Synthesis and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ nano-powders by pulse jet spray pyrolysis

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$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ nano-powders were successfully synthesized at 500°C through the pulse jet spray pyrolysis with use of a citric acid aqueous solution. As-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ nano-particles had spherical and irregular shapes with an average size of 50 nm. As-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ nano-particles had a spinel phase with high crystallinity and a homogeneous chemical composition. The carbon content was 10 wt % in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nano-powders. A 2032 type coin cell was used to examine electrochemical properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ anode. The discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ anode exhibited 170 at 1 C and 120 $\text{mAh}\cdot\text{g}^{-1}$ at 20 C, respectively. The discharge capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ anode maintained 96% of the initial discharge capacity after 500th cycle at 10 C and room temperature. The discharge capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ anode exhibited 160 $\text{mAh}\cdot\text{g}^{-1}$ at 10 C and 50°C and maintained 98% of the initial discharge capacity after 100th cycle.

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1. Introduction

Oxide materials are expected as an anode of lithium ion battery (LIB) for the energy storage of electric vehicles (EV), the electric storage and load leveling of the photovoltaic power generation. The solid electrolyte interface layer in the carbon^{1)–6)} anode for LIB is usually formed at the potential below 0.8 V. Approximately 9% volume expansion occurs during the rechargeable. The active lithium ion gradually is losing during the insertion of lithium. This results in increase of impedance and decrease both rechargeable capacity and life cycle of LIBs. For an application of EVs, oxide type anode is also noted as alternative materials for the anode because of safer and longer life cycle. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (denoted as LTO) shows the ionic crystal with low electronic conductivity. Adding carbon to LTO is however effective improvement in electronic conductivity. The carbon-added LTO (denoted as LTO/C) shows high electronic conductivity. It was reported that the LTO/C was as an anode material^{7)–9)} having a long plateau at about 1.5 V and exhibiting excellent cycle stability.

It was well known that the liquid phase reaction such as spray drying, spray pyrolysis, sol-gel led to the formation of the LTO/C powders.^{10)–12)} We have synthesized the LTO/C powders through the spray pyrolysis process. The spray pyrolysis leads to easily carbon adding to the LTO particles at one process including organic compounds in the mist. Carbon is formulated through the decomposition of the organic compound and dispersed in the LTO particles uniformly. The carbon can be existed in the mist without volatilization because the residence time of mist is very short in the spray pyrolysis. Ju et al. reported that the LTO/C powders derived from the spray pyrolysis exhibited higher rechargeable capacity and good cycle stability.^{13),14)} The spray pyrolysis offers spherical LTO/C powders with a sub-micrometer

size. The mist size atomized through ultrasonic vibration process is about 3 μm at 1.6 MHz according to Lang's equation.¹⁵⁾ The mist size generated by the commercially-used two-fluid nozzle is usually ranged from several μm to 20 μm .¹⁶⁾ It is difficult to synthesis the LTO/C powders with nano-size less than 100 nm by the pyrolysis at less than 1000°C due to oversize mist. To obtain higher rechargeable capacity at the high discharge rate, the LTO/C powders with nano-size less than 100 nm is required because the diffusion of the lithium ion is dependent on the particle size, i.e., the diffusion rate increases with decreasing the particle size. We noted that the nano-mist less than 100 nm was given by using a pulse jet. The sound wave is generated by the LPG (liquid propane gas) or city gas burning in the pulse jet engine.¹⁷⁾ When the mist derived from the two-fluid nozzle is introduced in the pulse jet engine room, the mist is break to less than 100 nm through the irradiation of sound wave. We can therefore expect that the various types of nano-powders are available in one operation in a very short time. This is also a promising process for a large scale production of nano-powders. In this paper, the particle characterization and the electrochemical properties of the LTO/C powders synthesized through the spray pyrolysis with the use of a pulse jet engine were described.

