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A novel $Li_4Ti_5O_{12}$/graphene/carbon nano-tubes hybrid material for high rate lithium ion batteries

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ABSTRACT

The $Li_4Ti_5O_{12}$/G/CNTs hybrid material was synthesized via a facile rheological phase reaction route. For comparison, the $Li_4Ti_5O_{12}$/G hybrid material was also prepared using the similar rheological phase method. The results showed that the $Li_4Ti_5O_{12}$/G/CNTs had better rate capability and cycling performance than that of the $Li_4Ti_5O_{12}$/G. At 0.2 C, the initial discharge capacity of the $Li_4Ti_5O_{12}$/G/CNTs was 172 mA h/g, and even at the high rate of 5.0 C and 10.0 C, it could still remain at 150 mA h/g and 144 mA h/g, respectively. Moreover, only less than 6% discharge capacity loss over 100 cycles at 10.0 C was observed. The outstanding electrochemical performances make it a promising anode material for high rate lithium ion batteries.

1. Introduction

Spinel lithium titanate ($Li_4Ti_5O_{12}$) has been demonstrated as a potential candidate for the anode electrode material in lithium ion batteries because it has some unique characteristics as compared with carbon based anode materials [1,2]. The $Li_4Ti_5O_{12}$ features a flat operation potential plateau and higher lithium intercalation–deintercalation potential of about 1.55 V versus Li/Li^+, which can effectively prevent safety problems associated with carbon-based anode materials [3]. Furthermore, the $Li_4Ti_5O_{12}$ possesses good structural stability with an almost negligible volume change during the Li^+ insertion and extraction processes, which suggests virtually unlimited cycle life [4]. All of these characteristics indicate that $Li_4Ti_5O_{12}$ is advantageous as an anode for use in high power lithium ion batteries with safety, long life and reliability. However, the low electronic conductivity (ca. 10^{-13} S/cm) of spinel $Li_4Ti_5O_{12}$ and the sluggish lithium ion diffusion in $Li_4Ti_5O_{12}$ result in the poor power performance of the $Li_4Ti_5O_{12}$ materials [5], preventing them from being widely used. In order to overcome the low electrical conductivity and further improve the rate capability of $Li_4Ti_5O_{12}$, several methods have been developed. These include synthesizing nanosized $Li_4Ti_5O_{12}$ particles [6], doping $Li_4Ti_5O_{12}$ with aliovalent metal ions [7] and forming a hybrid material consisting of $Li_4Ti_5O_{12}$ and a conductive second phase [8].

Graphene, with an extraordinary electronic transport property, a flexible structure, high mechanical strength and high surface area, has been regarded as one of the most ideal conductive carbon matrices for hybrid electrodes [9]. Recently, $Li_4Ti_5O_{12}$/graphene hybrid materials have been widely investigated as anode materials for LIBs [10–12]. In the hybrid materials consisting of graphene and $Li_4Ti_5O_{12}$, usually a small amount of graphene can play a vital role to improve the rate capability of $Li_4Ti_5O_{12}$ [13]. However, it is worth noting that there is no chemical bond formed between the $Li_4Ti_5O_{12}$ particles and the graphene, which has been proved by Shi et al. [14]. This indicates that there is still no effective contact between $Li_4Ti_5O_{12}$ particles and graphene, and which might cannot efficiently improve the rate capability of $Li_4Ti_5O_{12}$ via only adding graphene as the conductive carbon matrice. In the present study, a novel $Li_4Ti_5O_{12}$/graphene/carbon nano-tubes ($Li_4Ti_5O_{12}$/G/CNTs) hybrid material was synthesized via a facile rheological phase reaction route, and for comparison, the $Li_4Ti_5O_{12}$/graphene ($Li_4Ti_5O_{12}$/G) hybrid material was also synthesized by the similar rheological phase method (As we focus on comparing the electrochemical performances of $Li_4Ti_5O_{12}$/G/CNTs with $Li_4Ti_5O_{12}$/G and we have studied the $Li_4Ti_5O_{12}$/CNTs in our previous work (Solid State Ionics 2010; 181: 635-9), the $Li_4Ti_5O_{12}$/CNTs hybrid material would not discuss here.). We found that the $Li_4Ti_5O_{12}$/G/CNTs had better rate capability and cycling performance than that of $Li_4Ti_5O_{12}$/G. We believed that should be ascribed to that the CNTs in the hybrid material could act like

