

Preparation of particulate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ having excellent characteristics as an electrode active material for power storage cells

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Abstract

In recent years, lithium secondary batteries have been widely utilized as a power source for mobile electronics, but modifications are required to apply this type of battery to motor vehicles or energy storage purposes. Although the excellent cycle characteristics of lithium titanate have been verified for small cells, the high rate characteristics of this material should be improved if it is used as an active material in large batteries. The authors prepared very fine particulates of lithium titanate having an average size of 0.7 μm . The prepared lithium titanate shows superior high rate characteristics, as well as excellent cycle characteristics. A high capacity maintenance ratio of 99% was achieved at 1 C and 25 °C after the 100th cycle. Taking the discharge capacity at 0.15 C, that at 10 C was 86% at 25 °C, while that at 50 °C was 96%.

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1. Introduction

In recent years, lithium titanate has attracted attention as a superior electrode material for energy storage cells, because of the extremely small expansion and contraction during the charge and discharge phases, respectively, of the battery [1].

An important paper dealing with the spinel oxide $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$, $0 \leq x \leq 1/3$ was published by Deschanvers et al. in 1971 [2]. Since the early 1990s, this material has been electrochemically characterized by Colbow et al. [3] Ferg et al. [4], and Ohzuku et al. [5]. Among the various members of the series, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is semiconducting, and exhibits Li-insertion electrochemistry. The formal potential of Li insertion is 1.55–1.56 V for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [3–7]. This material accommodates Li with a theoretical capacity of 175 mAh/g based on the mass of the starting host material. According to previous publications [2–4,6–11], the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared by a solid-state reaction of stoichiometric amounts of TiO_2 and Li_2CO_3 or TiO_2 and LiOH , with heating at 800–1000 °C for 12–24 h. Zaghbi et al. prepared nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by high energy grinding

of the microcrystalline spinel using a ball mill, obtaining particles of 600 nm in size. However, the electrochemical performance was not significantly different among their materials [9].

In 2001, Ametucci et al. reported a nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibiting a very promising charging rate and stability in a hybrid cell with a supercapacitor-like counter electrode [12]. They prepared it by a high-temperature reaction of TiO_2 with Li_2CO_3 , but did not detail the method.

Recently Kavan and Grätzel reported on the Li-insertion activity of a nanosized spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared via a sol-gel route [13]. A thin-film electrode (2–4 μm) prepared from nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited excellent activity toward Li insertion, even at a charging rate as high as 250 C.

Recently we successfully developed fine particulates of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for secondary battery use. Hereafter this material is referred to as LT-FP.

The material gives a favorable smoothness to the electrode sheet, and high filling density. Furthermore, the charge–discharge characteristics as well as the cycle characteristics of the cell using this lithium titanate are satisfactory; an initial discharge capacity is greater than 165 mAh/g at 0.15 C and discharge capacity is above 86% at 10 C. The relative discharge capacity of this cell at 1 C after the 100th cycle was found to be about 99%. This paper deals with the findings obtained by the present study.

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2. Experimental procedures

2.1. Preparation of lithium titanate

2.1.1. Preparation of LT-FP

LiOH·H₂O was dissolved in water to prepare a 12 wt.% solution, then anatase type TiO₂ was added to achieve a molar ratio of Li:TiO₂ of 4:5. The mixed material was dried at 110 °C using a spray drier, and subjected to thermal treatment at 800 °C for 3 h to synthesize Li₄Ti₅O₁₂. The product was ground using a vibrating ball mill for 4 h.

2.1.2. Preparation of LT-2

The preparation of lithium titanate, LT-2, was done as follows. An aqueous solution containing 12 wt.% LiOH·H₂O was mixed well with anatase type TiO₂ at a molar ratio of Li:TiO₂ of 4:5. The mixed slurry was dried at 110 °C using a spray drier, then the dried product was heated at 875 °C for 6 h in an air atmosphere. The main difference between LT-FP and LT-2 is characterized by the grinding of the former lithium titanate using the vibrating ball mill.

