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Carbon Coating with Oleic Acid on $Li_4Ti_5O_{12}$

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Oleic acid was selected for carbon coatings on $Li_4Ti_5O_{12}$. The properties of $Li_4Ti_5O_{12}$/C were variable depending on the content of oleic acid. The multi-functional groups of oleic acid could orient properly to cope with the variable surface properties of $Li_4Ti_5O_{12}$, which could lead to dense carbon coatings. The low price and low toxicity of oleic acid were main advantages of the coating process. The structure and morphology of the as-prepared samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical performances including charge-discharge, cyclic voltammetry and Ac impedance were also investigated. The results revealed that the $Li_4Ti_5O_{12}$/C had a relatively smaller particle size and more regular morphology than that of $Li_4Ti_5O_{12}$. Carbon coating of using oleic acid as carbon source enhanced the ability of lithium ion diffusion in the electrode. It delivered a discharge capacity 164.67 mA h g^{-1} after 50 cycles for the $Li_4Ti_5O_{12}$/C. Carbon did not change the electrochemical process, instead enhanced the electronic conductivity. The reversible capacity and cycling performance were effectively improved.

Keywords: Lithium ion batteries , Anode material , Oleic acid, $Li_4Ti_5O_{12}$/C

1. INTRODUCTION

With the development of electric devices, especially electric vehicles (EV), power sources demanded higher power and higher energy density. However, traditional anode material graphite could not meet the requirements in terms of high power density, long cycle life, and safety. $Li_4Ti_5O_{12}$ (denoted as LTO) has attracted much attention as an anode material because of its appealing advantages such as little structural change (zero-strain insertion material) in charge-discharge process, outstanding cycling stability etc[1,2]. It has been considered as a promising alternative anode material to graphite. The LTO had a stable flat of Li insertion potential at about 1.55V (versus Li^+/Li), which was above the reduction potential of electrolyte solvent, thus it would not form SEI film at the interface. But LTO had low electronic conductivity (ca. 10^{-13} S cm^{-1}) and moderate lithium ionic diffusion coefficient (10^{-12} cm^2 s^{-1})[3,4] thus the high rate performance was not satisfied for commercial application.

Three typical strategies have been developed to overcome these problems. The first one was to synthesize nano-structured LTO[5-7].The nano-sized particle could shorten both the ionic and electronic transporting path, thus the kinetics of lithium ion intercalation was raised, therefore the electrochemical activity could be improved. The second one was to dope with cations and anions in Li, Ti and O (K^+, Mg^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Zr^{4+}, Mo^{4+}, V^{5+}, Ta^{5+}, F^- , Br^- and etc[8-24]). Substitution of a small quality of Li^+, Ti^{4+} or O^{2-} by supervalent ions could enhance electronic conductivity and reduce the electrode polarization. But the substitutional site of metal ions was not easy to be defined. The third one was to coat conductive materials on LTO, such as Cu[25], Ag[26] or metal nitrides[27]. But the cost of coating materials was expensive and the working procedure was complicated.

As one kind of surface modification method, Carbon-coating has been widely investigated because of its low cost and simple procedure. The carbon coating on active material could be processed to make better electrical contact among the particles. The coating could remarkably reduce 'dead zones' where active particles were coagulated or poorly networked with the carbon. Solid-state method has been widely employed to synthesize LTO/C composites [28,29]. But the higher temperature and the longer reaction time were required, in the meanwhile, the coating layer of solid-state method was not uniform. To overcome these drawbacks, solution method has been investigated to prepare LTO/C in this work. Till now, Sugar, carbon nanotubes, graphite, common organic compounds et al were selected for main carbon sources to coat LTO. Ogihara[30] et al. applied spray pyrolysis to the preparation of LTO/C anode powders. They selected lactic acid, malic acid, citric acid as carbon sources and reported that powders obtained via spray pyrolysis exhibited higher rechargeable capacity and good cycle performance. It was reported that the rechargeable property of $LiFePO_4$/C cathode had been improved using oleic acid as carbon source [31]. As far as we known, no research has been attempted to investigate oleic acid as carbon source to coat LTO. Oleic acid is a kind of larger sized unsaturated fatty acid, its multiple functional groups could favourably interact with LTO. Its low toxicity and low price were further reasons for its selection. However, it was unclear as to whether LTO/C prepared by using oleic acid as carbon source had a higher reversible capacity at high-rate charging-discharging. So the powder characterization and electrochemical properties of LTO/C anode materials synthesized by using oleic acid as carbon source were detailedly investigated in this work.

