



Short communication

Micron-sized, carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as high power anode material for advanced lithium batteries

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ABSTRACT

Spherical, high tap density, carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders are synthesized by a spray-drying process followed by a facile pitch coating. XRD, SEM, TEM analyses show that the carbon layer uniformly coats the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles without producing any crystalline changes. We demonstrate that the carbon coating significantly increases the electrical conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ making it an efficient, high rate electrode for lithium cells. The electrochemical tests in fact confirm that the 3.25 wt% carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode operates with ultra high rate capacity levels, i.e., 100 C and has excellent capacity retention and charge–discharge efficiency for a life extending over 100 cycles.

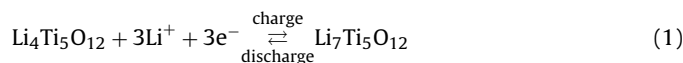
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1. Introduction

In the past few decades, lithium ion batteries (LIBs) have been the power sources of choice for popular mobile electronic devices, such as cellular phones, notebooks and MP3 players [1,2]. However, a profitable use of LIBs for large scaled energy storage applications requiring fast charge–discharging power rates [2], e.g., hybrid and electric vehicles (HEVs), renewable energy (wind and solar) plants, is still limited. Accordingly, exploration of new nanostructured electrode materials capable of improving the rate performance of LIBs by assuring enhanced kinetics of the solid-state diffusion of the Li^+ intercalation process as well as a high value of electronic conductivity [3], is needed. In addition, safety remains a top priority because these electrode materials are expected to perform under much more severe environments (such as those associated with HEVs and renewable energy storage systems) than those experienced in portable electronic devices.

A promising, safe anode alternative to the commercial carbon/graphite is the spinel-type $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO [4–11]. This material displays a two-phase electrochemical process associated with lithium insertion (charge) and extraction (discharge) in and out its

structure [12]:



evolving with a stable operating voltage centered on 1.5 V vs. Li/Li^+ . The interest in LTO is motivated by its the long cycle life, in turn associated with its very high structural stability. These unique properties in principle make LTO an anode much more suitable than graphite for the development of safe and long life batteries, especially if they are designed for operation at elevated temperatures [13]. However, despite these favorable properties, LTO does not yet meet all the requirements for being successfully used in high-rate batteries. A remaining issue that still prevents LTO from being commercially implemented is its low electrical conductivity at room temperature, resulting in poor rate performance [14–16].

This issue has been addressed by decreasing the material particle size to reduce the Li^+ diffusion path [17–20]. On the other hand, a decrease in particle size reflects into low powder tap density that in turn leads to a poor volumetric energy density. This additional issue has been addressed by coating nanosized LTO particles with conducting materials, e.g., carbon, to obtain electrodes combining high rate with compact morphology.

Recently, we reported that a carbon coating process, using a pitch carbon source with a π -bond sp^3 character, consistently improved the electrical conductivity of LiFePO_4 , this greatly enhances its electrochemical performance when used as electrode

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in lithium batteries [21–23]. We expect that the same approach may be extended to the LTO case with similar beneficial results. Accordingly, in this work we report a simple spray drying synthetic method to coat carbon on spherical LTO particles using pitch as the carbon source. We show that this procedure leads to the deposition of a uniform carbon layer that significantly increases the electrical conductivity of LTO (and thus, its rate capability) without affecting the crystalline structure.

2. Experimental

The spherical LTO powders were synthesized using a spray drying process followed by solid-state calcination. The synthesis of C-LTO was conducted in two steps. To be sure of obtaining a final material having high tap density (necessary for assuring high volumetric density) we first prepared dense LTO precursor powders and then proceeded with their coating, condition (necessary for assuring high rates).

For the precursor slurry, LiOH (Aldrich), anatase TiO₂ nanoparticles (Aldrich), and dispersant (5 wt%, relative to TiO₂) were dissolved in distilled water. The molar ratio of lithium to titanium was 4:5. The prepared precursor slurries and zirconia balls were mixed by a planetary mill at a speed of 300 rpm for 12 h. The homogeneously mixed slurries were atomized using a two-fluid nozzle at a pressure of 3 kg cm⁻² at 250 °C. The collected, spray-dried precursor powders were further calcined at 900 °C for 20 h under air to obtain still carbon-free LTO. For carbon coating, LTO was mixed with different amounts of pitch (2 wt% and 5 wt%) and calcined for 5 h at 750 °C in a furnace purged with Ar.

