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Effect of particle size and agglomeration of TiO_2 on synthesis and electrochemical properties of $Li_4Ti_5O_{12}$

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Abstract: The effects of the initial condition of synthesis on electrochemical properties of $Li_4Ti_5O_{12}$ were studied with the comparison among starting and final materials by SEM, XRD and electrochemical analysis methods. The influence of the solvents for mixing the starting material on the products was investigated. The results show that nano-sized $Li_4Ti_5O_{12}$ powder obtained by nano-sized TiO_2 with ethanolamine as solvent shows more excellent electrochemical performance. More than 95%, 91%, 85% and 71% of the nominal capacity is achieved respectively at 0.5C, 1C, 2C and 4C rate without excellent capacity fading after more than 30 cycles.

Key words: lithium titanate; $Li_4Ti_5O_{12}$, nano-TiO_2; solid-state synthesis

1 Introduction

The spinel lithium titanate has been extensively studied as a promising anode candidate presently[1−6]. Those researches show that $Li_4Ti_5O_{12}$ can accommodate Li-ions during the charging without a noticeable change in the lattice parameter and does not react with electrolyte for its high potential plateau at around 1.55V versus Li/Li^+. Consequently it offers excellent safe and cycle performance compared with carbonaceous materials used as anode active materials in commercial Li-ion batteries[7−8]. Moreover, the Li-ion diffusion coefficients, which is about 10 times higher than graphite, makes it more suitable as an negative electrode for high-power battery and electrochemical capacitors. However, the main drawback of $Li_4Ti_5O_{12}$ is the poor electronic conductance[9−10], which reduces the high-rate ability of the electrode and accordingly limits its applications in some fields. Many researches indicated that fine particle-sized spinel $Li_4Ti_5O_{12}$ exhibits more excellent rate ability with the higher number of lithium insertion sites and shorter length of Li-ion diffusion and electron transfer[11−13]. Consequently, there have been many studies focused on the synthesis of nano-sized $Li_4Ti_5O_{12}$[14−16].

As most of the compounds of Li sources such as lithium hydroxide ($LiOH·H_2O$) or lithium carbonate (Li_2CO_3) are discomposed or melted easily at a lower temperature while the titanate dioxide (TiO_2) reacts in solid phase during the solid-state synthesis process of $Li_4Ti_5O_{12}$. It is supposed that the particle size distribution of $Li_4Ti_5O_{12}$ powder may mainly depend on the grain size of TiO_2. In this study, the effect of the particle size of starting materials on the final material was discussed by the comparison of the raw material and products. The high-polar solvent ethanolamine was first used to disperse the nano-sized TiO_2 during synthesis progress of $Li_4Ti_5O_{12}$ compared with ethanol solvent.

2 Experimental

The $Li_4Ti_5O_{12}$ powder was prepared by three methods. Method A[14]: stoichiometic amounts of Li_2CO_3 (1−5 μm, Xinjiang Research Institute of Non-ferrous Metals), micro-sized anatase TiO_2(0.5−1.0 μm, Beijing Yili Fine Chemical Co.,Ltd.) and 10%(mass fraction) acetylene carbon black was mixed and milled for 30 h in agate jar at room temperature with ethanol as solvent. 8%(mass fraction) excess Li_2CO_3 was added to compensate for lithia volatilization during the high temperature heating. Method B is the same as method A

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but with nano-sized anatase TiO_2 (20−25 nm, Hangzhou Wanjing New Material Co., Ltd.) instead of the micro-sized TiO_2. Method C is the same as method B but with the ethanolamine instead of ethanol as solvent. The achieved slurries A and B were dried at 70 ℃ and the slurry C was dried at 180 ℃ to remove the solvent respectively. The resulting grey mixtures were preheated in a muffle furnace at 400 ℃ for 5 h in air and then sintered at 700 ℃ for 10 h, then cooled down to room temperature naturally to obtain the final powder. The above three products were named LTO-A, LTO-B and LTO-C corresponding to the method A, B and C, respectively.

The working electrode was prepared from a paste mixture of 83% $Li_4Ti_5O_{12}$, 8% polyvinyldifluorin (PVDF) binder, and 9% carbon black with N-N Dimethyl Foramide(DMP) as solvent. The paste was coated on copper foils and then dried under vacuum at 100 ℃ to make a working electrode. The cell was assembled in drying chamber, which consisted of the working electrode, a metal Li electrode, porous separator (celgard 2400) and 1.0 mol/L $LiPF_6$ ethylene carbonate (EC)/diethyl carbonate (DEC)(1:1) electrolyte. The initial open circuit voltage was about 3.1 V. The crystalline phase of the obtained $Li_4Ti_5O_{12}$ powder was identified by powder X-ray diffraction(XRD) using PANalytical X'Pert PRO MPD diffraction system (Cu K_α, 40 kV, 40 mA).