2. EXPERIMENTAL

2.1 Sample preparation

LTO/C composites were prepared by a solution method. $LiOH·H_2O$, $Ti(OC_4H_9)_4$ and oleic acid were used as reactants. Stoichiometric amounts of $LiOH·H_2O$ was dissolved in distilled water to obtain solution A. $Ti(OC_4H_9)_4$ was dissolved in ethanol obtain solution B. After the solution A and the solution B were mixed, adequate amount of oleic acid (the oleic acid to LTO mass ratio as 0.01,0.03,0.05, were labeled as LTO/C-1, LTO/C-2 and LTO/C-3 respectively) was added into mixed solution. After the ultrasonic dispersion, the mixed solution was heated and maintained at 80 ℃ under vigorous stirring until the solvent was evaporated. The product was dried at 80 ℃ for 12 h and yielded white precursors. The white precursors was calcined at 750 ℃ for 8 h in an argon atmosphere, then cooled in the furnace to room temperature.

2.2 Sample characterization

The crystal structures of LTO/C were characterized by X-ray diffraction (XRD, Rigaku D/MAX-RC) with Cu Kα radiation (λ = 1.5405 Å, 45.0 kV, 50.0 mA). The content of carbon was tested by TOC-VCPN- (SSM-5000A) analyzer. The morphology of particle was observed using a filed emission scanning electron microscope (FESEM, Quanta 200F, FEI). The particle size distribution was identified by laser particle size analyzer (OMEC LS900).The electrochemical characterizations were measured by charging and discharging over a voltage range of 1-2.5 V at different rates. The C rate was calculated from the weight and theoretical capacity of LTO. Cyclic voltammograms were recorded using a CHI604C electrochemical working station at a scanning rate of 0.2 mV s^{-1}. Ac impedance measurement was carried out using a 5.0 mV ac voltage signal in the 100 KHz to 10 m Hz frequency range in automatic sweep mode from high to low frequency.

The working electrodes were prepared by spreading the anode slurry (80 wt% of the active material, 10 wt% of polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP), and 10 wt% of carbon black) onto an aluminium foil followed by drying in vacuum at 120 ℃ for 12 h. A typical electrode disk contained 2.0-2.3 mg active material. The cells (CR2025) were assembled in an argon filled glove-box using lithium metal foil as the counter electrode. The electrolyte was 1.0 mol dm^{-3} $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v).

3. RESULTS AND DISCUSSION

Fig. 1 displayed the X-ray diffraction patterns of the obtained LTO/C powders with different content of oleic acid. All samples exhibited single phase of LTO with an ordered spinel indexed to the cubic $Fd\bar{3}m$ space group and were in accordance with JCPDS card No-26-1198. The sharp peaks in the patterns showed good crystallinity of electrode materials. But no diffraction response of the carbon in XRD patterns was observed due to its amorphous form and low content. The result obtained from the TOC determinator indicated that the amount of carbon in the LTO/C-1, LTO/C-2, LTO/C-3 samples were about 0.47%, 1.92%, 3.68% respectively.

The effect of different content of oleic acid on the particles size and morphology of prepared powders have been investigated by SEM. All the samples have a like spherical shape and without serious agglomeration, as can be seen in Fig.2. But the observed particle size of prepared LTO/C powders was different as the amount of oleic acid increasing from 1wt% to 5wt%. Guerfi[32] pointed out that the carbon additive could help to hinder the agglomeration of LTO particles and retard the growth of particles during sintering. When the remainder carbon in prepared LTO/C was relatively lower (LTO/C-1), the carbon layer could not completely coat LTO particle, uncovered surface of particle directly contacted and leaded to agglomerate during sintering, so the particles of bigger size were obtained (LTO/C-1).

