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Synthesis and Electrochemical Properties of Lithium Titanate Anode Materials Powders by Solid State Reaction of Li and Spherical TiO_2 Powders

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Abstract $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were synthesized by solid state reaction of Li_2CO_3 and spherical composite powders of carbon and TiO_2 (denoted as C/ TiO_2). C/ TiO_2 powders were synthesized by spray pyrolysis of using lactic acid aqueous solution. The particle characteristics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were determined by SEM, XRD and DTA-TG. DTA-TG showed that the carbon content was around 8 wt% in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. XRD revealed that the spinel structure (Fd3m) was obtained by heating at 750 °C under N_2 atmosphere. The first rechargeable capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode was about 160 mAh/g at 1 C. That of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode decreased to 90 mAh/g at 20 C. The rechargeable capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode decreased with increasing the rechargeable rate, but 81% of initial discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode was retained after 200 cycles at 1C.

Introduction

Recently, lithium ion batteries are expected as the energy storage for electric vehicles (EVs) and hybrid electric vehicles (HEVs), the load leveling of photovoltaic power generation. Various type carbons [1-6] have been used as an anode material because they have better safety characteristic and long life of cycles compared with lithium metal. It was known that the dendrite was formed on the carbon anode during the high rate charging. The solid electrolyte interface (SEI) layer on the carbon anode, which is usually formed at the potential below 0.8 V and accompanied over time with active lithium loss, an increase in impedance and a decrease in rechargeable capacity, cycle life of lithium ion batteries.

For an application of EVs and HEVs, the oxide type anode material is expected because of better safety. Spinel type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been demonstrated as an alternative anode material because it has a very flat potential plateau at around 1.5V and exhibited excellent cycle life due to the structure stability in the rechargeable process. However, it is difficult to homogeneously synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ because of low reactivity of lithium oxide and titanium oxide. So, in this work, Stoichiometric composition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was synthesized by solid state reaction of Li_2CO_3 and spherical C/ TiO_2 particles of the high surface activity by spray pyrolysis. In this paper, the powder characterization and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials synthesized by solid state reaction of Li and spherical TiO_2 powders were described in detail.

Experimental

Spherical C/ TiO_2 powders were synthesized by spray pyrolysis. Titanium tetraisopropoxide (denoted as TTIP) was used as starting reagent. The lactic acid was added to TTIP to prepare the aqueous solution. The lactic acid was also used as carbon source. A lactic acid was dissolved in distilled water to prepare aqueous solutions of 0.3 mol/dm³. The mist of aqueous solution was generated with ultrasonic atomizer (1.6 MHz) with 0.083 dm³/s of air carrier gas. The mist was pyrolyzed 650 °C. C/ TiO_2 powders were corrected by the cyclone. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were synthesized by solid state reaction of Li_2CO_3 and C/ TiO_2 powders. Li_2CO_3 and C/ TiO_2 were weighted out to attain the molar ratio of 4:5 (Li:Ti) and were mixed and then fired at 750 °C for 8 hr in electric

furnace under the nitrogen atmosphere. The morphology and microstructure of C/TiO_2 and $Li_4Ti_5O_{12}$ powders were determined with a scanning electron microscope (SEM, JEOL, JSM-6390). Specific surface area (SSA) of C/TiO_2 and $Li_4Ti_5O_{12}$ powders was measured by BET method using N_2 adsorption (SSA, BEL, BELSORP - miniII). The crystal phases of TiO_2 and $Li_4Ti_5O_{12}$ powders were identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100). The thermal decomposition behaviors of C/TiO_2 and $Li_4Ti_5O_{12}$ powders were observed by the differential thermal analysis (DTA) and the carbon content was determined by thermogravimetric analysis (TG) (DTA-TG, Shimadzu, DTG-60) the under the air at the heating rate of $5^\circ C/min$.