The particle morphology and average particle size of the starting material and final products were observed by scanning electron microscope (SEM) using the Hitachi S−4800 FE-SEM.

The electrochemical performance of the half-cells was evaluated using a battery test system LAND CT2001A model (Wuhan Jinnuo Electronics Co., Ltd.). The charge and discharging voltage range is from 1.0 to 2.5 V.

3 Results and discussion

3.1 SEM analysis

The SEM images of Li_2CO_3 powder, $Li_4Ti_5O_{12}$ powder and the gray mixture of Li_2CO_3, TiO_2 and acetylene carbon black prepared by method C are shown in Fig.1. The particle size of Li_2CO_3 is 1−5 μm. While the $Li_4Ti_5O_{12}$ powder size shown in Fig.1 is far smaller.

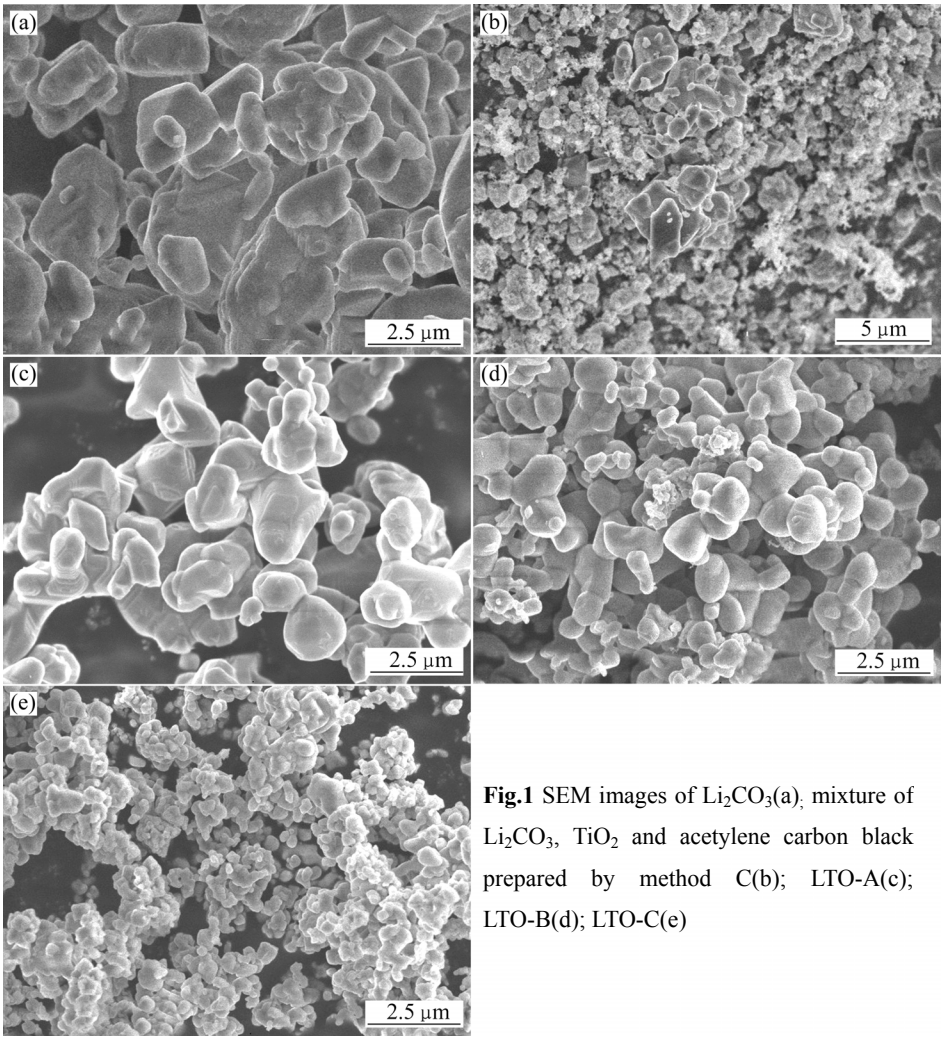

Fig.1 SEM images of Li_2CO_3(a), mixture of Li_2CO_3, TiO_2 and acetylene carbon black prepared by method C(b); LTO-A(c); LTO-B(d); LTO-C(e)