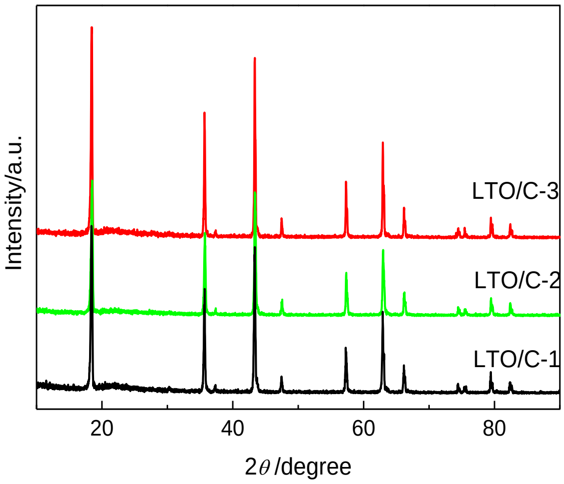

Figure 1. XRD patterns of LTO/C synthesized at different oleic acid addition

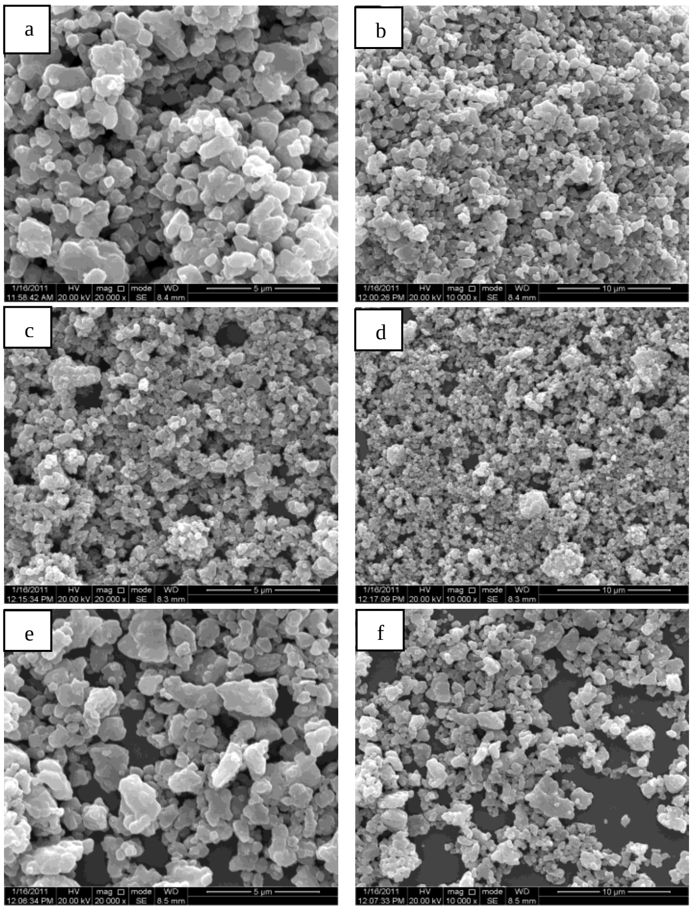

Figure 2. SEM images of LTO/C synthesized at different oleic acid addition a) 1mass%, 20000×; b) 1mass%, 10000×; c) 3mass%,20000×; d) 3mass%, 1000×; e) 5mass%, 20000×; f) 5mass%, 10000×