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bridges, which connected the isolated particles of $Li_4Ti_5O_{12}$ and the graphene, resulting in forming more effective conductive nets in the electrode and making the $Li_4Ti_5O_{12}$/G/CNTs have higher charge/ transfer kinetics than that of $Li_4Ti_5O_{12}$/G.

2. Experimental

Material synthesis: All materials and chemicals in the present study were purchased commercially and used as received. The CNTs are MWCNTs, with a diameter and length of about 20–30 nm and 2–3 μm, respectively, provided by Chengdu Organic Chemicals Co., Ltd (China). The graphene is reduced graphene-oxide, with a diameter of 5 μm and a thickness of 4.5 nm, also provided by Chengdu Organic Chemicals Co., Ltd (China). The purities (provided by the company) of the CNTs and the graphene are 97% and 95%, respectively. The $Li_4Ti_5O_{12}$/G/CNTs hybrid was prepared by using a rheological phase reaction route. The graphene, CNTs, Polyvinylpyrrolidone (PVP, used as dispersant), deionized water and stoichiometric amount of CH_3COO-$Li \cdot 2H_2O$ and anatase TiO_2 (n_{Li}:$n_{Ti}=0.82$) were mixed by high-energy ball milling method for 2 h to form a rheological phase slurry. The rheological phase slurry was then dried and calcinated at 800 °C for 8 h under Ar atmosphere to obtain the $Li_4Ti_5O_{12}$/G/CNTs. The total quantity of graphene and CNTs in the hybrid was given as 5 wt%, the mass ratio of the graphene and CNTs in the hybrid was 1:1. The $Li_4Ti_5O_{12}$/G hybrid was prepared by using the similar rheological phase approach as mentioned above and the quantity of graphene in the hybrid was also given as 5 wt%. Pristine $Li_4Ti_5O_{12}$ was also prepared by using the similar rheological phase reaction route.

Characterization: The X-ray diffraction (XRD) patterns of the as-prepared samples were recorded using the Philips X'Pert Pro MPD DY1219 with a Cu $K\alpha$ radiation source. The morphology and particle size were observed by scanning electronic microscopy (SEM FEI INSPECT-F).

Electrochemical measurements: The electrochemical performances were measured with coin cells on a BTS-5V2mA cell test instrument (NEWARE Electronic Co. Ltd) between cut-off voltages of 1–3 V. The working electrode was prepared by coating slurries (consist of 90 wt% active material, 5 wt% acetylene black and 5 wt% LA-132 binder (Chengdu Indigo Power Sources Co., Ltd. LA132 is a kind of aqueous binder for the cathode or anode materials of lithium ion batteries, which has excellent anti-oxidation ability and anti-reducibility. The major constituents of the LA132 are acrylonitrile copolymer and water.)) onto aluminum foil. Cell assembly was carried out in an argon-filled glove box using lithium metal as counter electrode, 1 M $LiPF_6$/EC:DEC:DMC (1:1:1 in volume) as electrolyte and Celgard 2400 as separator. The AC impedance spectrum was measured by using a Solatron 1260 Impedance Analyzer in the frequency range 10^{-2}–10^6 Hz with a potential perturbation at 10 mV.

