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Lithium titanate hybridized with trace amount of graphene used as an anode for a high rate lithium ion battery

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ABSTRACT

A novel $Li_4Ti_5O_{12}$ (LTO) electrode with a hierarchical carbon-based conducting network has been developed for high rate lithium ion battery. The unique network is constructed by graphene sheets (GS) that are not only dispersed among (inter-) but also inside (intra-) LTO particles, together with a thin carbon layer wrapping around the LTO particles. The intraparticle GS promotes the electron transfer inside LTO particles while the interparticle GS together with carbon coating bridges the particles guaranteeing fast electron transfer among LTO particles, which construct a highway throughout the whole electrode sheet. Quantitatively, only a trace amount of GS (~ 0.4 wt%) synergistic with carbon coating (~0.8 wt%) contributes to a more effective conducting network in the produced LTO electrode and as a result much better performance as compared to the LTO case with similar carbon coating but free of GS. Due to the effectiveness of the conducting network, even with a tap density as high as ~1.0 g cm^{-3}, the novel LTO possesses both excellent rate performance and cycling behaviors. The capacity of 123.5 mA h g^{-1} is obtained at a charge/discharge rate as high as 30 C and a very high capacity of 144.8 mAh g^{-1} is maintained even after 100 cycles at 10 C. Due to such a low fraction of carbon and a high tape density, the novel LTO electrode has a great practical application value in both the power and energy storage lithium ion batteries.

1. Introduction

The power density of carbon anode-based Lithium ion batteries (LIBs) is normally limited because of low Li ion diffusion coefficient and large polarization at high charge rate [1–6]. Another key issue of carbon anode LIBs would be the dendritic lithium growth on the carbon anode surface at high charge current because the cut-off potential of carbon anode approaches almost 0 V vs. Li^+/Li, which is close to the deposition potential of lithium metal. Spinel $Li_4Ti_5O_{12}$ (LTO), a promising anode, has a higher Li insertion potential (1.5 V vs. Li^+/Li) than that of commercial graphite anode (below 0.2 V vs. Li^+/Li). Therefore, deposition of lithium metal on LTO electrode can be avoided, which contributes to much better safety characteristics of LTO electrode [7]. Furthermore, the spinel LTO shows a very small volume variation during the charge and discharge process, consequently resulting in excellent cycle stability. However, the widespread application of conventional LTO is limited by its poor power performance resulted from its inherent insulating character and the low electrochemical kinetic process [8–10].

The kinetic behaviour of electrode can be improved by the introduction of nanostructure and the wrapping of conductive coating, which brings the required ionic and electronic conductivity to individual grains and accelerates the electrochemical kinetic process [11–13]. The formation of conductive networks among the LTO particles is another significant and efficient way to improve the conductivity of electrode for fast transfer of electrons [14]. Graphene sheets (GS), as flexible and thin carbon layers, is considered as an excellent conductive additive in the electrode and meanwhile can construct a conducting network following a "plane-to-point" model due to their flexible two-dimensional (2D) structure [15]. The GS can serve as a perfect 2D support for anchoring electrochemically active materials and an effective electronically conducting matrix, which also can hinder the agglomeration and growth of active particles during the calcination process and shorten the transport path of lithium ions and electrons [16,17]. Some studies have used GS to construct a conductive network in LTO electrode [18–25]. Both ion diffusion and electronic transfer can be greatly improved by

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Table 1
High rate charge and discharge performance of LTO/G and graphene content in the hybrids.

Sample	Preparation Method	ParticleSize (nm)	10 C Capacity ($mAhg^{-1}$)	GS (wt.%)
C-LTO/G(this work)	Hydrothermal	100-300	151	~0.4%GS additive + ~0.8% carbon coating
LTO microspheres/G[18]	Spray drying	50	104	5.91
LTO nanosheets/G[19]	Hydrothermal	/	>160	~6.45
LTO nanoplatelets/G[20]	Microwave-assisted solvothermal	3-5	135	28
LTO particles/G[21]	Solvothermal	~300	<100(5C)	0.7
LTO nanoparticles/G[22]	Heat treatment	100-400	140	5
LTO nanoparticles/G[17]	Hydrothermal	30	137	15.5
LTOnanofibers/G[23]	Electrospinning	/	130	1
LTOparticles/G[24]	Sol-gel	<100	137	8

hybridizing GS with LTO in nanoscale. Thus, as shown in Table 1, the nano-sized LTO/GS hybrid with short ion diffusion distance and good electron conduction are designed and prepared. However, the decrease of LTO particle size or too much GS fraction brings other problems in the practical applications, such as low volumetric energy density and difficulty in coating process on current collector when preparing electrode film [10,26]. Therefore, although the electrochemical performance of LTO is largely improved, it still remains challenges to optimize the electrode system: (*i*) how to balance the particles size and tap density; (*ii*) how to prepare a uniform and thin surface coating; (*iii*) how to construct conductive networks for LTO both intrapartically and interpartically.