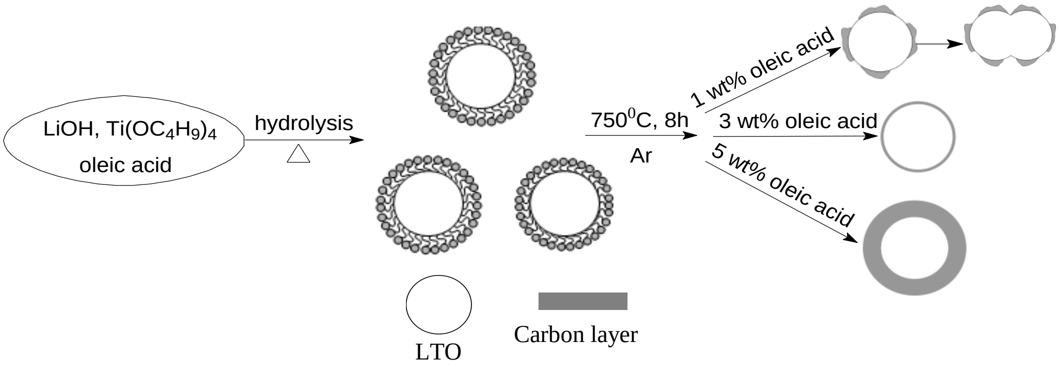

Figure 3. Schematic illustration for the formation procudure of LTO/C composite

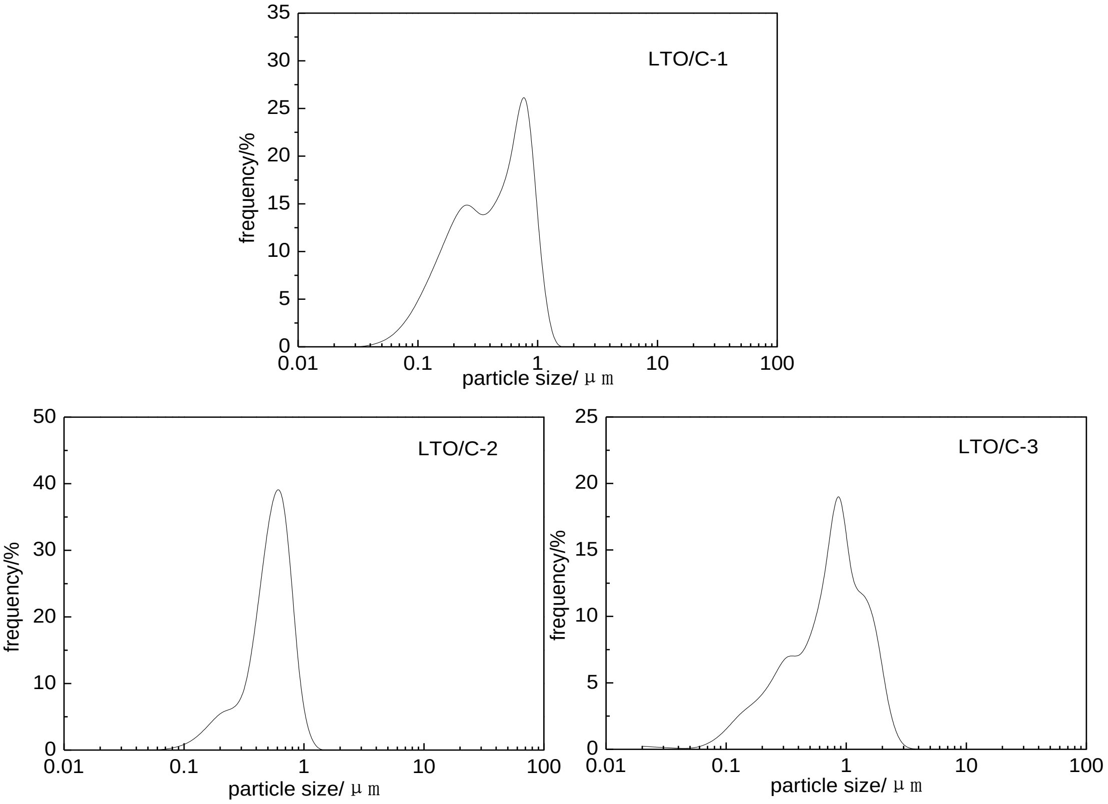

Figure 4. The particle size distribution of LTO/C powder

As the increasing of the remainder carbon, the uniform coated carbon layer could effectively prevent the LTO particles from directly contacting, so the particle size of LTO/C-2 was least. But the carbon layer of LTO/C-3 was relatively thicker, the particles size tended to growth slightly. The formation procedure of LTO/C was shown in Fig. 3.

To further determine this investigation, we ran particle size analysis on the typical samples. The particle size distribution of LTO/C powers was depicted in Fig.4.

As was seen in this figure, the average particle size was 760.8nm, 623.3 nm and 860.0 nm for LTO/C-1,2,3 respectively. The small and uniform particle was good for contact between active materials and electrolyte and then improved the electrochemical properties of the composites. Therefore, these results indicated indirectly that LTO/C-2 composite could give more advantages of electrochemical performance due to its well crystallization and suitable particle size.