The morphologies of carbon-free and carbon-coated LTO samples were analyzed via field-emission scanning electron microscopy (FE-SEM; JSM-6400, JEOL) and high resolution transmission electron microscopy (HR-TEM; JEM-2010, JEOL). Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Rint-2000 with Cu K α radiation. The diffraction data were obtained in the 2θ range of 10–80° with a step size of 0.03°. The specific surface area and pore volume were calculated by nitrogen sorption measurements with a Quantachrom Autosorb-1 after the sample had been degassed at 200 °C for 4 h. The electrical conductivity was measured using a direct volt–ampere method (CMT-SR1000, AIT Co.) using a four-point probe. The carbon content was determined by elemental analysis using an EA 110 CHNS-O automatic analyzer (CE Instrument).

The electrochemical measurements were performed using CR2032 coin-type cells. The electrodes were made by mixing carbon-free or carbon-coated LTO active materials with a carbon black conducting agent (super P and KS6) and a polyvinylidene fluoride (PVDF) binder at a weight ratio of 80:10:10 in a N-methyl-2-pyrrolidone (NMP) solution, the prepared slurry was coated onto Cu foil. Lithium metal was used as the counter electrode. The electrolyte was 1 M LiPF₆ solution in ethylene carbonate–diethyl carbonate (EC–DEC, 1:1 vol%, Panax E-Tec. Co., Ltd.) adsorbed in a porous polyethylene separator. The cells were charged and discharged at 25 °C between 1.0 V and 3.0 V voltage limits, by applying current densities ranging between 17.5 and 17,500 mA g⁻¹ (0.1–100 C-rate).

3. Results and discussion

Fig. 1 shows the XRD pattern of the synthesized carbon-free and carbon-coated with different amounts of pitch LTO samples. All the peaks are in good accordance with the standard patterns (JCPDS card no. 26-1198), demonstrating that the expected cubic spinel structure with a *Fd3m* space group was indeed obtained. As shown in Table 1, the cubic lattice parameters (*a*) of the carbon-free and of

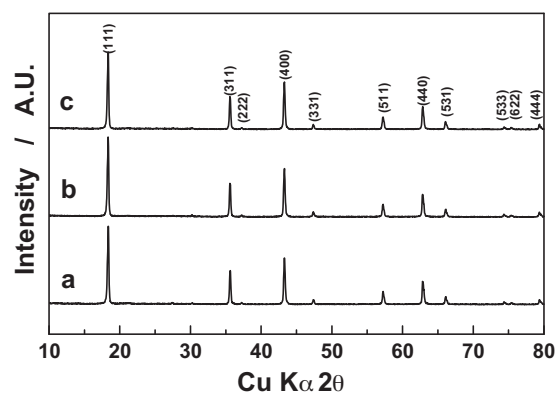


Fig. 1. X-ray diffraction patterns of the carbon-free and of pitch-coated Li₄Ti₅O₁₂ powders after heat treatment at 750 °C: (a) carbon-free, (b) 2 wt% pitch, and (c) 5 wt% pitch.

the 2 wt% and 5 wt% pitch-coated LTO were calculated to be 8.364 Å, 8.365 Å, and 8.365 Å, respectively, values which are consistent with previous reports [5,13].

The morphologies of the carbon-free and of the 5 wt% pitched-coated LTO samples were examined using SEM and TEM. The carbon-free LTO powders were white and had a spherical morphology with a diameter of 5 μm (Fig. 2a). The SEM image clearly demonstrates that the spherical LTO powders are composed of 100 nm-sized primary particles. We expect that this nanosized dimension, by reducing the Li⁺ ion diffusion path, may be very beneficial for enhancing the kinetics of lithium intercalation into the LTO host structure. As shown in Fig. 2b (referring to the 5 wt% pitch-coated sample), the spherical morphology and microstructures were maintained also after carbon coating at high temperature. In addition, the high resolution TEM image of Fig. 2c

