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High Tap Density $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Microspheres: Synthetic Conditions and Advanced Electrochemical Performance

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Abstract: Preparation of uniform spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with high tap density is significant to achieve a high volumetric energy density in lithium-ion batteries. Herein, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ micro-spheres with variable tap-density and tunable size distribution were synthesized by a newly designed industrial spray drying approach. The slurry concentration, sintering time and sintering conditions after spray, the effect of Li/Ti molar ratio on the lithium ion (Li^+) storage capability were investigated. A narrow particle size distribution around 10 μm and high tap-density close to 1.4 g cm^{-3} of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spheres can be obtained under the optimized conditions. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spheres can deliver much higher capacity of 168 mAh g^{-1} at 1 C-rate and show high capacity retention of 97.7% over 400 cycles. The synthetic conditions are confirmed to be critical for improving the electron conductivity and Li^+ diffusivity by adjusting the crystal and spatial structures. As-prepared high performance $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is an ideal electrode for Li-ion batteries or capacitors; meanwhile the presented approach is also applicable for preparing other kind of spherical materials.

Introduction

With the increasing demand for lithium ion battery (LIBs) in electric vehicles, the safety and energy density of LIBs become important to guarantee its worldwide commercialization and long driving distance.¹ Although the graphite is the most commonly used anode, it always suffers the severe safety problems, such as flammable risks and lithium plating in the fast (dis-)charge process.² Thus, seeking safer anode to replace graphite are being carried out intensively,³ and the spinel structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has attracted great attention.⁴ The large crystalline channels for Li^+ and a flat potential plateau at 1.55 V (vs. Li/Li^+) can facilitate the Li^+ (de-)intercalation, prevent the lithium plating, and suppress the electrolyte decomposition.⁵ Particularly, the

thermal stability of lithiated $\text{Li}_7\text{Ti}_5\text{O}_{12}$ is much higher than that of lithiated graphite (*i.e.*, LiC_6),⁶ because of its stable three-dimensional lantern structure constructed by the corner-interconnected octahedral TiO_6 . However, a relatively low conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$) and theoretical capacity of 175 mAh g^{-1} is still problematic for its application. Therefore, enhancing the rate capability and increasing the tap density to gain higher volumetric energy density is rather crucial for commercialization. So far, simultaneous improvement in rate capability and tap density of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is still greatly challenging.⁷

Recently, many excellent strategies, including the cation doping,⁸ conductive material modification,⁹ compounds addition,¹⁰ binder/electrolyte optimization,¹¹ particles tailoring to nanoscale levels,¹² etc. have been widely developed to improve the rate performances. However, the parameter of tap density is rarely discussed in most of the researches. The efforts of developing one scalable approach to produce high tap density $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is urgently needed, which is actually important for the practical applications. Generally, spherical particles with uniform size distribution and smooth surface always give rise to a higher tap density than that of irregular ones, and possess better fluidity and processing performance.¹³ Dahn and co-workers even reported that micro-sized particles with high tap density could have less reactivity at highly-oxidized state in respect of thermal stability.¹⁴ And also, the same for cathode in LIBs, high tap density spherical $\text{LiNi}_{1-x-y}\text{Co}_y\text{Mn}_2\text{O}_2$ particles can directly pave the way to its commercialization.¹⁵ Therefore, it is significant to prepare uniform, highly dispersive and spherical structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles.¹⁶

However, to date, most synthetic strategies are based on the solid-state and sol-gel approach, in which the uniformity of morphologies and desired high density are difficult to be controlled, particularly aiming for the scalable production. Alternatively, the spray drying method is being used to prepare uniform micro-sized spherical materials in a high production.¹⁷ Based on a newly designed spray approach, herein we successfully synthesize a series of tunable micro-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. The critical parameters, including the slurry concentration, molar ratio of Li/Ti, sintering conditions before and after spray drying were investigated systematically. Furthermore, a relationship between the synthetic conditions, and resultant structure, final lithium storage capability were correlated to the design of the advanced electrode materials. Spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ porous particles with a high tap density of 1.35 g cm^{-3} are prepared and exhibit an extremely robust rate capability and cycle ability.