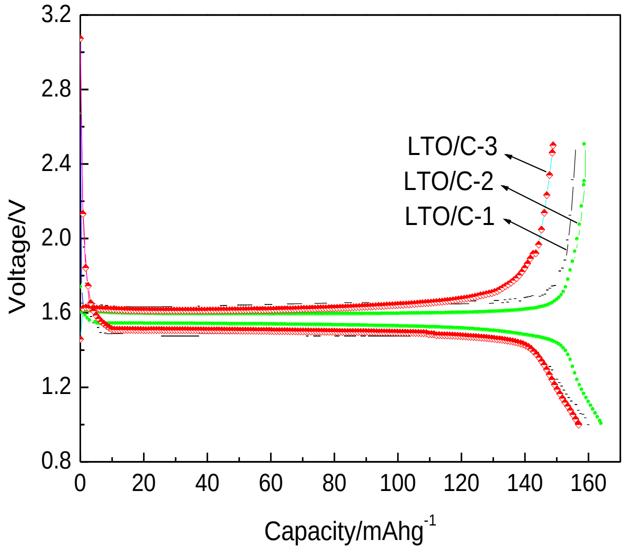

Figure 5. The initial charge and discharge curves of LTO/C synthesized at different oleic acid addition

The electrochemical characterization was carried out by charge–discharge tests and cycle voltammetry. Fig. 5 presented the initial charge/discharge curves of LTO/C-1, LTO/C-2, LTO/C-3 electrodes at 0.5 C between 1 V and 2.5 V versus Li. From the shape of the charge and discharge profiles, three kinds LTO/C electrodes exhibited a flat charge and discharge plateau at 1.47–1.72 V range, indicating the two-phase nature of the lithium insertion and extraction reactions between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$. As shown in Fig. 5, different anode properties were obtained from LTO/C with the additive amount of oleic acid varying from 0.01 to 0.05. LTO/C-2 exhibited higher capacities than other LTO/C. The reversible capacity reached 164.30 mA hg^{-1}, the value is very close to the theoretical capacity of LTO (175 mA hg^{-1}). Furthermore, the differences between the charge and discharge voltage plateau were smaller, which were representative of their good kinetics. The reason may lie in the increase of the electronic conductivity by coatin carbon. The electronic conductivities of the typical LTO/C-1, LTO/C-2 and LTO/C-3 powders were measured with the four-electrode method, and the data were listed in Table 1. Carbon coating on the surface of LTO particles could enhance the conductivity. The conductivities were almost six to seven orders of magnitude higher than that of pure sample. LTO/C-2 showed the highest electronic conductivity among three samples, reaching to about 5.8×10^{-6} S cm^{-1}.