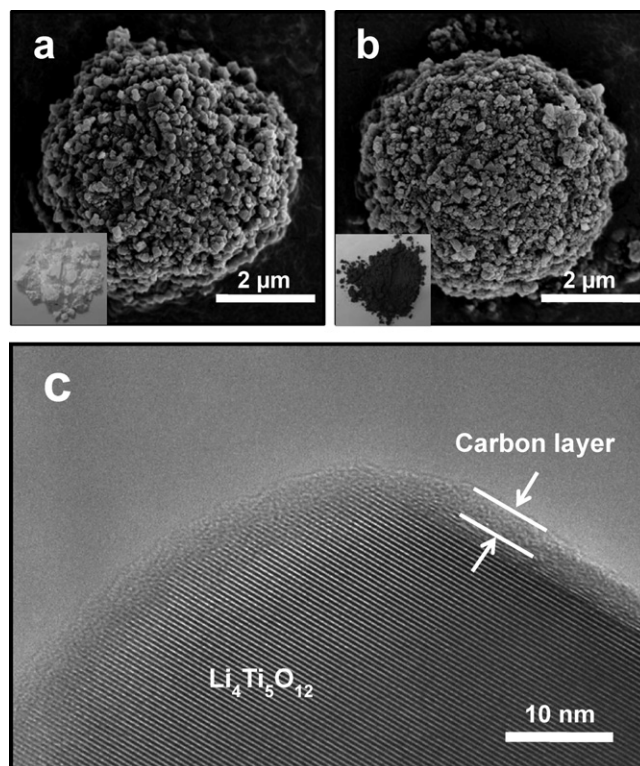


Fig. 2. SEM images of carbon-free (a) and 5 wt% pitch-coated Li₄Ti₅O₁₂ powders (b). High-resolution TEM images of the 5 wt% pitch-coated Li₄Ti₅O₁₂ after calcination at 750 °C (c).

Table 1
Physical properties of carbon-free and carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Carbon content ^a		Electronic conductivity (S cm^{-1})	Tap density (g cm^{-3})	Lattice parameters (\AA)
Before calcination	After calcination			
0%	0.00%	1.58×10^{-9}	1.10	8.364
2%	1.14%	2.38×10^{-3}	1.13	8.365
5%	3.25%	5.24×10^{-3}	1.15	8.365

^a The carbon content was obtained from the elemental analysis using EA 110 CHNS-O automatic analyzer (CE Instrument).

shows that a 3 nm-thick carbon layer uniformly coats the primary particles. We believe that this carbon film may consistently increase the electrical conductivity of LTO powders. Indeed, after the carbonization process at 750°C , the pitch was converted into carbon and the color of the LTO powders changed from white to black, suggesting a consistent increase in the electrical conductivity, with values increasing linearly with the amount of pitch. For example, the conductivity of the 3.25 wt% carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample was found to be $5.24 \times 10^{-3} \text{ S cm}^{-1}$, which is significantly higher than that of the carbon-free LTO, i.e., $1.58 \times 10^{-9} \text{ S cm}^{-1}$, thus transforming LTO from an insulator to an electrical conductor.

The pore size distributions of the carbon-free and carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were measured by nitrogen gas adsorption and desorption isotherms (Fig. 3) and analyzed by the Barrett–Joyner–Halenda (BJH) model. The results show that the BJH pore size distributions of both the carbon-free and carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are similar with narrow pore size distributions and a pore diameter ranging around 3–10 nm. However, the results also show that in the pitch-coated LTO (2 wt% and 5 wt%) the distribution of pores larger than 3 nm slightly decreased while the distribution of the pores below 2 nm slightly increased, indicating an average pore size decrease due to the formed carbon layer on the primary LTO particles. Accordingly, also the total pore volume decreased from $0.19 \text{ cm}^3 \text{ g}^{-1}$ for the carbon-free $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to $0.16 \text{ cm}^3 \text{ g}^{-1}$ for the 5 wt% pitch-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The BET surface area for the synthesized powders was $12.7 \text{ m}^2 \text{ g}^{-1}$ for the carbon-free LTO, $12.2 \text{ m}^2 \text{ g}^{-1}$ for the 2 wt% pitch-coated LTO and $12.1 \text{ m}^2 \text{ g}^{-1}$ for the 5 wt% pitch-coated LTO. Because the average pore size, as well as the total pore volume of pitch-coated LTO, is slightly lesser than those of carbon-free LTO, we can expect that also the porosity of carbon-coated LTO decreases.