3. Results and discussion

It can be observed from Fig. 1(a) that the X-ray diffraction patterns of the samples are similar, except for a weak peak in the
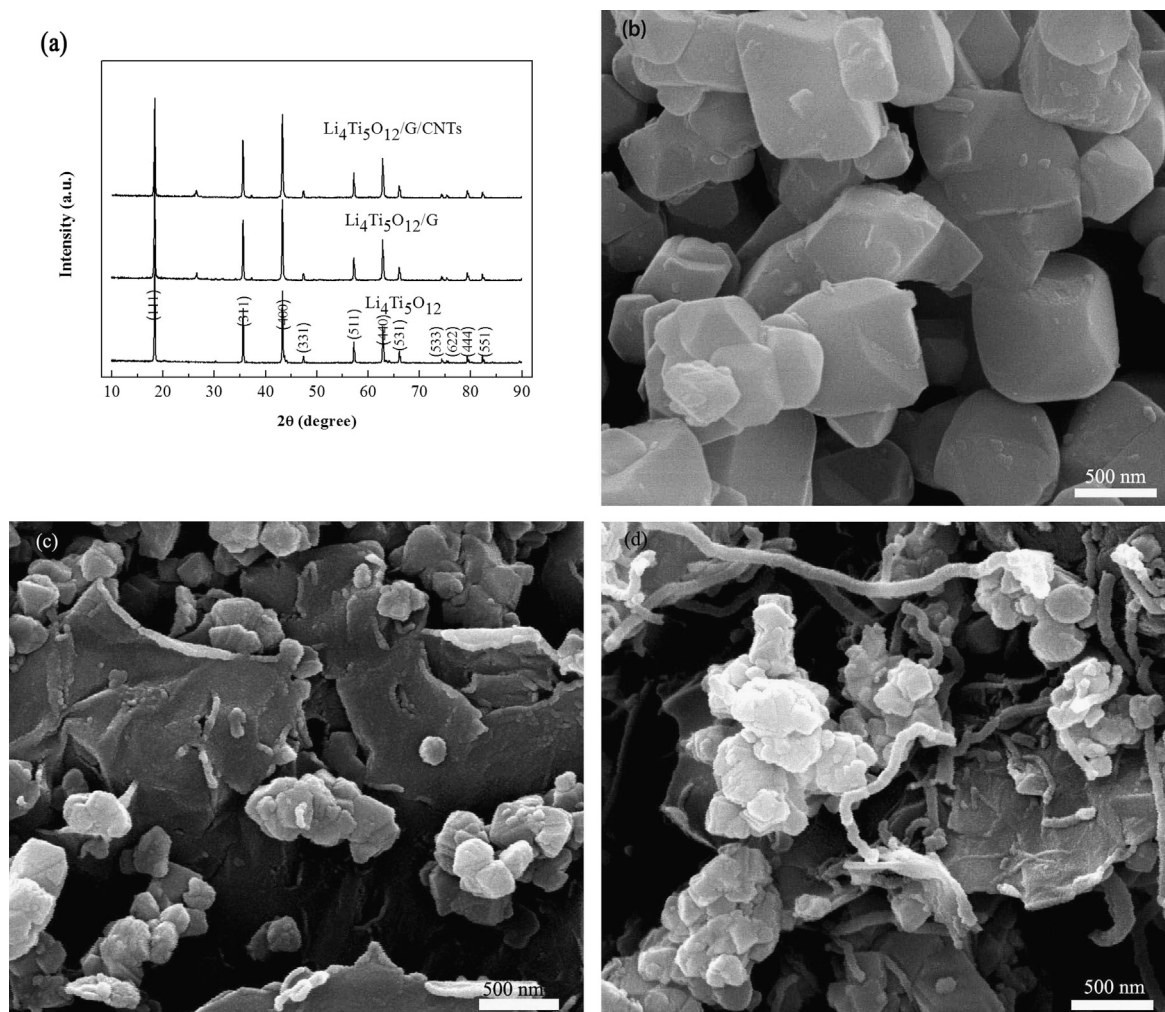

Fig. 1. (a) XRD patterns of the samples, (b) SEM image of the pristine $Li_4Ti_5O_{12}$, (c) SEM image of the $Li_4Ti_5O_{12}$/G, (d) SEM image of the $Li_4Ti_5O_{12}$/G/CNTs.