So it is supposed that there is no necessary relationship between them. Further more, the particle size of LTO-B(Fig.1(d)) and LTO-C(Fig.1(e)) synthesized by nano-sized TiO_2 are less than LTO-A(Fig.1(a)) prepared by micro-sized TiO_2. The results indicate that the particle size of $Li_4Ti_5O_{12}$ is not dependent on the particle size distribution of Li sources but on that of Ti sources. The influence of the dispersion of TiO_2 on the particle size of the final particles is also found. The nano-sized $Li_4Ti_5O_{12}$ is achieved by using ethanolamine as solvent, as seen in Fig.1(e). That is because the ethanolamine as a high-polar solvent is more efficient to disperse the nano-sized TiO_2 than ethanol and thus it can reduce the reunion of TiO_2 and generate a more homogeneous precursor, and consequently reduce the particle size of the products. It appears that the particle size distribution of $Li_4Ti_5O_{12}$ changes with that of TiO_2.

3.2 XRD analysis

The XRD patterns of the Li-Ti-O phases shown in Fig.2 correlate well with that reported in the Refs.[17−19]. Single spinel phase $Li_4Ti_5O_{12}$ is achieved with both methods B and C. While a weak diffraction peak appears at 2θ=27.4° in LTO-A , which indicate that the product prepared by method A contains a little amount of rutile phase TiO_2. During the react process, as shown in Fig.3, the TiO_2 powder, on one hand reacts with the near Li_2CO_3, on the other hand, transfers to the rutile phase and forms the impurity when they are not able to contact with Li_2CO_3. In our later studies, the peaks of rutile phase TiO_2 disappear when the heating temperature is greater than 723 ℃ for the good contact of the reactants provided by the Li_2CO_3 salt fusion. But the particle size of the products also increases with the increasing temperature, which is in agreement with previous literatures[20]. While at the same heating temperature in methods B and C, no impurities were found in the products, which indicates that the nano-sized TiO_2 and well mixed condition ensure good contact and complete reaction of the starting materials.

3.3 Electrochemical analysis

Fig.4 shows the charge-discharge curves of $Li_4Ti_5O_{12}$ samples prepared by methods A, B and C with voltage range of 2.5−1.0 V. The samples exhibit discharge capacities of 148.1, 163.7 and 161.8 mA·h/g respectively at 0.1C rate, and the initial efficiencies of charge-discharge are all above 97%. The voltage plates of all samples are about 1.55 V (vs Li^+/Li) with unapparent polarization, which is in agreement with literature values. The constant electrical potential is derived from the two-phase reversible reaction between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ during the charge/discharge progress according to the following reaction[21]:

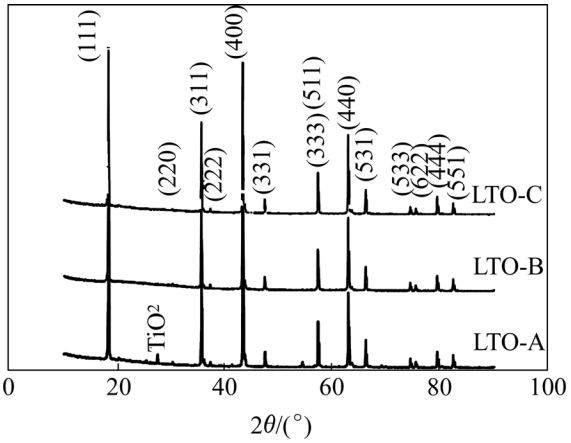

Fig.2 XRD patterns of $Li_4Ti_5O_{12}$ prepared by methods A, B and C

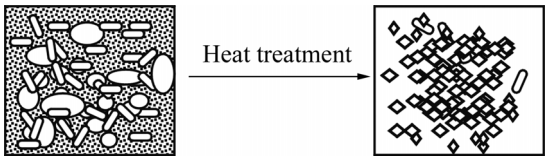

Fig.3 Schematic presentation of presence of impurity (⬭ presents TiO_2; ⬭ presents Li_2CO_3; ◇ presents $Li_4Ti_5O_{12}$; and black dots present acetylene carbon black)

$$(\mathrm{Li})^{8a}(\mathrm{Li}_{1/3}\mathrm{Ti}_{5/3})^{16d}(\mathrm{O}_4)^{32e} + \mathrm{e}^- + \mathrm{Li}^+ \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} (\mathrm{Li}_2)^{16c}(\mathrm{Li}_{1/3}\mathrm{Ti}_{5/3})^{16d}(\mathrm{O}_4)^{32e}$$