The electrochemical measurements were examined using CR2032 type coin cell. $Li_4Ti_5O_{12}$ powders were mixed acetylene black as a conducting agent and a polyvinyliden difluoride as a binder in the weight ratio of 80 : 10 : 10 to make a N-methyl-2-pyrrolidinone solution slurry. The prepared slurry was then coated on an aluminum foil using a doctor blade and dried under vacuum at $100^\circ C$ for 24 hr. Metal lithium sheet (Honjo chemical) was used as the counter electrode. The polypropylene sheet (Celgard 2400) was used as a separator. 1 mol/dm^3 $LiPF_6$ in ethylene carbonate /1, 2-dimethoxyethane (EC:DEC = 1:1, Tomiyama pure chemical) was used as the electrolyte. The cell was built up in globe box under an argon atmosphere. The rechargeable capacity and cycle stability of $Li_4Ti_5O_{12}$ anode were measured with a battery tester (Hosen, BTS2004) at between 1.0 V and 2.5 V.

Result and Discussion

Figure 1 shows typical SEM photographs of C/TiO_2 powders obtained by spray pyrolysis using TTIP aqueous solution. As-prepared C/TiO_2 powders had smooth surface. The particles had also spherical morphology and non-aggregation with broad size distribution. It was seemed that the particle microstruture was dense. No particles with irregular morphology or hollow microstructure were observed.

Figure 2 shows typical SEM photographs of $Li_4Ti_5O_{12}$ anode materials obtained by solid state reaction with Li_2CO_3 and C/TiO_2 powders. SEM showed that $Li_4Ti_5O_{12}$ anode materials had both spherical and irregular morphology and then changed to the rough particle surface. It was considered that the roughness of particle surface was formed by the crystallization of $Li_4Ti_5O_{12}$ with the volatile of carbon. SSA of C/TiO_2 particles determined by BET method was $4.6\text{ m}^2/\text{g}$.

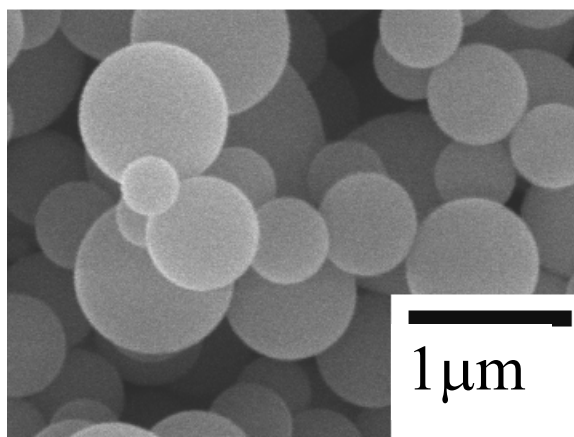


Fig. 1 SEM photograph of C/TiO_2 powders obtained by spray pyrolysis

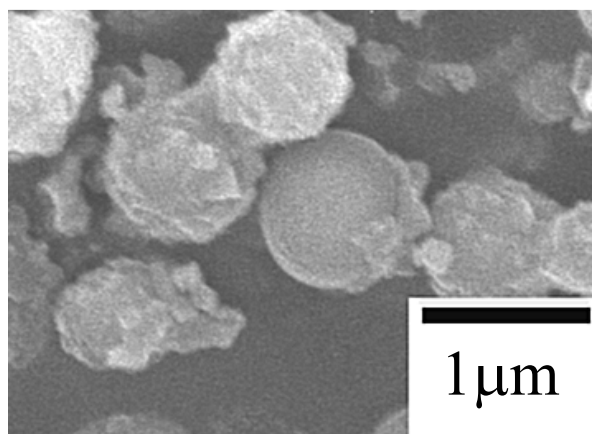


Fig. 2 SEM photograph of $Li_4Ti_5O_{12}$ powders obtained by solid state reaction