Table 1 shows the physicochemical properties of the carbon-free and carbon-coated LTO powders. As determined by CHN analysis, the residual carbon contents in samples containing 2 and 5 wt% pitch were 1.14 and 3.25 wt%, respectively. The carbon coating process, by leading to much tighter packing of the secondary particles, is expected to consistently improve the tap density of the LTO powders, to achieve the desired high rate combined with high density

feature, as indeed confirmed by the results of the electrochemical tests.

Fig. 4 compares the initial charge (Li^+ insertion)/discharge (Li^+ extraction) curves for the carbon-free and carbon-coated LTO run in a lithium cell at a constant current rate of 17.5 mA g^{-1} (0.1 C-rate) between 1.0 V and 3.0 V voltage limits. Both cells show a flat discharge plateau of 1.55 V (vs. Li/Li^+), which corresponds to the $\text{Ti}^{3+}/\text{Ti}^{4+}$ redox couple. However, the response of the 3.25 wt% carbon-coated LTO is quite different in terms of discharge capacity: the carbon-free LTO delivered at 17.5 mA g^{-1} a discharge capacity of 164.2 mAh g^{-1} while the 1.14 wt% and 3.25 wt% carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ delivered at the same rate higher values, i.e., 167.6 and 170.3 mAh g^{-1} , this latter value being very close to the theoretical capacity, i.e., 175 mAh g^{-1} . Even more impressive is the comparison of the volumetric capacities, derived from the respective tap density values. At a rate of 17.5 mA g^{-1} the carbon-coated LTO delivers $195.4 \text{ mAh cm}^{-3}$ while the carbon-free LTO gives only $180.6 \text{ mAh cm}^{-3}$. As shown in the inset of Fig. 4, the polarization (gap between the charge and discharge curves) decreased with increasing the carbon coating thickness. We believe that the enhanced electrochemical performance of the carbon-coated material is associated with the increase of its electrical conductivity [24–26].

The rate capability is another important parameter for evaluating an electrode material addressed to battery application. A constant current discharge test was performed on our LTO electrodes varying the rate from a 1 C (175 mA g^{-1}) to a 100 C (17.5 A g^{-1}) during discharge in the voltage range of 1.0–3.0 V. Fig. 5 illustrates the results in terms of capacity vs. cycle number. The discharge capacity of the carbon-free LTO dropped significantly with increasing C-rate, delivering a disappointed value of 61 mAh g^{-1} at 30 C. On the contrary, the response of the carbon-coated LTO is quite superior and, as expected, strongly dependent on the amount of the carbon coating, since this is directly linked to the value of the electrical conductivity. In particular, the 3.25 wt% carbon-coated LTO showed an outstanding rate performance delivering a discharge capacity as high as 170.2 mAh g^{-1} at a 1 C-rate (175 mA g^{-1}).

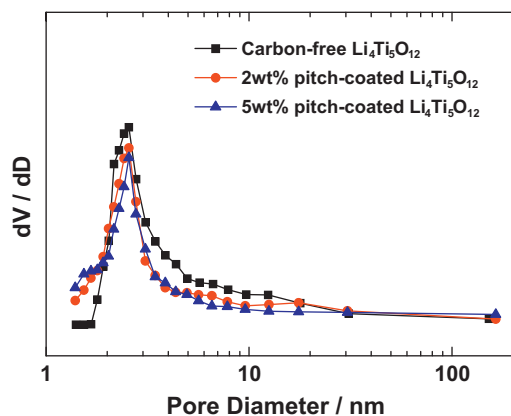


Fig. 3. Pore diameter distribution for the carbon-free, 2 wt%, and 5 wt% pitch-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders after calcination at 750°C .

