



Significantly enhanced electrochemical performance of lithium titanate anode for lithium ion battery by the hybrid of nitrogen and sulfur co-doped graphene quantum dots



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ABSTRACT

The paper reported a facile synthesis of lithium titanate/nitrogen and sulfur co-doped graphene quantum dots (LTO/N,S-GQDs). Tetrabutyl titanate was dissolved in tertbutanol and heated to refluxing state by microwave irradiation. Then, lithium acetate was added into the mixed solution to produce LTO precursor. The precursor was hybridized with N,S-GQDs in ethanol. Followed by drying and thermal annealing at 500 °C in Ar/H₂ to obtain LTO/N,S-GQDs. The synthesis creates fully crystalline interconnected porous framework composed of nanoscale LTO crystals. The unique architecture achieves to maximize the high-rate performance and enhance the power density. More importantly, the introduction of N,S-GQDs don't almost influence on the electrolyte transport, but greatly improve the electron transfer and the storage lithium capacity. The LTO/N,S-GQDs anode exhibits remarkably enhanced electrochemical performance for lithium ion battery. The specific discharge capacity is 254.2 mAh g⁻¹ at 0.1C and 126.5 mAh g⁻¹ at 10C. The capacity remains 96.9% at least after 2000 cycles at 2C. The battery performance is significantly better than that of pure LTO electrode and LTO/graphene electrode.

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1. Introduction

Lithium ion battery is popular electrochemical devices since its first commercialization by Sony Corporation in 1990s. It has been widely used in various portable electronic devices, including notebook personal computer, mobile phone, tablet and digital camera, due to its merits in terms of high operating voltage, high energy density, low self-discharge and the absence of memory effects. Its applications have been extended to electric vehicles and hybrid electrical vehicles to meet the environmental concerns [1]. As battery performance of lithium ion battery seriously depends on the electrode materials, the development of new electrode materials with high-performance has become the focus of lithium battery industry [2]. To date, graphite still is a main anode material for commercial lithium ion batteries. Graphite is rich in resources, low cost and high electronic conductivity, but it has low lithium ion diffusion coefficient, restricting its applications in high-power lithium ion battery. In addition, low operating potential below

0.2 V (vs. Li/Li⁺) may result in the growth of lithium dendrites on the anode surface in the overcharged state [3]. In the last decade, great effort has been paid to search for alternative anode candidates instead of conventional graphite electrode [4]. Currently, lithium titanate (LTO) is considered as the most promising one, because of its excellent safety characteristic and long lifetime. LTO anode provides many advantages such as excellent lithium ion insertion and extraction reversibility, negligible volume change and structural change during the charge and discharge process, and a flat potential plateau. The vital drawback for LTO is its intrinsic insulating property, leading to severe polarization discharged at high current density. This will bring a poor high-rate performance and limits its applications in high-performance lithium ion battery [5].

Several strategies have been successfully attempted to improve the electrochemical properties of LTO in the recent years [6]. The first is to fabricate nanoscale LTO crystals. The nanosizing effectively enhances the high-rate performance of lithium ion battery via shortening diffusion distance of lithium ions in the electrode materials. Fattakhova-Rohlfing et al. synthesized fully crystalline interconnected porous frameworks composed of ultra small LTO nanocrystals of a few nanometers in size [7]. These framework

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feature a gravimetric capacity of about 175 mAh g^{-1} at rates of 1–50C and can deliver up to 73% of their maximum capacity at unprecedented high rates of up to 800C without the deterioration up to 1000 cycles. However, the nanosizing inevitably leads to reduce the tap density, resulting in a low volumetric specific capacitance. This will greatly limit its applications in high-energy lithium ion battery. In addition, the production of nanoscale LTO crystals often requires a complex process, multi steps and serious control of the reaction conditions, which results in an obvious increase of product cost. The second is to introduce metal ions or atoms into LTO crystals. The doping can remarkably enhance the high-rate performance of lithium ion battery, owing to an improved electronic conductivity [8–11]. Czerwinski et al. developed a solid phase synthesis of the doping Ag into LTO [12]. The doped Ag atoms are distributed on the surface of LTO crystal as a conductive network, so as to enhance the high-rate capability. However, the doping may destroy the integrity of LTO crystal and result in the loss of zero strain characteristic to some extent. This will greatly shorten the battery life. The third is to hybrid with other conductive materials to form LTO-based composite [13]. The composite shows a better rate capability than pure phase LTO, owing to a better electronic conductivity [14]. Recently, graphene as a new type of carbon materials has becomingly received great concern for the LTO modification. Graphene nanosheets are 2D macromolecular carbon material with remarkable electronic conductivity, large specific surface area and good mechanical property. The characteristics make it become an ideal conductive additive and structural support for LTO crystals. The investigation has acquired great achievement through mixing, coating or loading graphene on the LTO crystals. Chen et al. do well works in the mesoporous LTO grown on the reduced graphene oxide and the discharge capacity is 132 mAh g^{-1} at 40C [15]. As graphene sheets are in the size of several microns to tens of microns, the coating such a large sheet on the surface of LTO crystals will hinder the entry of lithium ions into LTO crystal, leading to a remarkable decrease of the specific capacity. To resolve the problem, researchers had to convert 2D graphene into 3D graphene with special space structure or activated graphene with rich of mesopores for providing channels of the electrolyte transport. However, the building 3D graphene or activated graphene often requires a complex and time-consuming process. In addition, the use of large amounts of graphene also increases the cost, which are not in favour of the commercial process. More recently, graphene quantum dots (GQDs), single- or few-layer graphene with a tiny size of only several nanometers, have interesting optical properties due to tunable size and surface chemistry [16]. GQDs stand for a new type of QDs with the unique properties associated with both graphene and QDs, and have shown their value-added function in light emitting diode [17], supercapacitor [18], oxygen reduction reaction [19], solar cell [20] and sensors [21]. To the best of our knowledge, few report refers to the applications of GQDs in lithium ion battery.