curves of $Li_4Ti_5O_{12}/G$ and the $Li_4Ti_5O_{12}/G/CNTs$ at 26° (2θ) due to the graphene or graphene and CNTs in the hybrid material. Moreover, all peaks of the above samples can be indexed as spinel $Li_4Ti_5O_{12}$ according to JCPDS File No. 26-1198. These results indicate that the addition of graphene or graphene and CNTs in the precursor does not affect the formation of spinel $Li_4Ti_5O_{12}$ during heat-treatment process.
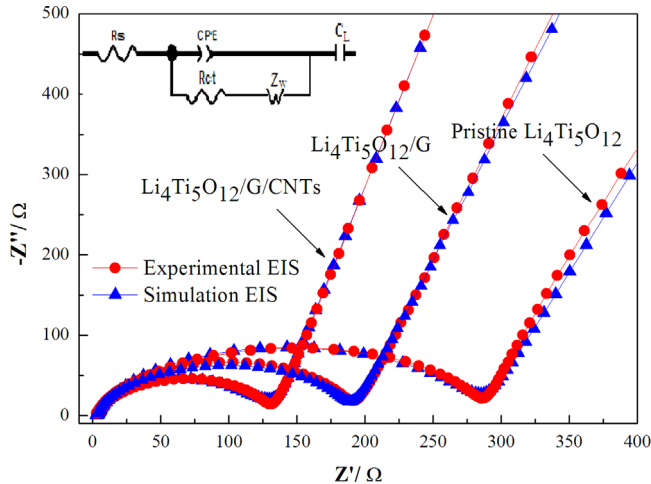

Fig. 2. AC impedance spectra with the equivalent circuit of the samples.

Table 1
Impedance parameters calculated from equivalent circuits.

Materials	R_s (Ω)	R_{ct} (Ω)	i^0 (mA/cm^2)
Pristine $Li_4Ti_5O_{12}$	2.864	286.5	0.090
$Li_4Ti_5O_{12}/G$	2.437	186.7	0.137
$Li_4Ti_5O_{12}/G/CNTs$	2.175	112.1	0.229

Fig. 1(b)–(d) show the SEM images of the pristine $Li_4Ti_5O_{12}$, the $Li_4Ti_5O_{12}/G$ and the $Li_4Ti_5O_{12}/G/CNTs$, respectively. It can be observed that the particle size of the $Li_4Ti_5O_{12}/G$ and the $Li_4Ti_5O_{12}/G/CNTs$ is obviously smaller than that of the pristine $Li_4Ti_5O_{12}$, which indicates that the addition of graphene or graphene and CNTs in the precursor could hinder the particle growth during the calcination process. Furthermore, Fig. 1(c) shows that most of the $Li_4Ti_5O_{12}$ particles cannot anchor on the surface of the graphene, and there is no effective contact between $Li_4Ti_5O_{12}$ particles and graphene. Fig. 1(d) also shows that most of the $Li_4Ti_5O_{12}$ particles cannot anchor on the surface of the graphene, nevertheless, the CNTs acting like bridges, which can connect the graphene and the isolated $Li_4Ti_5O_{12}$ particles, giving a more effective conductive connection between the graphene and the $Li_4Ti_5O_{12}$ in the hybrid material.

