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Full Length Article

Graphene supported $Li_2SiO_3/Li_4Ti_5O_{12}$ nanocomposites with improved electrochemical performance as anode material for lithium-ion batteries

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ABSTRACT

Graphene supported Li_2SiO_3@$Li_4Ti_5O_{12}$ (GE@LSO/LTO) nanocomposites have been synthesized via a hydrothermal route and following calcination. LSO/LTO nanospheres are adhered to the graphene nanosheets with the size of 50–100 nm, in which both LSO and LTO particles are attached together. When tested as the anode for lithium ion batteries, the initial discharge and charge capacities of GE@LSO/LTO are 720.6 mAh g^{-1} and 463.4 mAh g^{-1} at the current density of 150 mA g^{-1}. After 200 cycles, the discharge and charge capacities can be remained of 399.2 mAh g^{-1} and 398.9 mAh g^{-1}, respectively. Moreover, the charge rate capacities of GE@LSO/LTO composites retain 89.1% at the range of current density from 150 mA g^{-1} to 750 mA g^{-1}. And its recovery rates are 91.0% when the current density back to 150 mA g^{-1}. In addition, the reversible capacity and cycle stability of GE@LSO/LTO are better than that of LTO and LSO/LTO. The reasons can be attributed to the synergistic effect between GE and LSO/LTO as well as the features of GE supports.

1. Introduction

With the development of electric vehicles, communication devices and portable electronics, exploitation of advanced energy storage devices has attracted researchers' more attention. Lithium ion batteries (LIBs) are considered to be a promising candidate for clean energy storage due to their high electromotive force, long cycling ability, no memory effect, little self-discharge and design flexibility [1–7]. Development of the electrode material is a key factor for LIBs [8,9].

Spinel $Li_4Ti_5O_{12}$ (LTO), one of the alternative candidates, has been used as an anode material which has facile Li^+ storage properties in spite of low theoretical capacity (175 mAh g^{-1}). The crystalline structure of LTO could be the structure with Fd3 m space group, where O^{2-} is located at 32e sites, 3/4 of Li^+ is located at tetrahedral 8a sites and the rest of Li^+ with Ti^{4+} is located at octahedral 16d sites [10]. When Li^+ intercalating, the inserted lithium and Li^+ in 8a sites are migrated to the neighboring octahedral 16c sites, and form the structure of a rock salt ($[Li_2]_{16c}[Li_{1/3}Ti_{5/3}]_{16d}O_4$). When Li^+ de-intercalating, the lithium ions move back 8a sites again. The reaction can be described as follows [10,11].

$$Li_{(8a)}[Li_{1/3}Ti_{5/3}]_{(16d)}O_{4(32e)} + Li^+ + e \leftrightarrow Li_{2(16c)}[Li_{1/3}Ti_{5/3}]_{(16d)}O_{4(32e)}$$

In the reaction, 1 mol of $Li_4Ti_5O_{12}$ may be intercalated in 3 mol of lithium at most. The unit cell parameter of $Li_4Ti_5O_{12}$ is 0.836 nm while that of the generative $Li_7Ti_5O_{12}$ is 0.837 nm [12]. Thus, LTO may be regarded as a "zero strain effect" material, indicating its long cycle life. In addition, a charge and discharge potential at ~1.55 V vs. Li^+/Li of LTO makes it safer [13]. However, it has a low electronic conductivity (~10^{-13} S cm^{-1}) and a poor lithium ion diffusion coefficient (~10^{-15} cm^2 s^{-1}) which results in a poor rate capability [14–16]. Some approaches have been attempted to solve the problems. Tailoring the particle size of LTO can reduce the ionic and electronic transportation distance and enhances the electronic conductivity [17–19]. Additionally, the composites formed by coating or doping with additives in LTO can also improve the electrochemical properties of the electrodes, such as SiO_2-incorporated $Li_4Ti_5O_{12}$ [20], $Li_4Ti_{5-x}Sn_xO_{12}$ [21], carbon-encapsulated F-doped LTO composites [22], Mg-substituted $Li_4Ti_5O_{12}$ [23], $Li_{3.8}Cu_{0.3}Ti_{4.9}O_{12}$/CNTs [24], carbon-$Li_4Ti_5O_{12}$ [25,26], and so on. These dopants or coating materials can prevent the agglomeration of LTO particles and provide better electrical conductivity, thus further improve the electrochemical performance of LTO.