The fine product was subjected to determinations of tap density, average particle size and size distribution. For the determination of tap density, the JIS-K-5101 tap method was employed. Particle size and size distribution were measured with a Microtrack 9320-X100 made by Honeywell based on the laser diffraction-scattering method.

2.2. Preparation of coating material

To prepare the coating material used to determine cell characteristics, 82 weight parts of Li₄Ti₅O₁₂, nine weight parts of acetylene black (Denka black 75% pressed product of Denki Kagaku Kogyo) and nine weight parts of polyvinylidene fluoride (Kynar 301F made by Atofina) were mixed well, then pasted with *N*-methyl-2-pyrrolidone made by BASF at a solid concentration of 30 wt.% using a high share mixer for 30 min. Then the mixture was kneaded for 240 min using ϕ 1.0 mm glass beads by an Eiger motor mill, a product of Eiger Engineering. It is necessary to achieve sufficient contact between the active material and the conductive material and at the same time to ensure an electric current path from the active material to the collector to sufficiently draw out the characteristics of the active material. Since LT-FP is made up of very fine particulates of lithium titanate, it is necessary to use a fine conductive material to make contact using a beads mill to establish an enough kneading.

2.3. Measurement of charge–discharge curves of lithium ion cell

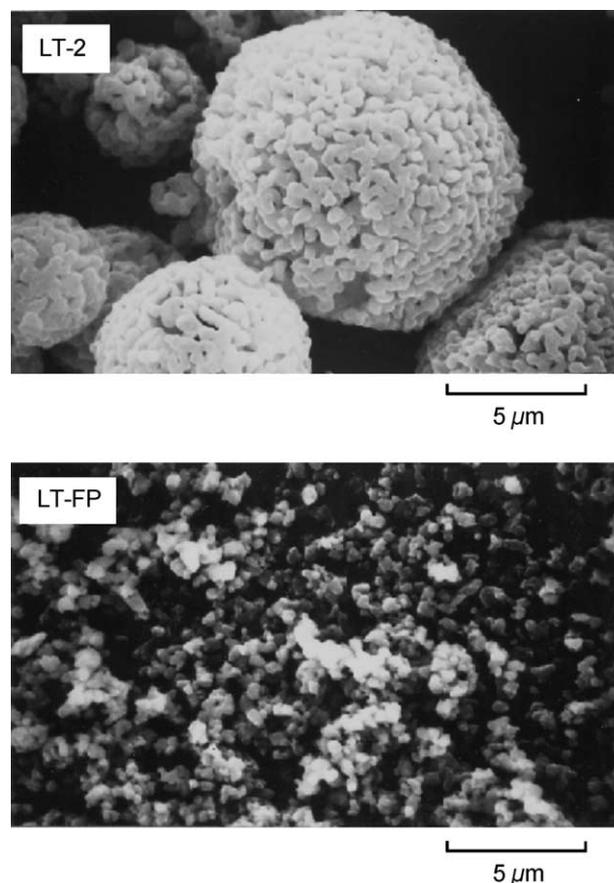
The coating material thus prepared was applied to 0.020 mm thick aluminum foil, a product of Mitsubishi Aluminum, using a doctor-blade to be 0.01 g/cm² thick after drying. After drying in vacua at 110 °C, the plated aluminum

foil was rolled and pressed to 80% of the original thickness of its coated material. One square centimeter disc was perforated and used as a cathode, while the anode used was a lithium metal disc. Then 1 mol/dm³ LiPF₆ dissolved with an equi-volume mixture of ethylene carbonate and dimethyl carbonate made by Kishida Kagaku was used as an electrolyte, and a porous membrane of polypropylene was used as a separator. The coin cell thus composed was subjected to discharge at a rate of 0.15 C to 1.0 V, then charge at the same rate to 3.0 V, repeating three cycles of these operations using the BTS-2004 W charge–discharge apparatus commercially supplied by Nagano. Then, the rate was changed to 10 C to discharge to 1.0 V.