2. Experimental procedure

Lithium nitrate (LiNO_3) and titanium iso-propoxide [$\text{Ti}(\text{iso-OC}_3\text{H}_7)_4$] were used as starting materials of LTO. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was used as a carbon source for conducting agent. The citric acid was dissolved in distilled water. LiNO_3 and $\text{Ti}(\text{iso-OC}_3\text{H}_7)_4$ were added in the citric acid solution at the stoichiometric ratio of LTO and stirred until a solution became transparent at the room temperature. The concentration of the starting solution range was from 0.1 to 0.5 $\text{mol}\cdot\text{dm}^{-3}$. The concentration of the citric acid was about 4 times of that of $\text{Ti}(\text{iso-OC}_3\text{H}_7)_4$. The schematic diagram of the pulse jet spray pyrolysis¹⁸⁾ is shown in Fig. 1. The nano-mist of the starting solution was generated

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Fig. 1. Schematic diagram of pulse jet spray pyrolysis apparatus.

through pulse jet engine (Ohkawara Kakohki) consisting of two-fluid atomizer and combustor. LPG was burn with a spark plug in the combustor and then the sound wave of 115 dB was irradiated at the combustion of $1000 \text{ kcal} \cdot \text{h}^{-1}$. The mist derived from two-fluid atomizer was broken down to form the nano-mist by the sound wave. The nano-mist was introduced into an alumina tube ($38 \text{ mm} \phi \times 1000 \text{ mm}$) in the electrical furnace with air carrier ($10 \text{ dm}^3 \cdot \text{min}^{-1}$). The residence time of the nano-mist and powders inside the alumina tube was as short as about 2 s. The temperatures of the electrical furnaces used to dry and pyrolysis were set to 200 and 500°C , respectively. When the nano-mist was dried and then pyrolyzed, as-prepared LTO/C particles were collected by the bag filter.

The particle morphology, microstructure and agglomeration of as-prepared powders were observed by a scanning electron microscope (SEM, Hitachi, S-2360). The average particle size was measured by a dynamic light scattering method (Otsuka Electronics, FPAR-1000). The chemical analysis of as-prepared powders was verified by an induced coupled plasma analysis (ICP, SII, SPS-7800). The crystal phase of as-prepared powders was identified on a powder X-ray diffraction (XRD, Shimadzu, XRD-6100). The carbon content was determined on a simultaneous thermogravimetry/differential thermal analysis (TG-DTA, Shimadzu, DTG-60). The anode was prepared with 80 wt % LTO/C, 10 wt % acetylene black (electronic conductor) and 10 wt % fluorine resin (binder). The slurry obtained was coated on the aluminum sheet using the doctor blade. Lithium sheet was used as a counter electrode. Porous polypropylene sheet was used as a separator. $1 \text{ mol} \cdot \text{dm}^{-3}$ LiPF_6 in ethylene carbonate/1,2-dimethoxyethane (EC:DME = 1:1 in volume ratio) was used as the electrolyte. A 2032 type lithium ion coin cell was assembled in a globe box under an argon atmosphere. The rechargeable capacity and cycle stability of LTO/C anode were measured with a battery tester (Hosen, BTS2004) at between 1 and 2.5 V.

3. Results and discussion

Figure 2 shows SEM photographs of as-prepared LTO/C powders obtained through the pulse jet spray pyrolysis. The concentration of the starting solution was $0.1 \text{ mol} \cdot \text{dm}^{-3}$ (the molar

Fig. 2. SEM photographs of the LTO/C particles obtained with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ (a) and $0.5 \text{ mol} \cdot \text{dm}^{-3}$ (b).

Fig. 3. TG-DTA curves of the citric acid.

ratio of $\text{Li}/\text{Ti} = 0.045/0.055$) and $0.5 \text{ mol} \cdot \text{dm}^{-3}$, respectively. The concentration of the citric acid 0.2 and $1 \text{ mol} \cdot \text{dm}^{-3}$, respectively. When the concentration ratio of the citric acid and $\text{Ti}(\text{iso-OC}_3\text{H}_7)_4$ was less than 4 times, although LTO/C nano-particles were also obtained, a long time range was required from 1 h to 24 h so that $\text{Ti}(\text{iso-OC}_3\text{H}_7)_4$ was dissolved in the citric acid solution. Furthermore, it was assumed that the carbon content decreased in the LTO/C and led to poor electrochemical properties of LTO/C. For all of these reason, the concentration ratio of the citric acid and $\text{Ti}(\text{iso-OC}_3\text{H}_7)_4$ needed to be set more than 4 times. SEM photographs showed that the LTO/C particles had the spherical and irregular shapes such as spheroidal and cubic in both samples. The average particle size of them measured with a dynamic light scattering method was approximately 50 nm. This finding suggests that the micro-mist (several micrometer) generated with the two-fluid nozzle is broken to 50 nm with the sound wave of 115 dB regardless of the concentration. So far, the LTO/C nano-particles less than 100 nm had not been directly prepared by the spray pyrolysis with an ultrasonic and a two-fluid nozzle. It was clear however that the LTO/C nano-particles could be prepared through the pulse jet spray pyrolysis.