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Furthermore, Li_2SiO_3 (LSO) is an ideal dopant due to its unique structure. The SiO_4 tetrahedra form zigzag chains, indicating that LSO has a three-dimensional path, which is favorable for the lithium ion diffusion. Moreover, LSO is a kind of chemically inert materials and has good structural stability in organic electrolyte [27,28], which will improve the rate capability and cycling stability and decrease the polarization of LTO.

Graphite has been widely used as a kind of commercialized anode materials for LIBs. But its low theoretical capacity (372 $mAhg^{-1}$) limits its further application in the large-scale energy storage fields [29]. At present, various kinds of novel carbon materials such as carbon nanotube [30], mesoporous carbon [31], carbon coating material (typically carbons) [32] and carbon black [33] have been used in LIBs. In all of these, as a two-dimensional crystal lattice sheet of carbon atoms with a honeycomb structure, graphene has been demonstrated to be desirable for good Li ion storage space and charge-transfer rate due to its superior electrical conductivity, large surface-to-volume ratio, high specific surface area of over 2600 $m^2\ g^{-1}$, mechanical strength and structure flexibility [34–36].

Thus, based on the previous research [37], we have developed graphene supported LSO/LTO (GE@LSO/LTO) nanocomposite by the hydrothermal method and following sintering as anode materials for lithium-ion batteries. The structure, morphology and the electrochemical properties of LSO/LTO and GE@LSO/LTO nanocomposites are characterized and further compared with LTO.

2. Experimental

2.1. Synthesis procedures

2.1.1. Synthesis of Si-TiO_2 sphere

The TiO_2 spheres were synthesized by the hydrolysis of tetrabutylorthotitanate ($Ti(OC_4H_9)_4$, TBOT, AR) [37,38]. Firstly, 400 mg of hydroxypropyl cellulose (HPC, AR) was dissolved in 2 mL of distilled water and 300 mL of ethanol under vigorous magnetic stirring. After that, 3 mL of TBOT and 40 mL of ethanol were mixed and then added into the above solution. After reacted at 85 °C for 90 min, the collected product was washed with distilled water and ethanol and dried at 60 °C to obtain amorphous TiO_2 spheres. Finally, the products were kept at 500 °C, 600 °C and 700 °C for 3 h in a furnace, which were labeled as T500, T600 and T700, respectively.

In addition, Si was provided by Harbin Te Bo Technology Co. Ltd., China Si particles present the nano spheres with a size from 30 to 50 nm and the purity is 99.9%. Si/TiO_2 sphere was prepared with the above-mentioned method with 300 mg of silicon as support. The final product was kept in a furnace at 600 °C for 3 h to obtain the precursor of LSO/LTO.

2.1.2. Synthesis of LSO/LTO sphere

The LSO/LTO sphere was synthesized by the hydrothermal method [18]. 900 mg of Si/TiO_2 sphere was dispersed in 20 mL of distilled water and 60 mL of ethanol under vigorous magnetic stirring. After adding a certain molar of $LiOH{\cdot}H_2O$, the mixture solution was transferred into a 100 mL of Teflon-lined stainless steel autoclave and heated at 180 °C for 18 h. After the reaction was finished, it was cooled down to room temperature naturally. The solid products were centrifuged, washed with distilled water and ethanol, and then dried at 60 °C under vacuum to obtain the precursors. Finally, the products were kept in a tube furnace at 600 °C for 3 h. The samples prepared at the molar ratio of LiOH:TiO_2 = 1.75:1, 4:1, 6:1 and 8:1 were named as LT1.75, LT4, LT6 and LT8, respectively. For comparison, LTO was also prepared via the above method but no silicon was added, and the molar ratio of LiOH and TiO_2 is set as1.75:1.