3. Results and discussion

3.1. Powder properties of Li₄Ti₅O₁₂

Scheme 1 shows a SEM photograph of the lithium titanate produced in the present study. The size distribution of this material is depicted in Fig. 1. As is seen in this figure, the average particle size of LT-FP determined by the laser diffraction-scattering method is 0.7 μ m, exhibiting the coefficient of variation (CV) of 48.4% on a volume basis.



Scheme 1. SEM photograph of Li₄Ti₅O₁₂ produced.

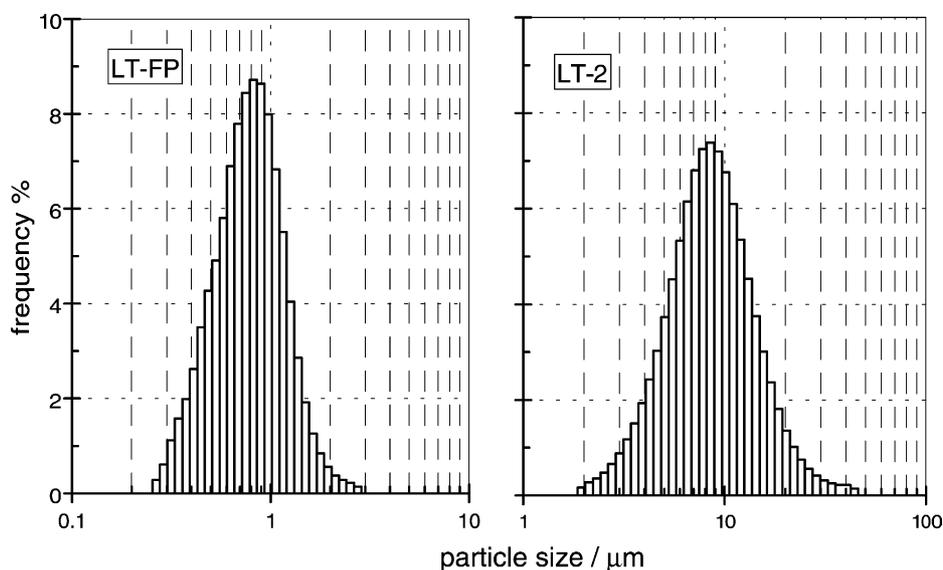


Fig. 1. Size distribution of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ produced.

The specific surface area determined by the BET method is $7.5 \text{ m}^2/\text{g}$. Bulk density determined is 0.4 g/ml , while tap density measured is 0.8 g/ml .

In contrast, the average particle size of LT-2 is $8.5 \mu\text{m}$, and its CV value is 54.4%. The specific surface area, bulk density and tap density of this material are $3.0 \text{ m}^2/\text{g}$, 0.3 , and 0.7 g/ml , respectively.

3.2. Charge–discharge characteristics

The discharge capacity of the cell, in which LT-FP was used, determined at the initial stage was larger than 165 mAh/g at 0.15 C . The cycle dependency of the coin cell was determined at 1 C . Fig. 2 shows the cycle dependency of charge–discharge curves determined when both the charge and discharge of the cell were conducted at 1 C . As is clear in this figure, no significant difference can be detected in charge–discharge curves from the 1–100th cycle, exhibiting very stable cycle characteristics.