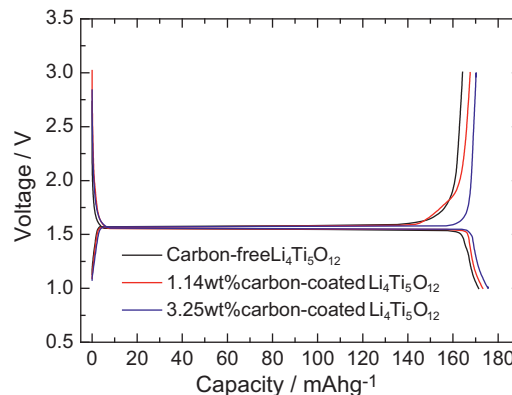


Fig. 4. Initial charge and discharge curves of carbon-free and carbon-coated (1.14 and 3.25 wt%) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes. 2032 coin-type half cells. Li metal counter electrode. Rate: 0.1 C (17.5 mA g^{-1}).

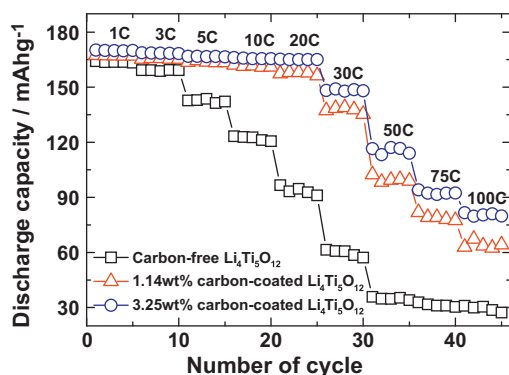


Fig. 5. Rate capability of carbon-free and carbon-coated (1.14 and 3.25 wt%) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes at rates ranging from 1 C (175 mA g^{-1}) to 100 C (17.5 A g^{-1}). The charging rate was 1 C.

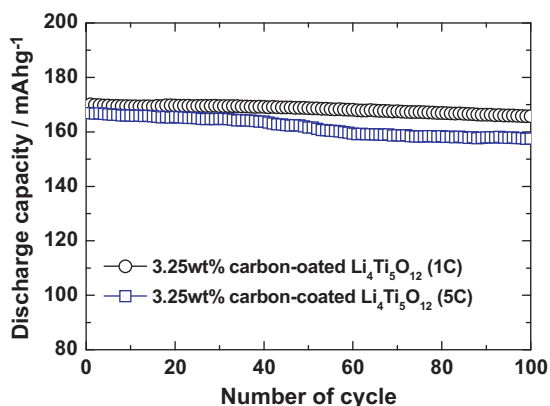


Fig. 6. Cyclability of the 3.25 wt% carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at rates varying from a 1 C (175 mA g^{-1}) to 10 C (1.7 A g^{-1}). The charging rate was 1 C.

Even if slightly decreasing by increasing the rate, the capacity remains impressively high keeping a value of 81.7 mAh g^{-1} at 100 C (17.5 A g^{-1}).

The cycling performance of these advanced carbon-coated LTO electrodes was also tested. Fig. 6 illustrates the response of the 3.25 wt% carbon-coated LTO in a lithium cell cycled at rates of 1 C and 5 C in the voltage range of 1–3 V. The initial discharge capacity of 170 mAh g^{-1} at a 1 C rate remained as high as 166 mAh g^{-1} after 100 cycles. Excellent cycling stability was also observed in the 5 C rate test, showing a capacity retention of 94.4% after 100 cycles.

4. Conclusions

Carbon-coated LTO electrodes with a spherical morphology and a particle size of approximately $6 \mu\text{m}$ were synthesized via a spray-drying and facile pitch coating process. The optimal carbon content was determined to be 3.25 wt%. By comparing the results here reported with those previously obtained on a LiFePO_4 carbon-coated material [22], we may assume that also the carbon on the coated layer over the LTO materials here discussed have the

same π -bond, sp^3 character. Indeed the 3.25 wt% carbon-coated LTO shows an excellent performance in terms of rate capability, cycling life and capacity retention. We believe that enhancement in electrical conductivity provided by the carbon coating accounts for the superior electrochemical behavior of the C-LTO electrodes that appear suitable for the application in batteries designed as storage systems in renewable energy plants and/or as power supplies for electric vehicles.

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