The AC impedance spectra of the $Li_4Ti_5O_{12}/G/CNTs$, the $Li_4Ti_5O_{12}/G$ and the pristine $Li_4Ti_5O_{12}$ are shown in Fig. 2, which are measured at the stable voltage of 1.55 V, respectively. The AC impedance spectra of the samples are simulated by Z-view software using same equivalent circuit. It can be observed that the experimental and simulated AC impedance spectra are almost coincident, which indicates that the AC impedance spectra of the samples all fit the equivalent circuit. According to the equivalent circuit, the depressed semicircle at high-middle frequency range represents the charge transfer resistance at the particle/electrolyte interface (R_{ct}). The slope line at low frequency corresponds to the Warburg impedance (Z_W). The R_s in the equivalent circuit is the resistance of the electrolyte, and the constant phase element (CPE) is placed to represent the double-layer capacitance. Table 1 shows the parameters of the recorded equivalent circuit, from which it can be observed that both the R_s and R_{ct} of the $Li_4Ti_5O_{12}/G/CNTs$ are smaller than that of the $Li_4Ti_5O_{12}/G$, whereas the exchange current densities ($i^0 = RT/nFR_{ct}$) of the $Li_4Ti_5O_{12}/G/CNTs$ is larger than the $Li_4Ti_5O_{12}/G$. These results indicate that the $Li_4Ti_5O_{12}/G/CNTs$ had higher charge/transfer kinetics than that of the $Li_4Ti_5O_{12}/G$, which should be attributed to that there is a more effective
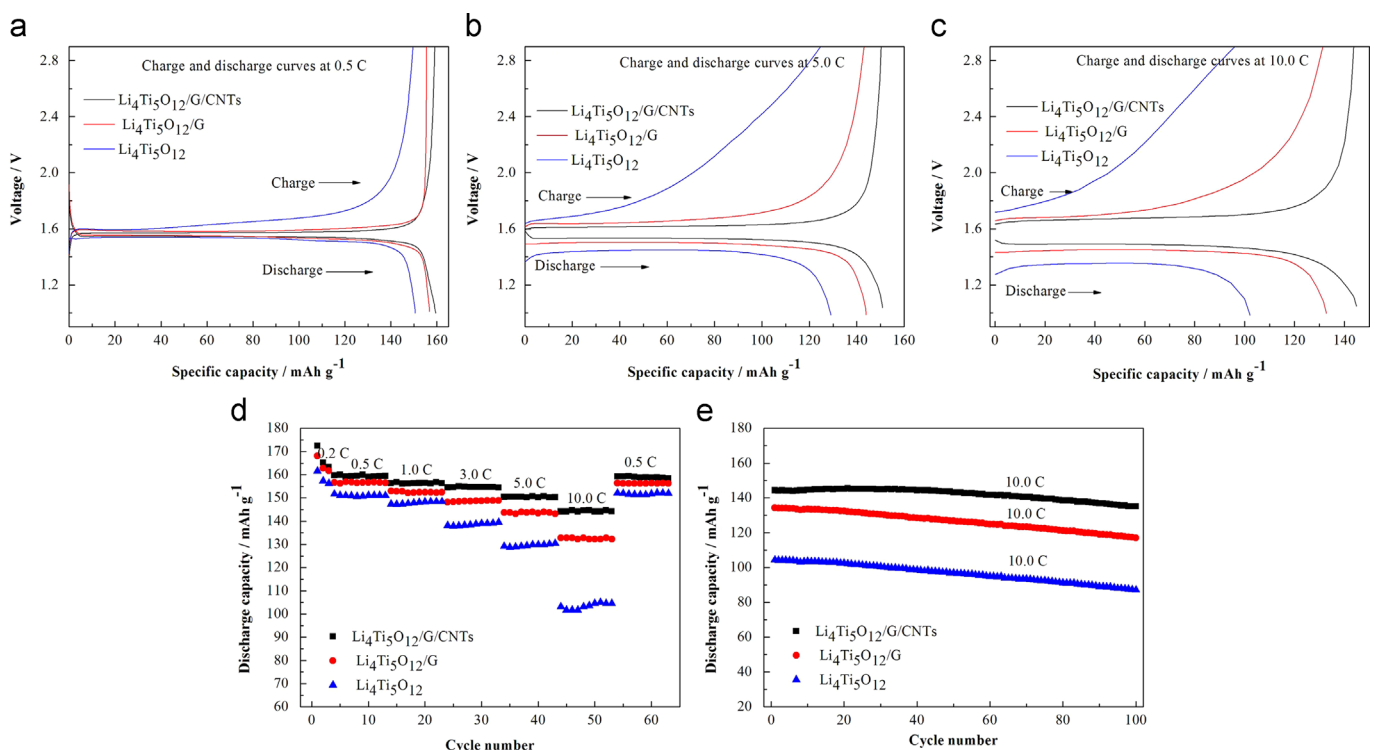