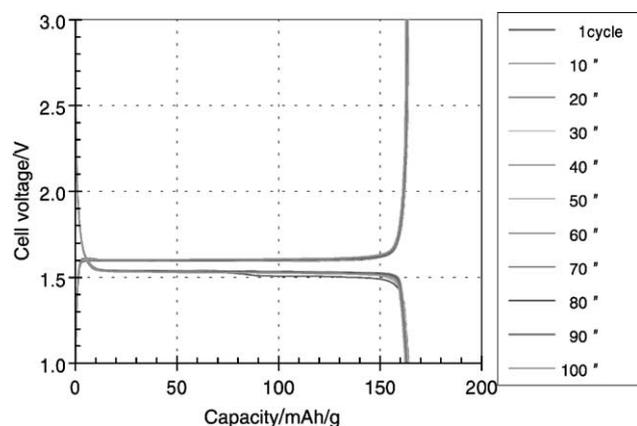


Fig. 2. Cycle dependency of charge–discharge curves obtained when charge and discharge were performed at 1 C (LT-FP).

The discharge capacity at 1.0 V of each cycle was plotted against cycle number. Fig. 3 depicts the results, showing a very stable cycle dependency at 1 C . Even after the 100th cycle, a relative capacity of 99% is obtainable. In contrast, it is around 5% lower except in the initial few cycles.

3.3. Effect of discharge rate on discharge capacity

One of the most important electrochemical characteristics required of a lithium ion cell for power storage use is a high rate of behavior. To know the rate behavior of the lithium titanate produced in the present study, charge–discharge curves were determined by changing the discharge current from 0.15 to 10 C . In these determinations, the charge current was maintained constant at 0.15 C .

Fig. 4 shows the charge and discharge curves obtained with LT-FP. Cell voltage is lowered by increasing discharge current. For example, it dropped to about 1.3 V at 10 C , while it was 1.5 V at 0.15 C . Also the discharge capacity exhibits a slight decreasing tendency on increasing discharge current.

Fig. 5 depicts the relationship between relative discharge capacity and discharge current. The discharge capacity determined at 0.15 C was taken as standard. On increasing the discharge current from 0.15 C , a slightly sharp decrease can be observed at the initial stage, but soon a linear decrease is exhibited whose slope is $0.12 \text{ mAh}/(\text{g C})$. At 10 C , relative discharge capacity was found to be 86%. In these experiments, we employed Li metal as the active anode material, so that it is unable to increase discharge current. This phenomenon can be attributed to the large difference of interface area between LT-FP particulates and an electrolyte to that of LT-2.

Fig. 6 depicts the relationship between cell voltage and discharge current for both LT-FP and LT-2. The lower cell voltage of LT-FP is far smaller than that of LT-2. This finding can be attributed to the large contact area between the particulates of LT-FP and conductive material due to the

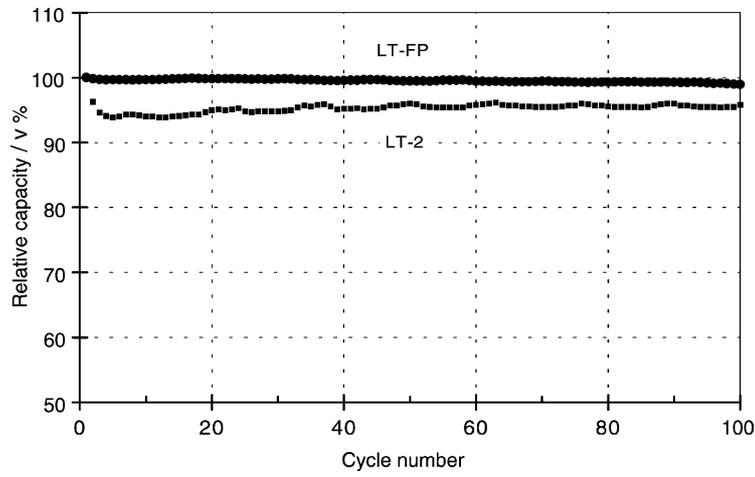


Fig. 3. Change in relative discharge capacity during the increase in cycle number.

