaction of further reduction product of metallic Li compound with Ti formed at the less noble potential than that of reaction (1). From the consideration of the observation of very small irreversible capacity of 1.6 mAh g^{-1} at such a low current density of 0.028 A g^{-1} to minimize the influence of the contribution of reaction polarization, the observed delivered capacity of test electrode is to be assumed to be equal to the amount of Li doped into $Li_4Ti_5O_{12}$. The change in the discharge capacity of $Li_4Ti_5O_{12}$ electrode in different solvents of BME and DME is shown in Fig. 7 together with the amount of doped Li of X in $Li_{4+X}Ti_5O_{12}$. The contribution capacity observed in the potential range from 0.0 and 1.0 V versus Li/Li^+ was eliminated for the plotted discharge capacity in order to focus only on the discussion of Li-doping reaction (1). The discharge capacity of electrode for BME is found to be more drastically increased than that for DME with the immersion time. The value of the former reaches to 161.3 mAh g^{-1} of which value is corresponding to $X = 2.77$ at the immersion time of 3.00 h. The value of the latter reaches to 144.1 mAh g^{-1}, corresponding to $X = 2.47$ at the same time. The chemical reaction is considered to be promoted by the

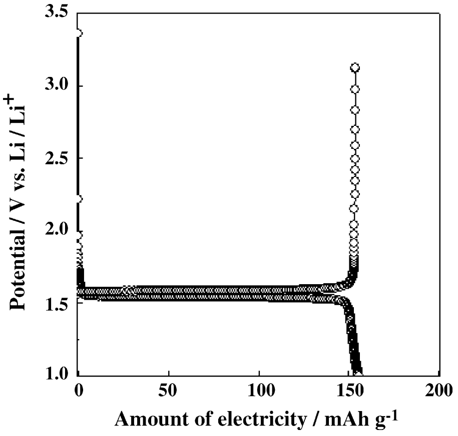

Fig. 4. Charge and discharge characteristics of $Li_4Ti_5O_{12}$ electrode with no Li doping process.

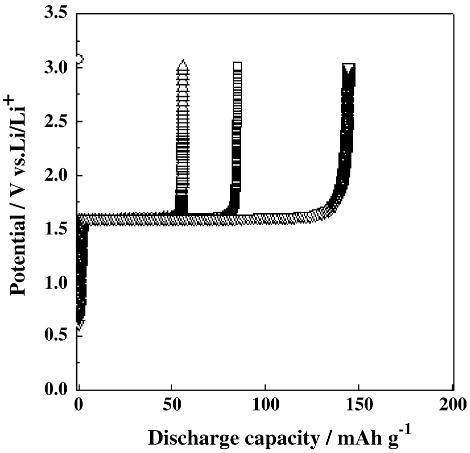

Fig. 6. Initial discharge characteristics of $Li_4Ti_5O_{12}$ electrode with immersion time of (◯) 0.00 h, (△) 0.17 h, (□) 0.50 h, and (▽) 3.00 h in Li-organic complex solution with DME solvent containing 0.25 mol dm^{-3} naphthalene.

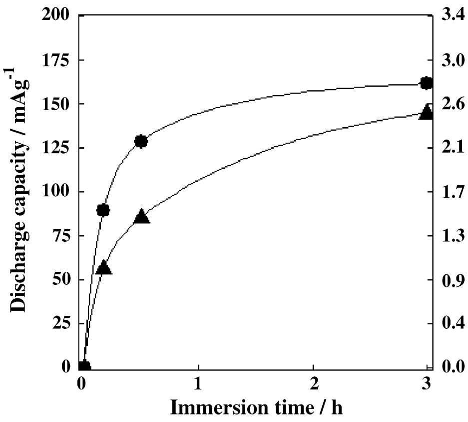

Fig. 7. Change in initial discharge capacity and Li doping amount of $Li_4Ti_5O_{12}$ electrode with different immersion times in Li-organic complex solution with (●) BME or (▲) DME solvent containing 0.25 mol dm^{-3} naphthalene.

following reaction

$$Li + C_8H_{10} \rightarrow [Li^+ C_8H_{10}{}^{\bullet -}] \quad (2)$$

$$Li_4Ti_5O_{12} + X[Li^+ C_8H_{10}{}^{\bullet -}] = Li_{4+X}Ti_5O_{12} + XC_8H_{10} \quad (3)$$

Namely, naphthalene serves as a catalyst function in reaction (2) followed by (3). In other words, the reaction mechanism of Li-doping is considered to be through the process of insertion of Li^+ ion in addition to an electron from naphthalene radical anion with electron affinity in ether solvent in which the radical ion is transformed into the original naphthalene after Li-doping into $Li_4Ti_5O_{12}$. The function of naphthalene is therefore regarded to be catalyst for the reaction mechanism.

