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Graphene oxide/lithium titanate composite with binder-free as high capacity anode material for lithium-ion batteries

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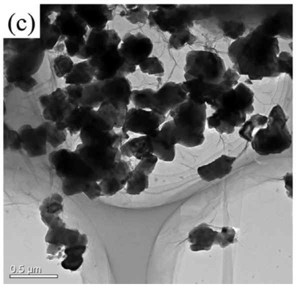
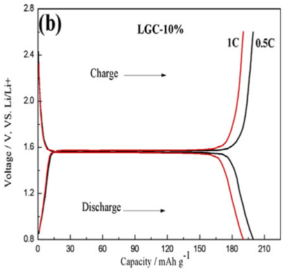
HIGHLIGHTS

- LTO particles well dispersed among graphene oxide nanosheets.
- Graphene oxide can replace the polymer binder.
- LGC-10% electrode has a higher reversible Li-storage specific capacity.
- LGC-10% electrode exhibits an excellent rate and cycling performance.

GRAPHICAL ABSTRACT





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ABSTRACT

A series of composites of $Li_4Ti_5O_{12}$ particles well dispersed among graphene oxide (GO) nanosheets as binder-free anode materials for high capacity and rate lithium-ion batteries are prepared and investigated. The morphology, microstructure and elemental compositions of the as-prepared composites are characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Electrochemical tests reveal that the electrode with GO content 10% presents a reversible Li-ion storage specific capacity of 201 mAh g^{-1} at 0.5C (1C = 175 mA g^{-1}), and the specific capacity still maintain in 162 mAh g^{-1} even at 30C. Moreover, this composite exhibits an excellent cycling stability, with a first charge capacity of 162 mAh g^{-1} at 30C and less than 3% loss after 300 cycles. The addition of GO provides the additional capacity via oxygen-containing functional group and nano-cavity, additionally, replacing the CMC by GO, which makes the composite with CMC binder-free, speeds up the lithium ion diffusion in anode materials.

1. Introduction

As one of the most promising anode materials for the application of power sources to replace graphite or carbon in electric vehicles (EV), hybrid electric vehicles (HEV) and plug-in hybrid vehicles (PHEV) [1,2], spinel $Li_4Ti_5O_{12}$ (LTO) has been investigated in recent years due to its zero volume change, no formation of solid electrolyte interphase layer and metallic lithium during discharge/charge processes, high working potential of the redox couple Ti^{4+}/Ti^{3+} (ca. 1.55 V vs. Li/Li^+), excellent safety and thermal stability [3,4]. However, the low specific capacity (175 mAh g^{-1} for theoretical and 160 mAh g^{-1} for actual) and poor intrinsic electronic conductivity of LTO, seriously hinder its large-scale application as high energy density and rate performance batteries [5].

In order to overcome the shortcomings of LTO material mentioned above, many efforts have been made, such as particle size reducing [6–9], ion doping [10–13] and carbon coating

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[14–18], etc. Nevertheless, the actual specific capacity of LTO is hard to exceed 170 mAh g^{-1}.

As the precursor of graphene, GO has been proved to have good electrochemical performance in our previous work [19,20] such as a higher lithium storage capacity than traditional graphite and $Li_4Ti_5O_{12}$ anode materials. In addition, GO is also easy to form self-assembly membrane instead of polymer binder.

In this work, commercial LTO, GO (made in our own laboratory) and conductive carbon black were applied to fabricate LTO composites (nominated as LGC), and in these novel composites, LTO can play a great role in holding back stack of GO sheets, in stabilizing electrochemical property and providing Li-ion storage capability. GO, can not only play the role of the Li-ion storage, but also the effect of binder. So the LGC composites can be directly used as electrodes without adding any other binders, and present a very high reversible capacity.

2. Experimental

2.1. Preparation of GO and LGC composites

Commercial LTO powders (Chengdu Xingneng New Materials Co., LTD) and 4A-Zeolite (Kelong Chemical Reagent Crop. Chengdu China) were used in our study. GO was synthesized from high-purity natural flake graphite (about 200 meshes, Changsha Shenghua Research Institute, 99.999%) by a modified Hummers method [21,22]. And the colloidal dispersion of GO in deionized water was prepared with the aid of ultrasound (20 kHz ultrasound probe) treatment about 30 min to give a stable amber dispersion. Conductive additive used in the composites was Super-P carbon black (40 nm, 62 m^2 g^{-1}, TIMCAL Graphite & Carbon). The LTO slurry was prepared by mixing adequate deionized water with LTO, CMC and conductive carbon black (in a LTO/CMC/conductive carbon black weight ratio of 80:10:10) via vigorously stirring for 3 h and the LGC slurries with different proportions were prepared with the same method (in a LTO/GO/conductive carbon black weight ratio of 70:20:10, 75:15:10, 80:10:10, 85:5:10 and 87:3:10). In addition, in order to determine the influence of GO and CMC binder-free, the other two electrodes have been prepared (in a LTO/GO/CMC/conductive carbon black weight ratio of 80:5:10:5, 75:5:10:10, nominated as LGCC-1, LGCC-2, respectively).