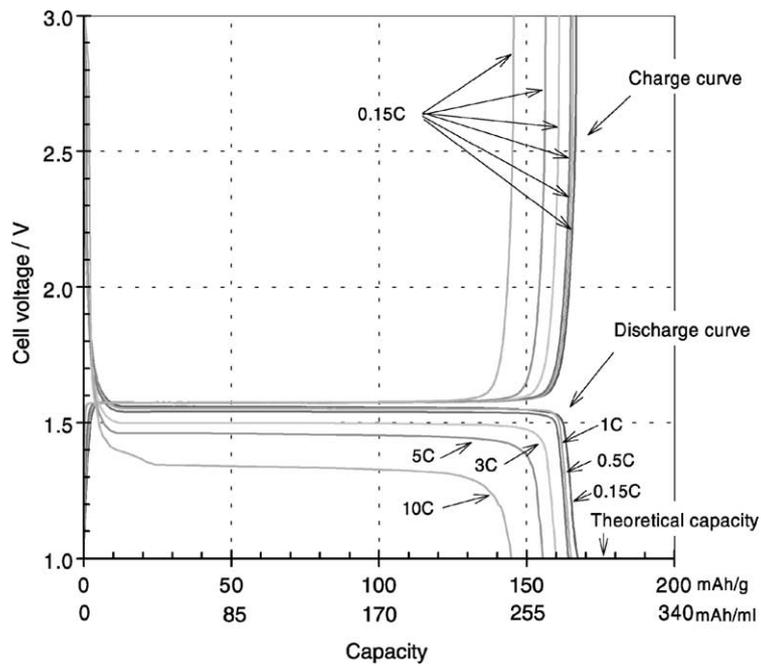


Fig. 4. Charge–discharge curves determined at different discharge currents (LT-FP). (Charging of the cell was carried out at a constant 0.15 C.)

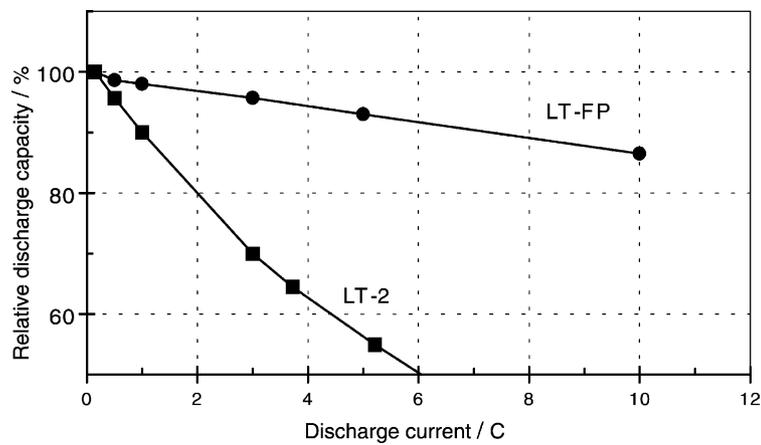


Fig. 5. Effect of discharge current on relative discharge capacity.