In this work, we report an easy method to synthesize a novel carbon-coated $Li_4Ti_5O_{12}$/graphene (C-LTO/G) hybrid with a unique hierarchical conductive network and high tap density (~1.0 g cm^{-3}) (Fig. 1). In this C-LTO/G hybrid, only 0.8 wt% carbon coating layer cooperated with 0.4 wt% GS as interpartical or intrapartical conductive components. That is, with much less carbon fraction as compared to those reported previously, an effective carbon-based conductive networks is constructed throughout inside and outside LTO particles. Cetyltrimethyl ammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$, abbreviated as (CTAB) was chosen as surfactant and a carbon source to make sure a uniform surface coating layer formed on the surface of LTO particle. The uniform surface coating layer (~0.8 wt %) coordinated with intraparticle and interparticle GS (~0.4 wt %) can construct an effective carbon-based hierarchical conductive networks in LTO/G hybrid, which promotes the large size LTO to present excellent rate and cyclic performance. As shown in Table 1, its specific capacity at charge/discharge rate of 10 C is amongst the largest capacity ever reported LTO/graphene hybrids containing much higher graphene content.

2. Experimental

2.1. Synthesis of C-LTO/G with hierarchical conductive networks

The aqueous dispersion of graphene oxide (GO) nanosheets was prepared in accordance with the procedure reported previously [27]. In a typical preparation process of C-LTO/G with hierarchical conductive networks, 11.2 mg GO was dispersed in 30 mL deionized water, and 0.39 g CTAB was added into the GO solution. Then, 5.9 mL tetrabutyl titanate (TBT) was added in above mixture stepwise with the assistance of sonication. After that, 1.56 g lithium acetate was dissolved in 10 mL purified water and was added to the above mixture suspension under sonication. The finally formed mixture suspension was transferred into a 60 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 24 hours. LTO-precursors which contained GO and organic compounds was obtained after the hydrothermal treatment. After drying in an oven at 80 °C, the LTO-precursors were finally calcined at 700 °C for 7 hours in argon filled atmosphere to obtain the C-LTO/G with hierarchical conductive networks. In order to exhibit the significant role of graphene for constructing the unique network both intra-/inter-LTO particles, C-LTO was prepared by a similar procedure without the addition of GO for comparison.

2.2. Material characterization

The structure and phase composition of the obtained samples were characterized by X-ray diffraction measurement (XRD, Rigaku D/max 2500/PC using CuKα radiation with λ=1.5418 Å), the diffraction data was collected at step mode over the angular range of $10^\circ \sim 80^\circ$ with a step 0.02°. The microstructure and morphologies of the prepared samples were examined with field emission scanning electron microscopy (FE-SEM, HITACH S4800) at 10 kV and transmission electron microscopy (TEM, JEOL, JEM-2100F), at an accelerating voltage of 200 kV. The Zeta potential and the particle size distribution of sample were measured using a Malvern Zetasizer Nano ZS (Malvern Instruments, Ltd.) at a temperature of 25 °C. The tap density of the sample was analyzed using a tap-densitometer (DP-Geopyc 1360, micrometrics Co.). Raman spectra were recorded with a labRAM HR800 (France, Jobin Yvon) using 532 nm laser as the excitation source.

2.3. Electrochemical characterization

Rate and cycling performance were carried out by galvanostatic testing CR2032-type coin cells assembled in argon filled glove box (Mbraum). The coin cells used the prepared C-LTO/G or C-LTO as cathode material, lithium foil as anode, and polypropylene (Celgard 2500, Celgard Inc., USA) as separator. The prepared hybrid C-LTO/G or C-LTO, acetylene black and polyvinylidene fluoride (PVDF) binder were mixed homogeneously in a weight ratio of 80:10:10 and dissolved in N-methyl-2-pyrrolidinone (NMP) solvent. The formed slurry was uniformly coated on a copper foil current collector and dried under vacuum at 80 °C for 6 h. The electrolyte employed was 1 M $LiPF_6$ solution in ethylene carbonate and diethyl carbonate (EC/DEC) (volume ratio: 1:1). The assembled cells were galvanostatically charged and discharged under different current densities between 1.0 V and 2.5 V using a Land 2001A battery testing system at room temperature. The electrochemical impedance spectrum (EIS) of the assembled cells was measured by using an electric IM6ex impedance analyzer in the frequency range of 10^{-2}-10^5 Hz. The impedance was measured at half state of charge by applying a 5 mV ac oscillation. Cyclic voltammetry (CV) experiment was carried out with a VMP3 multichannel electrochemical workstation at a scanning rate of 0.2 mV s^{-1} in the range of 1-2.5 V vs. Li^+/Li.

3. Results and discussion

As the precursors of GS, amphiphilic GO can be partially ionized to form GO anions and hydrogen cations in aqueous solution [27,28]. Therefore, GO aqueous solution (pH = 4, zeta = -50.8 mV) can be viewed as an anionic surfactant. CTAB as a typical cationic