The carbon content in as-prepared LTO/C nano-powders was approximately 10 wt % from the TG curve in a TG-DTA. **Figure 3** shows TG-DTA curves of the citric acid. The endothermic peaks which were attributed to the decomposition of hydroxyl group were observed at around 200°C on the DTA curve. The exothermic peak which was attributed to the combustion of carboxyl group observed at 470°C on the DTA curve. The citric acid therefore is almost pyrolyzed at 500°C in the pulse jet spray pyrolysis and the chemical species such as carbon, CO, CO_2 and H_2O are generated accordingly. When the concentration of the starting solution and citric acid was 0.1 and $0.2 \text{ mol} \cdot \text{dm}^{-3}$, the carbon content determined on the calculation was approximately 10 wt %. The carbon content in as-prepared LTO/C nano-powders was in agreement with calculated value. It was

Fig. 4. XRD pattern of the LTO/C nano-powders obtained with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ (a) and $0.5 \text{ mol}\cdot\text{dm}^{-3}$ (b).

considered that the release of carbon was not occurred from the nano-mist during the pyrolysis at 500°C , since the residence time of nano-mist was very short (2 s) in an alumina tube.

Figure 4 shows the XRD patterns of LTO/C powders obtained with 0.1 and $0.5 \text{ mol}\cdot\text{dm}^{-3}$, respectively. The XRD revealed that the diffraction patterns of as-prepared LTO/C powders were identified with a spinel structure (space group: $\text{Fd}\bar{3}\text{m}$) and other crystal phases such as TiO_2 , LiNO_3 were not detected. It was found that the high crystalline LTO/C nano-powders could be obtained at the short residence time of 2 s regardless of the concentration. This finding suggests that lithium ion and titanium ion are homogeneously mixing in each nano-mist in which is played a role as the nano-reactor. Furthermore, it was considered that the solid state reaction of lithium and titanium ion and the decomposition of citric acid rapidly occurred during the pyrolysis. When the chemical composition of LTO/C powders obtained with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ was measured on a ICP analysis, the molar ratio of the lithium ion and the titanium ion in the LTO/C powders was 0.046:0.055 and this result was in agreement with that of the starting solution composition (0.045:0.055). It was considered that the chemical composition of the LTO/C nano-powders was not influenced by the sound wave generated in the pulse jet engine.

The electrochemical properties of the LTO/C nano-powders were examined. **Figure 5** shows the rechargeable curves of the LTO/C anode obtained with 0.1 and $0.5 \text{ mol}\cdot\text{dm}^{-3}$, respectively. The charge and discharge rate set both in 1 C. The typical long plateau attributed to the reduction/oxidation of $\text{Ti}^{4+}/\text{Ti}^{3+}$ couple was observed at about 1.55 V in the rechargeable curves. The charge and discharge capacity were estimated based on the chemical composition of LTO. When the LTO/C anode obtained with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ was examined, the charge and discharge capacity of the LTO/C anode were 171 and $170 \text{ mAh}\cdot\text{g}^{-1}$ at 1 C, respectively and was close to the theoretical capacity of LTO ($175 \text{ mAh}\cdot\text{g}^{-1}$). The efficiency of the charge and discharge was 99%. When the LTO/C anode obtained with $0.5 \text{ mol}\cdot\text{dm}^{-3}$ was examined, the charge and discharge capacity of the LTO/C anode were 168 and $167 \text{ mAh}\cdot\text{g}^{-1}$ at 1 C, respectively. The concentration did not affect the charge and discharge capacity of the LTO/C anode. This resulted in that the particle characteristics such as particle size and crystallinity were about same for each sample. This excellent result suggests that the percolation path between carbons is formed in the LTO/C nano-particles and then the conductivity of the LTO/C is improved. In future, we will clarify the distribution of carbon in the LTO nano-particles with an auger electron spectroscopy.

Fig. 5. Rechargeable curves of the LTO/C anode obtained with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ (a) and $0.5 \text{ mol}\cdot\text{dm}^{-3}$ (b) at 1 C.