Table 1. Electronic conductivity of prepared samples

Sample	κ(S·cm-1)
LTO/C-1	7.9×10-6
LTO/C-2	5.8×10-6
LTO/C-3	3.1×10-7

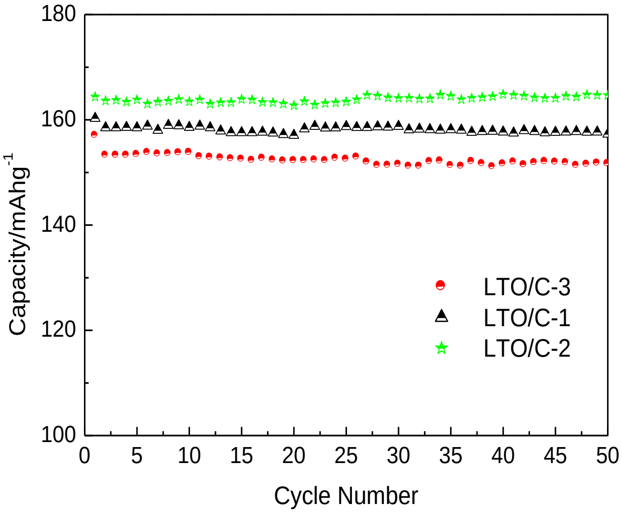

Figure 6. The cycle curves of LTO/C synthesized at different oleic acid addition

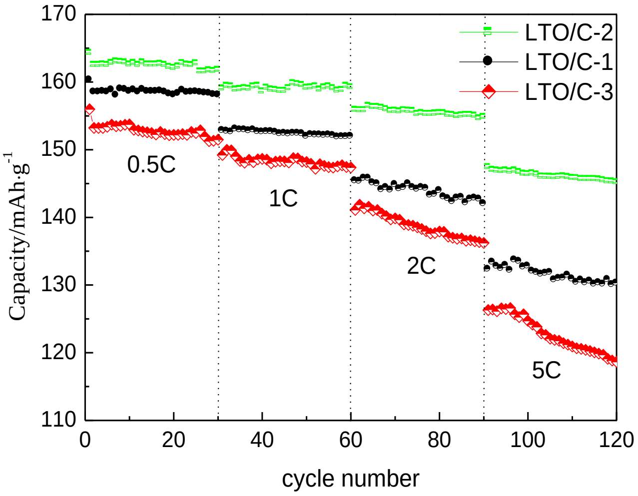

Figure 7. Cycling performances of LTO/C under the different oleic acid addition at different rate

The cycling performance curves of LTO/C electrodes at 0.5 C were plotted in Fig.6. According to the test, the cycling stability of three kinds of LTO/C was all excellent, although the reversible specific capacity was different. The electrodes were almost no loss of capacity after 50 circulations.

In order to show the high rate discharge ability of as-prepared LTO/C, the variation in discharge capacity with cycle for LTO/C electrodes at different rates from 0.5 C to 5 C were depicted in Fig.7. It could be seen from Fig.7 that LTO/C-2 showed the best cycling stability at high rate. The discharge capacity of about 161.76 mA hg^{-1} was obtained after 30th cycle at 0.5C rate and this value was lowered to 159.21mA hg^{-1},154.82 mA hg^{-1}, 145.17 mA hg^{-1} at the rate of 1 C, 2 C, 5 C. The result indicated that 3 wt% oleic acid as carbon source has significantly improved rate capacity and cycle stability of the LTO material.

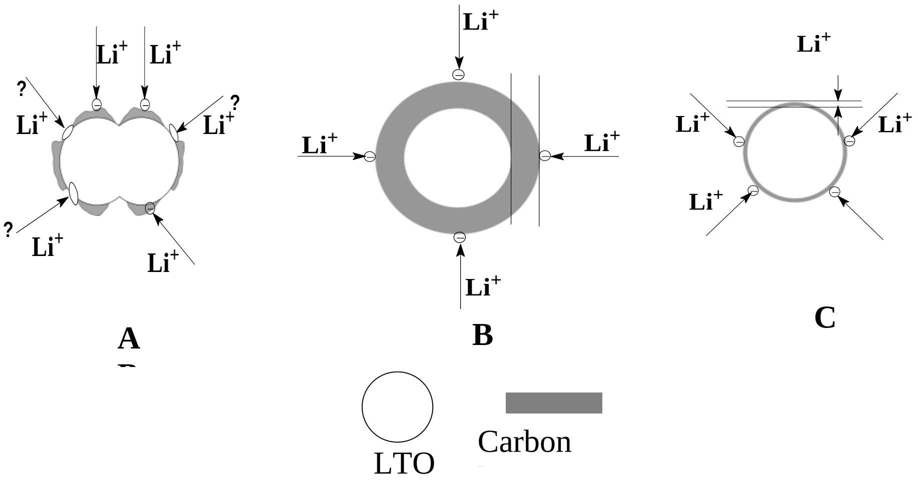

Figure 8. Schematic presentation of the electrochemical reaction path on three LTO/C particles