Results and Discussion

Influence of slurry concentration

The spray drying procedure is presented in Figure 1a, where the

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regime of solid slurry concentration is one of the critical factors to prepare $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spheres with a uniform distribution and high tap density (Figure 1b). A relatively high slurry concentration can facilitate the aggregation of seeds and the growth of spherical particle, while a dilute concentration gives rise to the loosely packed particles (Figure 1c-d). To explore the key conditions, different slurry concentrations of 0.15, 0.28 and 0.35 g mL^{-1} were selected. The quasi-spherical particles rich of surficial vacancies can be obtained at a low concentration of 0.15 g mL^{-1} . As a result, the loose structure gives rise to a low tap density of 0.66 g cm^{-3} (*i.e.*, P-1 sample). Increasing the concentration to 0.28 and 0.35 g mL^{-1} leads to the formation of the spherical particles with dense structure and larger size, which are abbreviated as P-2 and P-3, respectively. The average particle size of P-1, P-2 and P-3 are 7, 10 and 12 μm , respectively (Figure 2d), and the XRD pattern is completely consistent to the typical fingerprint structure of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$. However, the tap-density of P-2 (*i.e.*, 0.82 g cm^{-3}) and P-3 (*i.e.*, 0.83 g cm^{-3}) is much higher than that of P-1 (Figure 3a). Considering only a little bit increase in tap density as increasing the concentration from 0.28 to 0.35 g mL^{-1} , in this case, the slurry concentration is therefore selected to be around 0.28 g mL^{-1} , under which the capability of pumps can guarantee a uniform spray drying and also avoid the clogging problem resulted from the high viscosity of suspension.

Figure 1. (a) Schematic diagram of spray drying procedure and (b) Critical parameters determining the morphology and structure of particles. The aggregation of primary particles for spherical particles from (c) the dense and (d) dilute slurry respectively. Inset of (a) is the digital graph of nozzle.

Effect of sintering time

The effect of sintering time for precursors on tap density was further investigated (*i.e.*, the slurry concentration, 0.28 g mL^{-1}). A long sintering time is benefit to the crystal growth of primary particles. The intensity of diffraction peaks of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ become stronger as increasing the sintering time (Figure 2e), but there is no obvious change in tap-densities of 0.87-0.89 g mL^{-1} (Figure 3a). The morphologies of P-4, P-5 and P-6 with the sintering time of 1 h, 4 h and 8 h were demonstrated in Figure 2f-h, and the size distribution varied from 12 to 10 μm , respectively (Figure 2i). They all have a spherical morphology, particularly the P-4 sample consists of numerous uniform nano-sized primary particles which can facilitate the fast lithium diffusion for high rate capability. Overall, considering the negligible difference in the tap density as increasing the sintering time, sintering 1 h is more than enough for the solid-state reaction and consequently can reduce the energy-consumption.

Effect of sintering conditions after spray

To make the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spheres having an appropriate particle size, morphologies and high tap-density, the effect of sintering conditions after spray drying is further discussed (Figure 3b). Thermally treating P-4 sample under a high temperature of 800-900 $^{\circ}\text{C}$ give rise to a higher degree of crystallinity; meanwhile the spherical particle sizes of LTO-1 (800 $^{\circ}\text{C}$), LTO-2 (850 $^{\circ}\text{C}$) and LTO-3 (900 $^{\circ}\text{C}$) were gradually decreased from 11.5 (*i.e.*, P-4) to 10.6, 9.8 and 8.5 μm respectively (Figure 4a-f). This is mainly attributed to the shrink of spheres, which caused by the mutual molten growth of primary particles at a high sintered temperatures. As a result, the volume of microspheres is reduced, thereby giving rise to increased tap densities of 1.00, 1.20 and 1.40 g cm^{-3} (Figure 3b), respectively. The SEM images of the individual microspheres of LTO-based samples (Figure

Figure 2. SEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles prepared from different slurry concentration. (a) P-1, (b) P-2, (c) P-3 and (d) size distribution profiles of P-1, 2 and 3) sample sintering for 2h. SEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles with different sintering time before spray. (e) Typical XRD patterns of samples. (f) P-4 for 1h, (g) P-5 for 4h and (h) P-6 for 8h. (i) size distribution profiles of P-4, 5 and 6) sample.

Figure 3. Tap density of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles with varying the synthetic conditions of (a) Sintering time of precursors at 800 °C before spray, (b) Sintering temperatures after the spray and tuneable Li/Ti ratio. (c) A comparison of tap density with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in previous literatures. The cloverleaf demonstrates the optimized conditions for P4 and final LTO-4 prepared under the Li/Ti ratio of 0.75.