In the study, we focus a facile synthesis of lithium titanate/nitrogen and sulfur co-doped graphene quantum dots (LTO/N,S-GQDs). The as-prepared hybrid gives fully crystalline interconnected porous framework composed of nanoscale LTO crystals. The unique architecture and the introduction of N,S-GQDs create both ultrafast electron transfer and electrolyte transport and an enhanced specific capacity. The LTO/N,S-GQDs anode exhibits a prominent advantage of specific capacity, high-rate performance and cycle stability.

2. Experimental

2.1. N,S-GQDs preparation

N,S-GQDs were prepared by thermal treatment of molecular organic salts with the mixed carbon source and the surface modifier in the single precursor [16]. In a typical preparation

procedure, the mixture of citric acid (100 mmol) and L-cysteine (90 mmol) was dissolved in the deionized water (50 ml). Then, it was evaporated at 80°C until dry. The resulting thick syrup was hydrothermally heated in the Teflon-equipped stainless-steel autoclave at 220°C for 4 h and a heating rate of $10^\circ\text{C min}^{-1}$. The collected black syrup sample was neutralized with 1 M NaOH solution to pH 7 and finally dried by freeze drying to obtain a solid N,S-GQDs product. In addition, a common GQD was synthesized by using the same procedure unless no addition of L-cysteine.

2.2. LTO/N,S-GQDs synthesis

Synthesis of LTO/N,S-GQDs includes the preparation of LTO precursor (p-LTO) and hybrid of p-LTO with N,S-GQDs and LTO/N,S-GQDs. In a typical procedure, 20 g of tetrabutyl titanate (TBT) were dissolved in 150 ml of tertbutanol (TBA). The mixed solution was transferred into a HWL07-3 microwave reactor and then heated to refluxing state using microwave irradiation (300 W). Followed by adding the lithium acetate solution dissolved 4.9 g of lithium acetate (LiAc) in 20 ml of the deionized water into the mixed solution to form p-LTO. After 20 min, the solvent was removed from the reaction system by distillation. The collected p-LTO was dried at 200°C for 2 h. After that, the p-LTO was mixed with the N,S-GQDs solution dissolved 0.4 g of N,S-GQDs in 50 ml of ethanol with the help of ultrasonic wave. Followed by drying and thermal annealing in Ar/H₂ (95:5) atmosphere at 500°C with the temperate ramp rate of $10^\circ\text{C min}^{-1}$ for 12 h to obtain the LTO/N,S-GQDs product. To study on the effect of N,S-GQDs on the electrochemical property, LTO/GQDs or LTO-c) was prepared by the same procedure unless the use of GQDs instead of N,S-GQDs or no addition of N,S-GQDs. To compare the effect of graphene and N,S-GQDs on the battery performance of LTO, another hybrid, LTO/graphene (LTO-G), was also fabricated by the same procedure except for use of the same amounts of graphene oxide instead of N,S-GQDs.

2.3. Material characterization

Scanning electron microscope (SEM) was performed using HITACHI S4800. Transmission electron microscope (TEM) was performed by a JEOL 2010. X-ray diffraction (XRD) was measured on the D8 Advance with a Cu K α radiation. Raman measurements were carried out using a InVia laser micro-Raman spectrometer. X-ray photoelectron spectroscopy (XPS) was performed by PHI 5700 using Al KR radiation. Fluorescence lifetime intensity decay of LTO/GQD and N,S-GQDs in aqueous solution was measured on the FLS 920 steady state and transient state fluorescence spectrometer (Edinburgh Instruments, England) with excitation at 370 nm and emission at 452 nm.

2.4. Electrochemical measurements

Electrochemical properties of LTO materials were evaluated using 2016 coin cells. The active materials were mixed with super P conductive carbon and polyvinylidene fluoride (PVDF, Sigma-Aldrich) at weight ratio of 8:1:1 in N-methylpyrrolidone (NMP, Sigma-Aldrich) solvent to form uniform slurries, which were then coated on copper foils. The loading density of active materials was about 2.0 mg cm^{-2} . Subsequently dried in a vacuum oven at 120°C overnight and rolled by using a rolling machine, these working electrodes were incorporated into 2016 coin cells, in which Li foils were serviced as the counter and reference electrode, Celgard 2400 as the separator, and a mixed solvent of ethylene carbonate, dimethyl carbonate and diethylene carbonate (1:1:1) containing of 1 M LiPF₆ as the electrolyte. The assembly process was conducted in an argon-filled glove box having O₂ and H₂O contents below 0.1 ppm. Discharge-charge tests were performed at a potential

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