Fig. 3. Galvanostatic charge and discharge curves (a)–(c), rate capability (d) and cycling performances (e) of the samples.

conductive connection within the hybrid material of $Li_4Ti_5O_{12}$/G/CNTs.

Fig. 3(a)–(c) show the galvanostatic charge and discharge curves of the $Li_4Ti_5O_{12}$/G/CNTs, the $Li_4Ti_5O_{12}$/G and the pristine $Li_4Ti_5O_{12}$ at the rates of 0.5 C, 5.0 C and 10.0 C, respectively. There, it can be observed that the margins between the charge and discharge plateau potentials of the $Li_4Ti_5O_{12}$/G/CNTs are obviously smaller than those of the $Li_4Ti_5O_{12}$/G and the pristine $Li_4Ti_5O_{12}$, which suggests that the $Li_4Ti_5O_{12}$/G/CNTs electrode has the smallest electrode polarization. Fig. 3(d) shows the cyclic performances of the samples at different rates between 1 V and 3 V. It can be observed that the $Li_4Ti_5O_{12}$/G/CNTs exhibits higher discharge specific capacity at different rates as compared with the $Li_4Ti_5O_{12}$/G. For example, at 0.2 C, the initial discharge specific capacity of the $Li_4Ti_5O_{12}$/G/CNTs is 172 mA h/g, which is close to the theoretical value of the spinel $Li_4Ti_5O_{12}$ (175 mA h/g). And even at 5.0 C and 10.0 C, it can still remain at 150 mA h/g and 144 mA h/g, respectively. Whereas, for the $Li_4Ti_5O_{12}$/G, at 0.2 C, its initial discharge specific capacity is 168 mA h/g, while at high rate of 5.0 C and 10.0 C, its discharge specific capacity is only 143 mA h/g and 132 mA h/g, respectively. These results indicate that the $Li_4Ti_5O_{12}$/G/CNTs has better rate capability than that of the $Li_4Ti_5O_{12}$/G, which should be ascribed to that the $Li_4Ti_5O_{12}$/G/CNTs has better electronic conductivity than $Li_4Ti_5O_{12}$/G. For evaluating the cycling stability of the samples, they are further charge–discharged at a current rate of 10.0 C for another 100 cycles after the progressive rate tests mentioned in Fig. 3(d). The results are shown in Fig. 3(e), from which it can be observed that the $Li_4Ti_5O_{12}$/G/CNTs shows the best cycling performance. After 100 charge–discharge cycles, its discharge capacity remains at 135 mA h/g, and the capacity retention ratio is 93.6%.

4. Conclusions

A novel $Li_4Ti_5O_{12}$/G/CNTs hybrid material was synthesized via a facile rheological phase reaction route. For comparison, a $Li_4Ti_5O_{12}$/G hybrid material was also synthesized by the similar rheological phase approach. The results showed that there was no effective contact between $Li_4Ti_5O_{12}$ particles and graphene in the $Li_4Ti_5O_{12}$/G hybrid material because most of the $Li_4Ti_5O_{12}$ particles could not anchor on the surface of the graphene. However, in the $Li_4Ti_5O_{12}$/G/CNTs hybrid material, as CNTs could act like bridges, which connected the graphene and the isolated $Li_4Ti_5O_{12}$ particles, giving a more effective conductive connection. The $Li_4Ti_5O_{12}$/G/CNTs had higher charge/transfer kinetics than the $Li_4Ti_5O_{12}$/G, which resulted in its rate capability and cycling performance were better than that of the $Li_4Ti_5O_{12}$/G.

Acknowledgements

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