2.2. Materials characterization

The morphology and structure of the obtained samples were determined by scanning electron microscopy (SEM; INCA Penta-FETx3) and transmission electron microscopy (TEM; JEM-100CX JEOL). Using Al/K_α radiation ($h\nu = 1486.6$ eV), X-ray photoelectron spectroscopy (XPS; PHI5600 Physical Electronics) was performed to determine elemental compositions and assignments of carbon peaks. X-ray diffraction (XRD) patterns were obtained from X'Pert MPD DY1219 using Cu/K_α radiation ($\lambda = 1.5406$ Å).

2.3. Electrochemical measurements

The working electrode was prepared as follows. First, LTO, GO dispersion (GO amount calculated according to solid content) and conductive carbon black were mixed according to the fixed proportion and ground with ethanol as solvent to form a uniform slurry, then coated onto a Cu foil and dried under vacuum at 105 °C for 12 h (the thickness and density of working electrodes are almost uniform). After the foil was cut into disks (10 mm in diameter) and pressed, coin cells were assembled with lithium metal as the counter electrode and a Celgard 2400 was employed as separator in a glove box filled with Ar gas. The electrolyte obtained from Capchem. Technology (Shenzhen) Co., Ltd. consists of a solution of 1 M $LiPF_6$ in ethylene carbonate, dimethyl carbonate, diethyl carbonate (EC/DMC/DEC, 1:1:1, in volume). Galvanostatic discharge/charge experiments were carried out on an automatic galvanostatic charge–discharge unit (Land CT 2001A, Wuhan, China) under different current densities between 0.8 and 3.0 V at 25 °C. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted on PARSTAT 2273 Electrochemical System (Princeton Applied Research, USA). In the case of CVs, the potential range was recorded from 0.8 to 3.0 V at different scanning rates. The EIS measurements were performed at the input signal amplitude of 10 mV (vs. open circuit potential) and the frequency ranging from 10^5 Hz to 10^{-2} Hz, and the measured data were fitted by Z-View software (Scribner Associates Inc.). All the measurements mentioned above are based on the total mass of the active material (for LTO, LTO particles is the only based material for calculation of the capacity of mAh g^{-1}, while that of the LGC electrodes include the LTO and GO).

3. Results and discussion

Fig. 1 illustrates the schematic of preparation process for LGC composites. GO and LTO are dispersed by ultrasound in alcohol to form GO dispersion and LTO suspension, respectively, and then the well-dispersed GO dispersion is added into the obtained LTO suspension. After 1 h vigorous stirring together with conductive carbon black, the mixture is heated at 70 °C to remove the solvent. Finally, a grey slurry of LGC composite is obtained. Five kinds of LGC composites (LTO/GO/conductive carbon black weight ratio of 70:20:10, 75:15:10, 80:10:10, 85:5:10 and 87:3:10) and the other two LGCC electrodes (LTO/GO/CMC/conductive carbon black weight ratio of 80:5:10:5, 75:5:10:10, nominated as LGCC-1, LGCC-2, respectively) are gained with the same method (the compositions of working electrode in detail are shown in Table 1) and tested in coin type cells. As shown in Fig. 2, the reversible charge capacity of the LTO is about 163 mAh g^{-1} at 0.5C, with the increasing of the addition of GO, the charge capacity of LGC composites increases gradually. When the content of GO is 10%, it presents the highest reversible capacity and the best cycling stability. Further increase the GO content, the capacity of LGC will begin to decline. Because when the content of GO is too much, it will be easy to stack and has lower charge capacity (Fig. S1 of Supplementary materials). However, appropriate content of GO can be separated easily by LTO particles, so the LTO and GO can play a synergy effect and show the maximum capacity. In order to express easily and intuitively, the content of GO for 10% is referred to as LGC-10%.

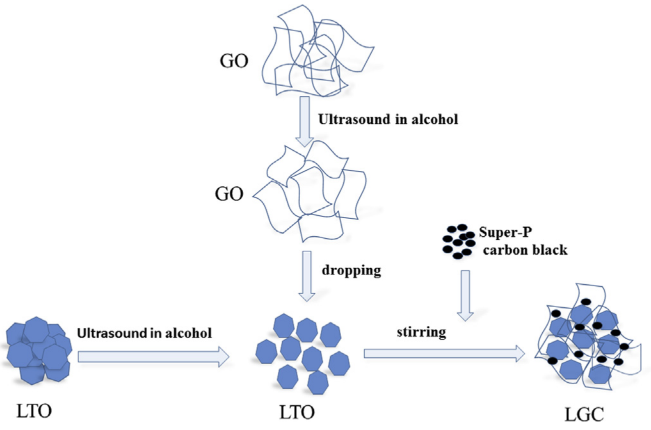

Fig. 1. Schematic of the preparation process for LGC composites.