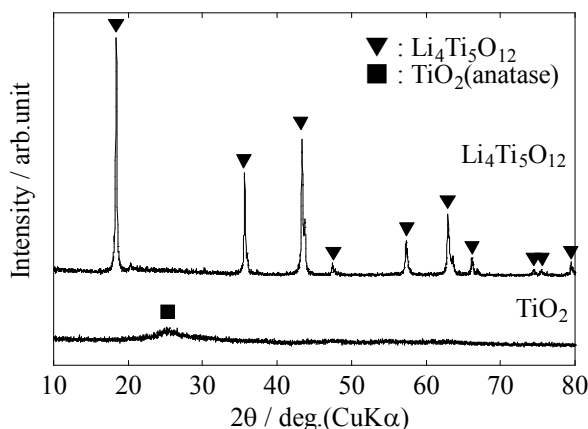
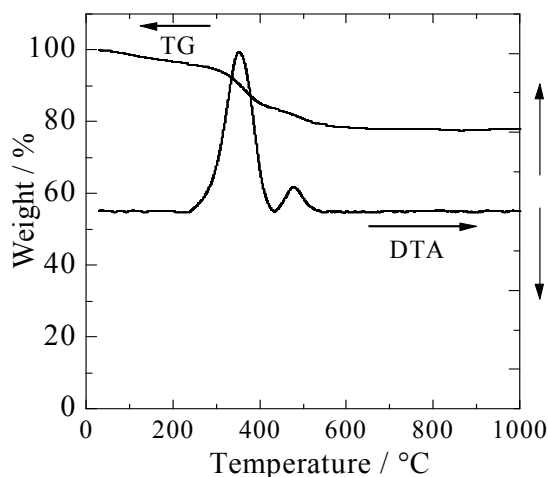
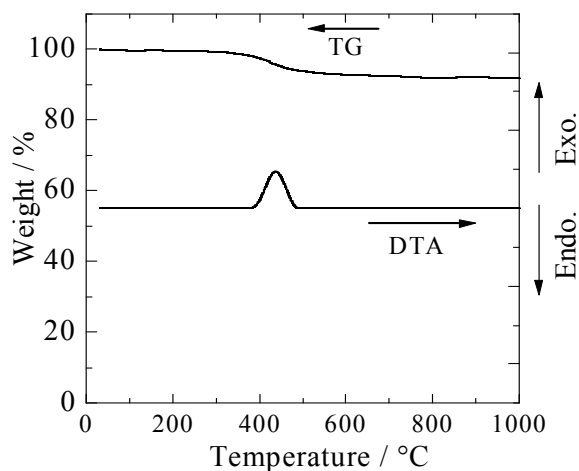


Fig. 3 XRD patterns of C/TiO_2 powders and $Li_4Ti_5O_{12}$ powders

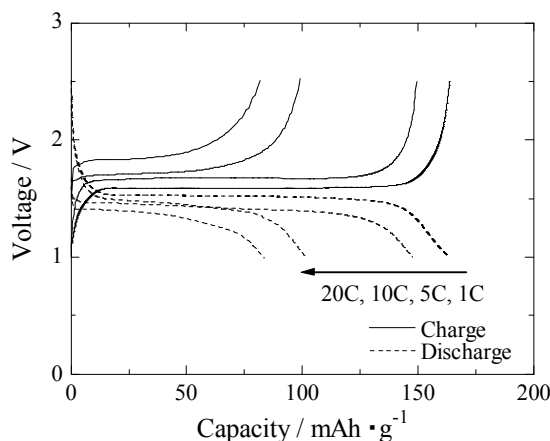
Fig. 4 DTA-TG curve of C/TiO₂ powdersFig. 5 DTA-TG curve of Li₄Ti₅O₁₂ powders

On the other hand, that of Li₄Ti₅O₁₂ anode materials decreased to 89.3 m²/g. It was considered that the increase of SSA was due to the change of particle surface with the volatile of carbon.

Figure 3 shows XRD patterns of C/TiO₂ powders and Li₄Ti₅O₁₂ powders. An anatase phase was slightly observed in XRD patterns. On the other hand, the crystal phase of spinel (space group: Fd3m) was observed in the Li₄Ti₅O₁₂ powders and was well crystallized. The other impurity phases were not observed. Figure 4 shows DTA-TG curves of as-prepared C/TiO₂ powders. DTA-TG curves showed that two exothermic peaks were observed in DTA curve. These peaks corresponded to the volatilization of carbon (350 °C) and the crystallization of anatase (400 °C). A weight loss of them was about 20 wt% at 600 °C in TG curve. This suggested that the carbon content in TiO₂ powders was 20 wt%. Figure 5 shows DTA-TG curves of Li₄Ti₅O₁₂ anode materials. One exothermic peak was observed in DTA curve. This peak corresponded to the volatilization of carbon (430 °C). A weight loss of Li₄Ti₅O₁₂ powders was about 8 wt% at 600 °C in TG curve. 12 wt% of carbon was lost from Li₄Ti₅O₁₂ powders by the solid state reaction.