The charge (de-intercalation) capacities of the half cells at different rate range from 0.1 to 4C are shown in Fig.5. As shown in Fig.5, sample LTO-A shows only 148.1 mA·h/g capacity, and only 70 mA·h/g is obtained at 4C for sample LTO-A corresponding to the existing impurity and large size. However, 161.3 mA·h/g and 163.8 mA·h/g are obtained for sample LTO-B and LTO-C respectively and there is no distinguished difference of the capacities at the low charge-discharge current between them. Furthermore, with the charge-discharge rate increasing, the difference between sample LTO-B and LTO-C become notable. More than 20 mA·h/g capacities are obtained for sample LTO-C than LTO-B though they have the similar XRD patterns. The reason should be the particle size distribution of $Li_4Ti_5O_{12}$. Fine particle sized $Li_4Ti_5O_{12}$ are more favorable to fast Li insertion/extraction. Sample LTO-C prepared by the nano-sized TiO_2 as Ti source and with ethanolamine as solvent for mixing, shows about 71% capacity of the 0.1C capacity at 4C. There is almost no capacity fading after 30 cycles at different current. About 95%, 91%, 85% of the initial capacity are achieved at 0.5C, 1C and 2C respectively.

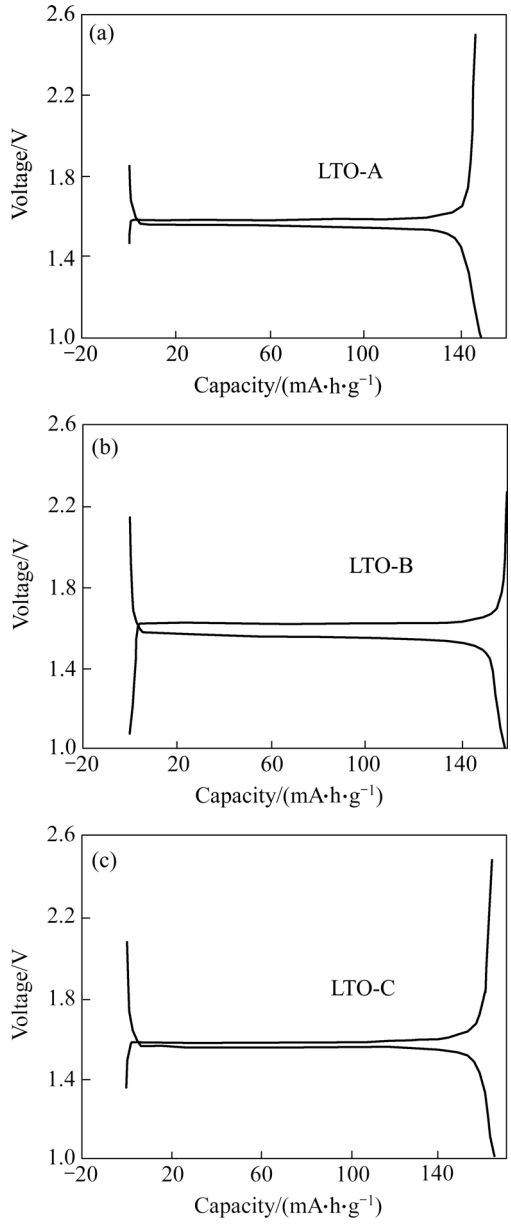

Fig.4 First charge and discharge curves of $Li_4Ti_5O_{12}$/Li half cells at 0.1C rate

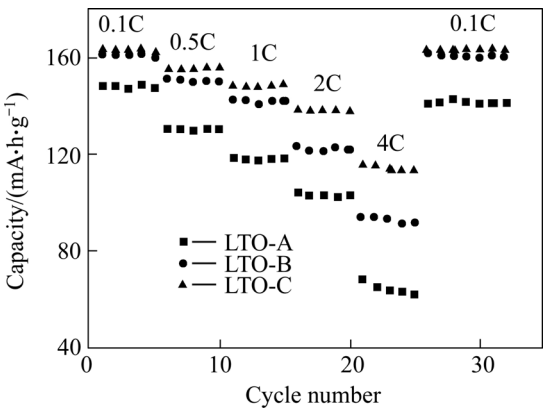

Fig.5 Charge (extraction) capacities in different rate as function of cycle number for cells shown in Fig.4

4 Conclusions

1) The particle size distribution of $Li_4Ti_5O_{12}$ is more dependent on that of Ti sources than on that of Li sources.

2) Ethanolamine is more effective to reduce the agglomeration of nano-sized TiO_2 than ethanol and subsequently the nano-sized $Li_4Ti_5O_{12}$ is generated.

3) Nano-sized $Li_4Ti_5O_{12}$ shows more excellent electrochemical performance than micro-sized ones, especially at high charge-discharge rate.

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