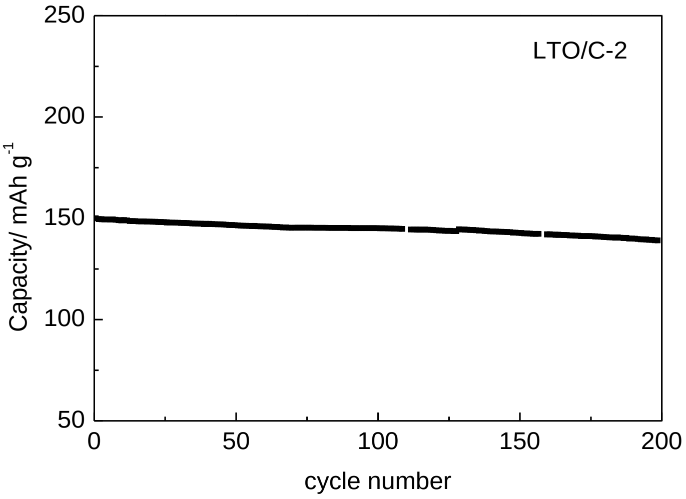

Figure 9. the cycle performance of LTO/C-2 sample at 5C rate

LTO/C-2 had better rate performance than other LTO/C. It attributed to LTO/C-2 sample having smaller particle size and more uniform coating layer than LTO/C-1 and LTO/C-3. The particle surface of LTO/C-1 could not form homogeneous coated layer (as shown in Fig. 8 A), which led to a noncontinuous electronic conducting and the larger particles size tend to lower the kinetics of diffusion. As a result, polarization was increased during charge and discharge, thus reduced the specific capacity and high rate performance. Moreover, the thick coating layer(as shown in Fig. 8 B) restricted the efficient charge transfer/transport; thus the specific capacity decreased, especially at high rates. These results showed that appropriate additive amount of oleic acid could decrease particle size and form uniform coating layer (as shown in Fig. 8 C). This morphology could reduce the distance of lithium ion diffusion and augment the contact surface of electrode/electrolyte, which improved the electronic conductivity of the electrodes and lowered the electrode polarization at high rate, resulting in good cycle stability and high rate performance.

The cyclical stability of the LTO/C-2 at 5 C rate was shown in Fig. 9. Even after 200 cycles, the capacity retention was about 92.65% at the high rate of 5 C. These phenomena indicated that carbon coating enhanced its rate capacity and cycle stability. It attributed to LTO/C-2 sample having smaller particle size and more homogeneous carbon layer than other LTO/C.

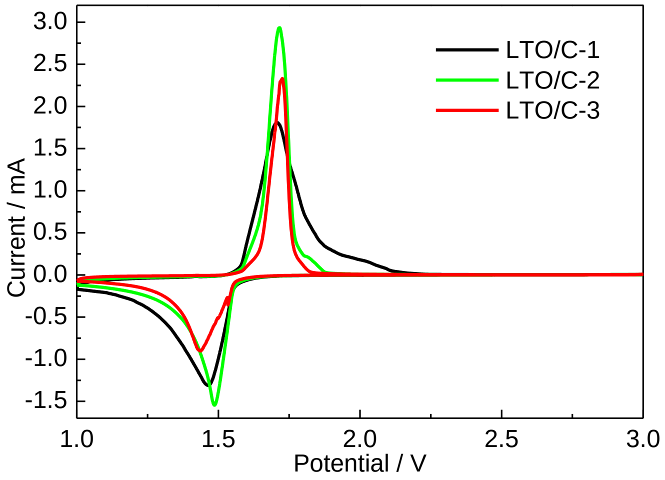

Figure 10. Cycle voltammograms of cells using the LTO/C-1, LTO/C-2 and LTO/C-3 samples as electrode materials

Table 2. Values of the CV peaks for LTO/C-1, LTO/C-2 and LTO/C-3 samples

Samples	φpa (V)	φpc (V)	Δφp (mV)
LTO/C-1	1.708	1.464	244
LTO/C-2	1.717	1.486	231
LTO/C-3	1.726	1.436	290