4a-c) illustrate that the primary particles were partially molten to form a continuous solid framework, and the primary particle size increased from ca. 200 nm for LTO-1, 450 nm for LTO-2, to 800 nm for LTO-3, respectively. These results suggest that the primary particle was rearranged under a high temperature treatment, giving rise to an integral connection of the primary particles towards high tap density and crystallinity (Figure 3b). Note that, the specific surface areas and average pore diameters of LTO-based sample are 4.2, 2.1, 0.9 m² g⁻¹ and 37.2, 37.8, 38.1 nm, respectively. The surface features of LTO-3 is inferior comparing to those of LTO-1 and LTO-2, because the stacking and completely molten of primary particles induced by the high temperature. Thus, the temperature of 850 °C is appropriate for enhancing the tap density. The porous particles consisting of interconnected primary nanoparticles are beneficial to fast Li⁺ diffusion capability and high Li storage due to the shorter Li⁺ diffusion route and a full utilization of empty channels assisted by the complete wetting of electrolyte.

Importance of Li/Ti molar ratio

With the aforementioned conditions, the effect of Li/Ti molar ratio on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was determined by changing the ratio from 0.75, 0.80 to 0.85, respectively. The actual molar ratio determined by the ICP was 0.72, 0.77 and 0.81, which is a little bit lower than the raw ratio due to the evaporation of Li source in the calcination. The products of LTO-4 and LTO-5 were prepared with the ratio of 0.75 and 0.85, while LTO-2 is attained using the

ratio of 0.8. The spherical particle size is gradually increased as increasing the Li/Ti molar ratio. The average size and tap density of LTO-4 and LTO-5 microspheres is about 9 μm, 10 μm and 1.35, 1.32 g cm⁻³, respectively (Figure 3b). The tap density of LTO-4 is much higher than that of most LTO materials reported before (Figure 3c).¹⁸⁻²⁰ Even other LTO reported in previous literatures have a little bit higher tap density, most synthetic strategies only enable a low production in the laboratory and mainly focused on nano-size LTO.²¹ Note that the primary particles of LTO-4 are a little larger in size than that of LTO-5 and have a relative smoother surface, being favorable for gaining high tap density. There is no obvious variation in the porosity and crystallinity of the samples as tuning the Li/Ti ratio (Figure 4g-l). That is, all the samples possess the porous structure that is more than enough to allow the fast penetration and distribution of electrolyte within the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. Benefiting from the spherical morphology, porous structure and fine dispersion, the high tap density of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles is significant to achieve a high volumetric capacity in LIBs. In addition, except having effect on the structure, the different Li/Ti ratio can also give rise to quite different lithium storage capability. As confirmed by the corresponding XRD peak around 26.7° (inset of Figure 4m), TiO_2 is formed in the LTO-4 sample. Note that the co-existence of TiO_2 in LTO-4 may enhance the performance of the material because of the following reasons: (i) additional capacity contributed from TiO_2 , which has higher

Figure 4. (a-c) SEM images and (d-f) size distribution of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles prepared from P-4 sample at the different temperatures of (a, d) 800 °C, LTO-1, (b, e) 850 °C, LTO-2 (Li/Ti = 0.8), and (c, f) 900 °C, LTO-3. SEM images and size distribution of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles prepared from the different Li/Ti ratio of (g-i) 0.75, LTO-4 and (j-l) 0.85, LTO-5 at 850 °C.

Figure 5. Electrochemical performances of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles in lithium battery. (a) Comparative rate capabilities and (b) typical voltage vs. capacity profiles of LTO-4 sample and (c) cycle test at 1C. (d) Comparative cycle performances of LTO samples and (e) the typical EIS analysis.

theory capacity of 336 mAh g^{-1} than 175 mAh g^{-1} of LTO;²² (ii) the improved electronic conductivity of LTO-4 by TiO_2 with better electronic transport ability;²³ (iii) the improved kinetics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ towards faster Li^+ intercalation assisted by the TiO_2 .²⁴