Fig. 6. Rechargeable curves of LTO/C anode at rechargeable rate indicated.

Figure 6 shows the rechargeable curves of the LTO/C anode at the rechargeable rate indicated. The rechargeable test was examined up to 20 C. The rechargeable capacity of the LTO/C at the plateau anode decreased with increasing the rechargeable rate. The voltage of the LTO/C anode at the plateau decreased to 1.35 V at 20 C. It was considered that the high current led to the large ohmic polarization. These results indicated that the lithium ion cell had a high AC impedance at a rechargeable rate more than 10 C. The discharge capacity of the LTO/C anode was $150 \text{ mAh}\cdot\text{g}^{-1}$ at 10 C. The efficiency of charge and discharge was 98%. The retention ratio of the discharge capacity for 1 C was 88%. The discharge capacity of the LTO/C anode was $120 \text{ mAh}\cdot\text{g}^{-1}$ at 20 C. The efficiency of charge and discharge was 70%. This result suggests that the effects of high conductivity and the rapid diffusion of lithium ion due to nano-sized LTO/C are spoiled by the large ohmic polarization under the high current. Furthermore, it was considered that the agglomeration of LTO/C nano-particles occurred in the anode and then led to the reduction of the ionic or electronic conduction. The LTO/C anode will exhibit a superior rechargeable rate performance if the carbon content, particle size and state of agglomeration are improved in the LTO nano-particles.

Figure 7 shows the relation between the cycle number and the discharge capacity of the LTO/C anode at 1 and 10 C, respec-

Fig. 7. Relation between the cycle number and the discharge capacity at 1 C (a) and 10 C (b).

Fig. 8. Relation between the cycle number and the discharge capacity at 10 C and 50°C.

tively. The discharge rate was the same as the charge in the cycle test. The cycle test was conducted up to 500th cycle at room temperature. The discharge capacity of the LTO/C anode still maintained 96% of the initial discharge capacity after 500th cycle at 1 C. On the other hand, when the discharge rate was 10 C, the discharge capacity of the LTO/C anode maintained 96% of the initial discharge capacity. It was clear that the LTO/C anode had no large capacity fade even high discharge rate. The LTO/C nano-particles showed a high stability of structure in the fast intercalation of lithium ion. It is expected that LTC/C anode will show good cycle performance at higher rate more than 20 C.

Figure 8 shows the relation between the cycle number and the discharge capacity of the LTO/C anode at 50°C. The cycle test was conducted at 10 C up to 100th cycle, while the coin cell was heated at 50°C on the hot plate. The discharge capacity of the LTO/C anode indicated $160 \text{ mAh} \cdot \text{g}^{-1}$ and the cycle life of it was also stable. It was well known^{19)–21)} that the LTO/C anode had high cycle stability even elevated temperature. The discharge capacity of the LTO/C anode maintained 98% of initial discharge capacity after 100 cycles. It was clear that LTO/C anode had excellent cycle stability at 50°C as well as room temperature. The discharge capacity and cycle stability of LTO/C anode at 50°C was superior to that at 25°C. This finding indicates that the electric conductivity of the LTO/C is raised at 50°C and the crystal structure of LTO was had a high stability during the intercalation of lithium ion even 50°C.

4. Conclusion

LTO/C nano-powders were successfully synthesized through the pulse jet spray pyrolysis with an aqueous solution with a citric acid. LTO/C nano-powders with average particle size of 50 nm and the high crystallinity were rapidly obtained regardless of the concentration. The carbon content in LTO/C estimated by TG-DTA curves was 10 wt% and in agreement with the calculated value. ICP analysis showed that the molar ratio of Li/Ti in the LTO was in good agreement with that in the starting solution. The discharge capacity of the LTO/C anode was $170 \text{ mAh} \cdot \text{g}^{-1}$ at 1 C. The LTO/C anode had a high discharge capacity of $120 \text{ mAh} \cdot \text{g}^{-1}$ at even 20 C. The discharge capacity of the LTO/C anode maintained 96% of the initial discharge capacity after 500th cycle at 1 and 10 C. The LTO/C anode exhibited also excellent cycle stability at 50°C. In future, we highly expect that the pulse jet spray pyrolysis should be applied as the preparation technique of the various oxide nano-particles for electronics and catalyst other than battery materials.

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