To better understood the electrochemical behaviors of LTO/C and the effect of different additive amount of oleic acid on electrochemical performance, cyclic voltammetry of the LTO/C-1, LTO/C-2 and LTO/C-3 electrodes at a scan rate of 0.2 mV s^{-1} between 1 V and 3 V were shown in Fig.10. The figure clearly exhibited that all the investigated samples had similar redox peaks, suggesting that coating carbon did not change the electrochemical reaction process of LTO in the voltage range of 1-3 V. But their intensities of the redox peaks were different. The intensities of the redox peaks for LTO/C-2 were much higher than other LTO/C, indicating the higher electrochemical reactivity of LTO/C-2 electrode. Furthermore, the peak profiles of LTO/C-2 were more symmetric and sharp. LTO/C-2 exhibited an anodic peak at 1.717 V and corresponding cathodic response at 1.486 V. The potential intervals of LTO/C-2 is 0.231 V, is least. As for cyclic voltammetry, the potential interval between anodic peak and cathodic peak was an important parameter to value the electrochemical reaction reversibility [28,33]. The sharp and symmetrical peaks appeared at around 1.45 V and 1.73 V could be attributed to the redox of Ti^{4+}/Ti^{3+}. In addition, values of the CV peaks were listed in Table 2. The potential differences between anodic and cathodic peaks for LTO/C-1, LTO/C-2 and LTO/C-3 were 244 mV, 231 mV, 290 mV respectively, suggesting that the lower electrode polarization and higher lithium-ion diffusivity was in solid state body of sample LTO/C-2. These phenomena further confirmed that appropriate amount of oleic acid was beneficial to the reversible intercalation and de-intercalation of lithium-ion in this synthesized anode material.

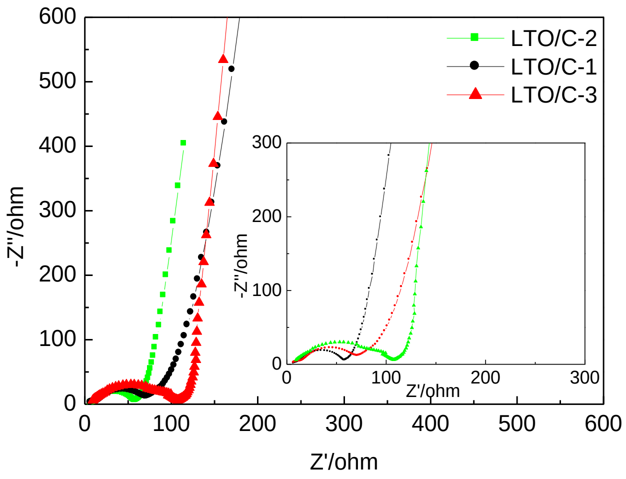

Figure 11. AC impedance spectra of LTO/C electrodes measured at open circuit potential ~3.0V *vs.* Li/Li^{+}

The resistance and the electrochemical reaction properties of electrodes were further examined by Ac impedance, EIS measurements were performed to monitor changes in electrolyte/LTO/C interface resistance at 0.5 C rate upon cycling. The open-circuit voltages were about 3.0 V when the cells were in the initial state. Fig. 11 presented the electrochemical impedance spectra of LTO/C/Li cells. Each curve consisted of a depressed semicircle in the high-middle frequency region. It was well known that the cross-section value of impedance spectra on the real Z’ axis at highest frequency was the resistance R_s, which corresponded the resistance of electrolyte mainly. For three systems they were very similar. The semicircle in the high middle frequency region was normally related to the complex reaction process over the electrolyte/anode, which might also include the particle contact resistance, charge-transfer resistance and corresponding capacitances. It could be seen that the resistance of LTO/C was variable with the difference of oleic acid addition. The dosage of oleic acid was excessive or insufficient, the resistant of electrodes were all increased, indicating that appropriate oleic acid as carbon source coated on LTO particle surface was favorable to the electrical conductivity. The oblique line in the low frequency region was corresponding to the diffusion of the lithium ions into the bulk of the anode material of the so-called Warburg diffusion [34,35].

4. CONCLUSIONS

Well crystallized LTO/C composites with different carbon content have been prepared by a solution method with oleic acid as carbon resource. The initial amount of the oleic acid was a critical factor which determined the electrochemical performance of as-prepared LTO/C electrodes. Carbon coatings with oleic acid exhibited competitive performance compared with other carbon coatings. The carbon source was cost-effective and environmentally benign. LTO/C-2 showed very good performance. The discharge capacities was 145.17 mA h g^{-1} with C rates of 5 C and the capacity retention was about 92.65 % at the high rate of 5 C after 200 cycles. It was clear that oleic acid coating sample enhanced the capacity retention and cycle stability especially at high charge–discharge rates, meanwhile the electrode of LTO/C-2 had lower polarization and higher lithium ion diffusivity. The carbon coating improved surface reaction kinetics. These results further demonstrated that the active interaction model with oleic acid worked well with LTO.

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