For the further understanding of the chemical reaction rate constant involved in the above-mentioned Li-doping reaction, the calculated value $\ln(1/1 - Y)$, where Y is mole ratio of resultant $Li_{4+X}Ti_5O_{12}$ to starting material $Li_4Ti_5O_{12}$, is also shown in Fig. 8 as a function of root of immersion time in the Li-organic complex solution with BME and DME solvents. It was turned out that the value $\ln(1/1 - Y)$ is increased linearly with root of immersion time and the slope of the distinct straight line on BME is larger than that on DME. The slope of line is regarded to be corresponded to the rate constant k of reaction (3) as the rate determining process. The relation is empirically derived as follows

$$\ln(1/1 - Y) = kt^{1/2} \quad (4)$$

The rate constant calculated from the data on BME and DME were 5.10 and 2.78 × 10^{-4} $S^{-1/2}$, respectively. Thus, the chemical reaction was found out to be strongly dependent on the kind of solvent used for the Li-organic complex solution. The rate constant of chemical reaction has been also estimated in the case using BME and DME solvents as described above. The amount of doped Li X for $Li_{4+X}Ti_5O_{12}$ ($X > 0$) is controllable at room temperature from the selection of solvent and naphthalene concentration for the Li-organic complex solution as shown in Fig. 1. The Li-doped product will be able to combine non-lithiated positive active material such as FeOOH, NiOOH, and MnO_2 to realize new Li-ion cells.

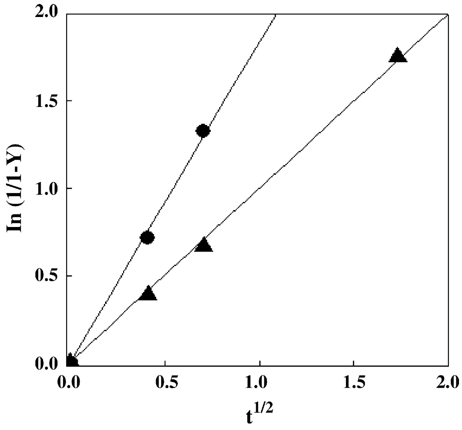

Fig. 8. Slope of distinct straight line in the relationship between $\ln(1/1 - Y)$ and $\sqrt{t}$ of $Li_4Ti_5O_{12}$ electrode in Li-organic complex solution with (●) BME or (▲) DME solvent containing 0.25 mol dm^{-3} naphthalene. Y is molar fraction of Li-doping materials of $Li_7Ti_5O_{12}$ and t is immersion time.

4. Conclusions

$Li_{4+X}Ti_5O_{12}$ ($X > 0$) negative active material has been successfully synthesized by a new chemical Li-doping method into $Li_4Ti_5O_{12}$ with immersion at room temperature in Li-organic complex solution obtained by dissolving metallic Li and naphthalene in different solvent of BME or DME. The reaction mechanism of Li-doping is considered to be through the process of insertion of Li^+ ion in addition to an electron from naphthalene radical anion with electron affinity in ether solvent in which the radical ion is transformed into the original naphthalene after Li-doping into $Li_4Ti_5O_{12}$ so that naphthalene serves as a catalyst function in the chemical Li-doping reaction.

The chemical reaction was found out to be strongly dependent on the solvent used for the Li-organic complex solution. The value $\ln(1/1 - Y)$, where Y is mole ratio of resultant $Li_7Ti_5O_{12}$ to starting material $Li_4Ti_5O_{12}$, was found out to be increased linearly with root of immersion time and the slope of line using BME is larger than that using DME. The rate constant calculated from the slope of this distinct straight line for BME was found out to be greater than that for DME, and the value was 5.10 and 2.78 × 10^{-4} $S^{-1/2}$, respectively. The Li-doped product of $Li_{4+X}Ti_5O_{12}$ ($X > 0$) was also found to be controllable at room temperature by the selection of appropriate solvent and naphthalene concentration for the Li-organic complex solution. Therefore, the new chemical method will be extended to the application for non-lithiated positive active material of FeOOH, NiOOH, and MnO_2 for lithium secondary cells with metallic lithium or its alloy resulting in the realization of new lithium-ion cells.

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