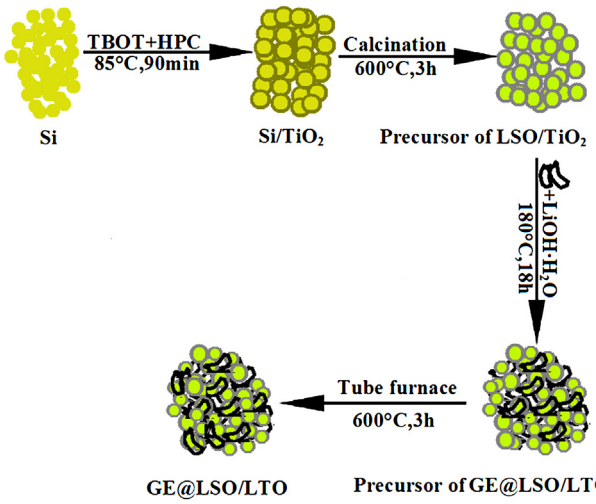

Fig. 1. The schematic diagram of the formation of GE supported LSO/LTO composite.

2.1.3. Synthesis of GE@ LSO/LTO

Graphene oxide was prepared by modified Hummers and Offeman's method according to the reported method [34]. GE@ LSO/LTO was prepared through above-mentioned method for LSO/LTO sphere, during which 300 mg of graphene oxide was added as support and the molar ratio of LiOH and TiO_2 was set at 6:1. Fig. 1 illustrates schematically the steps for the formation of GE supported LSO/LTO composite. The reaction could be summarized as the following.

$$Ti(OC_4H_9)_4 + 4H_2O = Ti(OH)_4 + 4C_4H_9OH \quad (1)$$

$$Ti(OH)_4 + Ti(OC_4H_9)_4 = 2TiO_2 + 4C_4H_9OH \quad (2)$$

$$Ti(OH)_4 \Leftrightarrow TiO_2 + 2H_2O \quad (3)$$

$$Si + O_2 = SiO_2 \quad (4)$$

$$5TiO_2 + SiO_2 + 6LiOH = Li_2SiO_3 + Li_4Ti_5O_{12} + 3H_2O \quad (5)$$

In the first step the Si/TiO_2 was formed through the hydrolysis of Ti ($OC_4H_9)_4$ as shown in Eqs. ((1)–(3)). SiO_2/TiO_2 is formed by the calcination of Si/TiO_2 (Eq. (4)). LSO/LTO is formed by hydrothermal method (Eq. (5)). Lastly, GE@ LSO/LTO is obtained by the calcination in a tube furnace. In addition, LSO/LTO spheres could be grown on the graphene sheets because the effect of an electrostatic adherence could take place between GE and Ti^{4+} [39].

2.2. Characterization

The structure and morphology of the samples were characterized by X-ray diffraction analysis (XRD, X'Pert MPD PRO, PANalytical Company, Almelo, Holland), scanning electron microscope (SEM, NoVaTM Nano 250, FEI Company) and field emission transmission electron microscope (FETEM, Tecnai G2 F20, FEI Company). XPS analysis was characterized by X-Ray photoelectron spectroscopy (K-Alpha, ESCALAB 250, Thermofisher Co., USA). The fourier transform infrared spectroscopy (FTIR) spectra of the samples were obtained by using Model NIcolETiS10 fourier transform spectrometer (Thermo SCIENTIFIC Co., USA) with a 2 cm^{-1} resolution in the range of 400–4000 cm^{-1}. The nitrogen adsorption/desorption isotherms of the samples were measured at 77 K by a Quantachrome Instruments Autosorb IQC (USA), and the surface area was determined using the Brunauer-Emmett-Teller (BET) formalism. The pore size distribution was computed from the by the original density functional theory (DFT) model.