Electrochemical Performance

The comparative rate capability of LTO-based samples is summarized in Figure 5a-b. The capacities of LTO-1 and LTO-3 dropped dramatically as increasing the rate, which is only 77 and 30 mAh g^{-1} at the 5 C-rate, respectively. The rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ annealed at 850°C (LTO-3) increases obviously at high C-rates, and a capacity of 121 mAh g^{-1} can be obtained at 5 C-rate. On the other hand, the Li/Ti molar ratio of the initial mixture also has largely effect on the capacity. The LTO-4 obtained with the Li/Ti molar ratio of 0.75 exhibits the highest capacity. The capacities of 173, 172, 171, 167, 152, 143 and 121 mAh g^{-1} can be obtained at the rates of 0.1, 0.2, 0.5, 1, 2, 3 and 5 C, respectively. The capacity can recover to 170 mAh g^{-1} , as the current density is switched back to 0.2 C. The rate capability well demonstrates that a high sintering temperature at 850°C with an appropriate Li/Ti ratio is critical to improve the performances of the LTO-based materials.

The cycle performances of LTO-based samples are further demonstrated in Figure 5c-d. The LTO-1 and LTO-3 obtained at 800°C and 900°C , only has the low capacity retention of 63.8% and 75%, respectively. The inferior performance of LTO-1 is mainly attributed to the lower crystallization which cannot provide enough fine channels for the Li^+ intercalation/de-intercalation. While for the sample of LTO-3, the larger primary particle size around 800 nm would be an obstacle for the fast Li^+ diffusion and electron transport since the natural electronic conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is low ($<10^{-9} \text{ cm}^2 \text{ s}^{-1}$).⁷ The Li/Ti molar ratio of the initial mixture also shows impact on the cycle performance. The LTO-4 with a Li/Ti molar ratio of 0.75, can deliver the highest capacity of about 168 mAh g^{-1} even after the 400 cycles at 1 C-rate, and its capability retention ratio is as high as 97.7%. Note that at the same conditions, the capacity of LTO-5 obtained with a high Li/Ti ratio is only 133 mAh g^{-1} , and the capacity retention is 91.6%. The Li/Ti molar ratio in the initial mixture for LTO-4 is 0.75, the insufficient Li_2CO_3 would cause the formation of the impurities such as rutile/anatase TiO_2 in LTO-4. As aforementioned, the TiO_2 would functionalize as a

promoting additive in LTO-4, not only to increase the capacity, but also to improve the rate capability of the material. In the case of LTO-5, the Li/Ti molar ratio in the initial mixture is 0.85, which is slightly higher than the stoichiometric Li/Ti molar ratio in $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Thus, TiO_2 would not be expected to be formed in LTO-5, leading to a low capacity and detrimental capacity retention.

It should be pointed out that the capacities of all as-prepared LTO spherical particles are much higher than that of LTO Reference (i.e., 60 mAh g^{-1} at 1C, 30.4 mAh g^{-1} at 5 C) obtained without spray drying process. A rather low capacity retention of 83.5% after 400 cycles at 1 C-rate were obtained for LTO Reference, fully demonstrating the advantages of the porous structure obtained by the spray drying strategy. The difference in the electrochemical performance of LTO-based samples was further investigated by electrochemical impedance spectra (EIS) at the charged state (Figure 5d). The semi-circular at the high frequency and the slope at the low frequency represent the resistance and Li^+ diffusivity within the electrode, respectively.²⁵ The resistance of LTO-4 is substantially lower and its Li^+ diffusion rate is much faster than others. Those are responsible for its higher rate capability and better cycling stability. By contrast, the LTO-5 electrode has a high resistance, indicating that the inferior electron conductivity and Li^+ diffusion are affected by the high Li/Ti molar ratio. The LTO Reference demonstrates the lowest Li^+ diffusion constant due to the irregular interspace structure.

Conclusions

Spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles with high tap density and excellent electrochemical properties were synthesized based on a newly designed spray drying method. The synthetic conditions, resultant structure and final lithium storage capability are crucial to optimize the performance of the electrode materials. It is demonstrated that, In particular, the TiO_2 formed with a low Li/Ti molar ratio of the initial mixture can largely enhance the capacity and rate capability of the material. As-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spherical particles under the optimized conditions can deliver a high capacity of 168 mAh g^{-1} and achieve excellent capacity retention of 97.7% even after the 400 cycles at 1 C-rate. In addition, the cost-effective, scalable and feasible spray drying strategy may provide a new approach to prepare other kind of electrode materials with high volumetric energy density.