Figure 6 shows the rechargeable curves of Li₄Ti₅O₁₂ anode at the rechargeable rate indicated. The rechargeable capacity of Li₄Ti₅O₁₂ anode was determined by correcting the carbon content in Li₄Ti₅O₁₂. The typical long plateaus were observed at approximately 1.5 V in the rechargeable curves. The charge and discharge capacity of Li₄Ti₅O₁₂ anode was about 160 mAh/g at 1 C and corresponded to 90 % of theoretical capacity (175 mAh/g). The discharge capacity of Li₄Ti₅O₁₂ anode was higher than that of Li₄Ti₅O₁₂ anode obtained by spray-drying of rutile type TiO₂ and Li₂CO₃ using polyvinyl butyral as a carbon source [7]. It was considered that the carbon was homogeneously blended in TiO₂ particles by spray pyrolysis. On the other hand, this value was close to that of carbon-coated Li₄Ti₅O₁₂ [8], Li₄Ti₅O₁₂ prepared by sol-gel [9, 10] and spray pyrolysis [11]. The rechargeable efficiency of Li₄Ti₅O₁₂ anode was approximately 99%. This value was higher than those of carbon-coated Li₄Ti₅O₁₂ and sol-gel or spray pyrolysis. The discharge capacity of Li₄Ti₅O₁₂ anode decreased to about 80 mAh/g with increasing up to 20 C and corresponded to 50 % of 1 C. It was observed that a difference of voltage between charge and discharge increased with increasing the rechargeable rate. These results suggested that the impedance of Li₄Ti₅O₁₂ anode became high in the coin cell.

Figure 7 shows the relation between cycle

Fig. 6 Rechargeable curves of Li₄Ti₅O₁₂ anode materials at rechargeable rate indicated

number and discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode at the rechargeable rate indicated. The rechargeable test was conducted with up to 200 cycles at 25 °C. It was clearly shown that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode had excellent cycle stability from 1 C to 20 C. The discharge capacity was maintained over 90 % of its initial discharge capacity after 200 cycles at 1C. It was considered that the spinel structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ had high stability for the intercalation of Li^+ ion during the rechargeable process. The retention of the initial discharge capacity decreased to 150 mAh/g, 100 mAh/g and 80 mAh/g at 5 C, 10 C and 20 C, respectively. They maintained 88 %, 81 % and 64 % of initial discharge capacity after 200 cycles. It was confirmed that the cycle stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode was higher than that of sol-gel and spray pyrolysis.

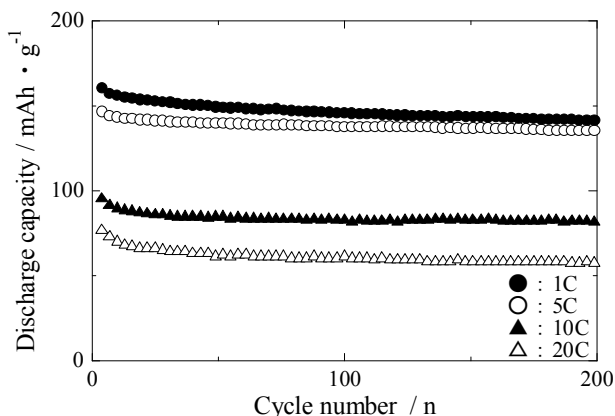


Fig. 7 Relation between discharge capacity and cycle number at rechargeable rate indicated

Conclusion

Spherical and non-aggregated C/TiO₂ powders were prepared by spray pyrolysis using aqueous solution of TTIP with lactic acid. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were synthesized by solid state reaction of Li_2CO_3 and C/TiO₂ powders. After the solid state reaction, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders with irregular morphology and rough particle surface were obtained. XRD revealed that the crystal phase of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders was in good agreement with the spinel structure. DTA-TG showed that the carbon content of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders was 8 wt%. The electrochemical measurement of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode revealed that the dischargeable capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode was 160 mAh/g at 1 C and the rechargeable efficiency was approximately 99%. The rechargeable capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode decreased with increasing the rechargeable rate, but the cycle stability of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode was maintained at higher rechargeable rate.

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