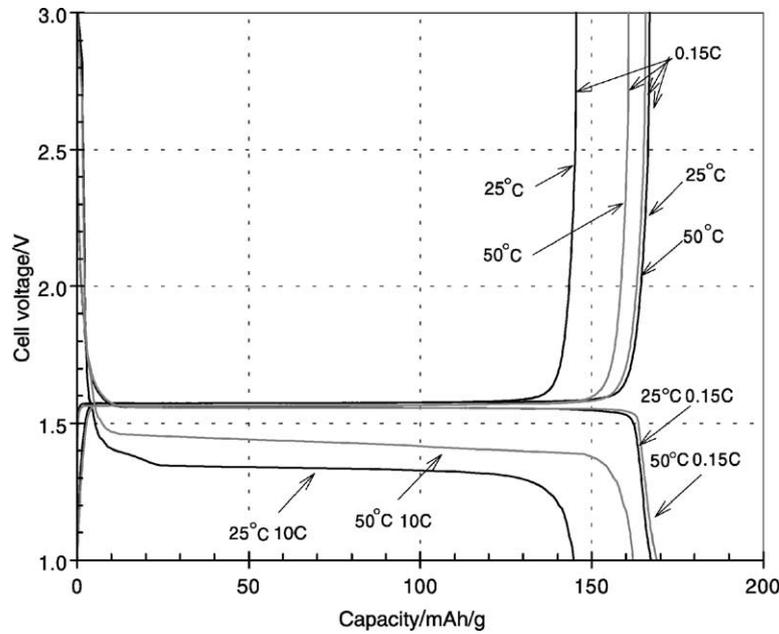


Fig. 6. Effect of temperature on discharge characteristics (LT-FP).

monodispersed state of LT-FP at the primary particle level, and thus internal resistance can be decreased.

3.4. Effect of temperature on discharge characteristic of LT-FP

It is important to know the temperature dependency of the lithium ion cell characteristics in connection with the practical use of the cell.

The charging of a lithium ion cell composed LT-FP was done at 0.15 C, while discharging was done at either 0.15 or 10 C. Temperature studied were 25 and 50 °C. The results determined are shown in Fig. 7. As is clear in this figure, the elevation of temperature results in an increase in discharge capacity. For example, the discharge capacity at 0.15 C was 167 mAh/g at 25 °C and that was 169 mAh/g at 50 °C. At 10 C, those values were 144 mAh/g at 25 °C and 162 mAh/g at 50 °C.

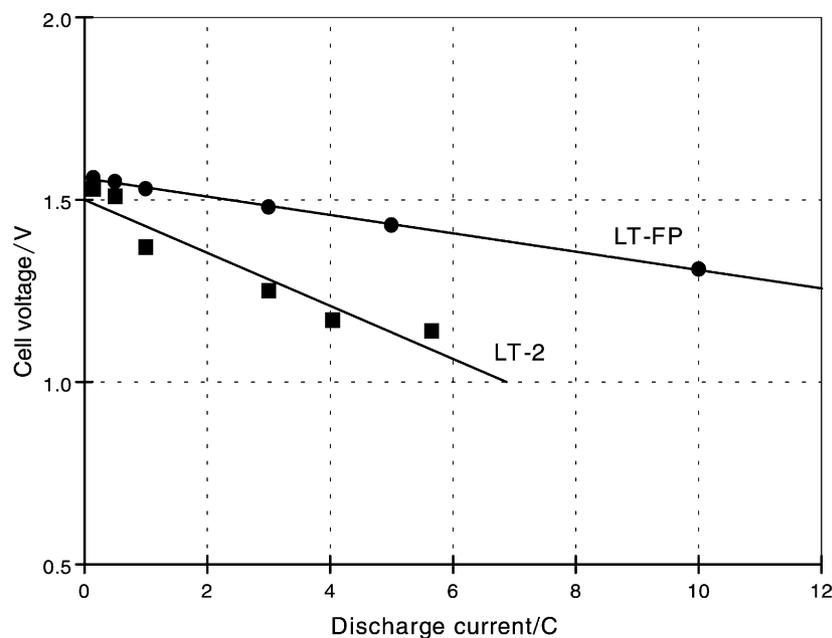


Fig. 7. Effect of discharge current on discharge cell voltage (LT-FP).

4. Conclusions

- (1) Fine lithium titanate particulates, LT-FP, having an average size of 0.7 μm and sharp size distribution of CV value of 48.4% on a volume basis were prepared.
- (2) The capacity maintenance ratio of LT-FP was 99% at 1 C and 25 °C after the 100th cycle.
- (3) When the discharge capacity of LT-FP determined at 0.15 C was taken as standard, the discharge capacity at 10 C was 86% at 25 °C, while that at 50 °C was 96%.
- (4) Compared to LT-2, the high rate capacity of LT-FP was greatly improved.

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