Experimental Section

Materials Preparation: Stoichiometric amounts of Li_2CO_3 and anatase-type TiO_2 (molar ratio of Li/Ti, 0.8) were ball-milled for 3 h in industrial ethanol to obtain a uniform suspension. Then, the suspension was dried at 110°C for 4 h and then sintered in muffle furnace at 800°C for 2h, giving rise to solid $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. Different amount of as-prepared solid particles was dispersed into de-ionic water and ball-milled for 3 h to form suspension with different concentrations of 0.15, 0.28 and 0.35 g mL^{-1} . After spray drying at 220°C , self-assembled $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microspheres with tunable tap densities and size distributions were obtained and abbreviated as P-1, P-2 and P-3. Alternatively, changing the sintering time from 2 h to 1, 4 and 8 h were named as P-4, P-5 and P-6, respectively. Finally, the P-4 sample was further annealed at different temperatures of 800, 850, and 900°C for 8 h in muffle furnace, giving rise to new series of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, named as LTO-1, LTO-2 and LTO-3 respectively. Besides, the molar ratio of Li/Ti in the raw materials Li_2CO_3 and anatase-type TiO_2 were tuned to 0.75 and 0.85, and the products of

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LTO-4 and LTO-5 were obtained through the similar procedure of LTO-2. For comparison, non-spray dried counterpart (named as Normal LTO) was prepared by direct annealing of the ball-milled slurry under the similar conditions. A detail comparison is listed in Figure 3.

Spraying Process: The spray drying equipment (YC-015) is manufactured by the Shanghai Pilotech Instrument and Equipment Co., Ltd. The nozzle geometry is round with internal diameter of 1mm (inset of Figure 1a). The main procedure for spray drying is illustrated in Figure 1a. Firstly, the feed slurry was pumped to the nozzle (2 in Figure 1a) and then sprayed into aerosol droplets by the centrifugal atomizer (3 in Figure 1a). And then, the moisture of slurry was evaporated immediately to form spherical powders when the hot air flowing through the heating tube (1 in Figure 1a). The spherical powders were separated and collected from the drying gas by cyclone separator (4 in Figure 1a). Finally, the wasted gas was pumped out by the induced draft fan (5 in Figure 1a) and released after the filter treatment (6 in Figure 1a).

Materials Characterization: The crystal information was acquired by X-ray powder diffraction (XRD) using an X'Pert-ProMPD (Holand) D/max- γ X-ray diffractometer with Cu K α radiation ($\lambda = 0.154178$ nm). The morphology was observed using a scanning electron microscopy (SEM, EVO 18, Germany or Hitachi S-4800, Japan). The distribution of particle size was identified with a laser particle size analyzer (HORIBA LA-960). The N₂ adsorption/desorption isotherms were obtained via a Quadrasorb 2MP (Micromeritics Instrument Corp.) surface area & porosity analyzer at 77 K. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

Electrochemical Measurement: As-prepared Li₄Ti₅O₁₂ microspheres were tested in half battery using the CR2032 type coin cell. The working electrode was prepared as below. Typically, the active material, acetylene black and poly-vinylidene fluoride (PVDF) with the weight ratio of 8:1:1 were mixed in N-methyl-2-pyrrolidone (NMP) to form a uniform slurry and then casted on the copper foil. The loading of active material on the electrode is about 1.3 mg cm⁻². The casted electrode was dried in vacuum oven at 80 °C overnight and punched into circular pieces. Metallic lithium foil was applied as the counter electrode versus the Li₄Ti₅O₁₂ electrode and they are separated by the Celgard 2400 separator, in which the electrolyte of 1.0 M LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC, v/v = 1:1) was used. Electrochemical impedance spectroscopy (EIS) was tested under a charged status after the 10th cycle within 100 KHz-10 mHz using CHI660E electrochemical workstation.

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Keywords: Anode • Lithium battery • Li₄Ti₅O₁₂ • Spray drying • Spherical particles

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Spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles with high tap density and excellent electrochemical properties are synthesized based on a newly designed spray drying method. A detail description of synthetic conditions, resultant structure and final lithium storage capability is explored to design advanced electrode materials.

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High Tap Density $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Microspheres: Synthetic Conditions and Advanced Electrochemical Performance