



Outstanding rate capability and long cycle stability induced by homogeneous distribution of nitrogen doped carbon and titanium nitride on the surface and in the bulk of spinel lithium titanate



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ABSTRACT

N-doped carbon and TiN composite conductive structure with homogeneous distribution on the surface and in the bulk of spinel lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) nanoparticles is prepared via a simple one-step chemical vapor deposition assisted solid-state route in the presence of layered structure sodium titanate nanotubes as the titanium source and ethylenediamine as the carbon and nitrogen source. Results indicate that as-fabricated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples containing N-doped carbon and TiN composite conductive structure exhibit markedly improved electrochemical properties as compared with pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Particularly, the electrode made from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ containing N-doped carbon and TiN composite conductive structure obtained after 60 min of treatment in the presence of ethylenediamine has a high capacity of $162 \text{ mAh} \cdot \text{g}^{-1}$ at a charge/discharge rate of 20C as well as a substantial capacity of 92% and a capacity retention of 75% after 2500 cycles at 10C, showing superior electrochemical performance and great potential as an anode material for high-rate lithium-ion batteries. The enhanced electrochemical performance of the composite electrodes can be attributed to the small size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles as well as the uniform distribution of N-doped carbon and TiN composite conductive structure on the surface and in the bulk of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles.

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1. Introduction

There is an increasing demand for batteries with a high energy density and power density used in electric vehicle (EV) and hybrid electric vehicle (HEV). Lithium ion batteries have high energy density, but their energy density is dramatically reduced at high charge/discharge rates. It is usually believed that very high power rates of electrochemical systems can only be achieved with supercapacitors which trade high power for low energy density, since supercapacitors store energy only by surface adsorption reactions of charged species on an electrode material [1]. Therefore, it remains a challenge to establish storage technology that combines the rate performance of supercapacitors with the energy density of lithium-ion batteries [2].

In recent years, spinel lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) has attracted great attention as an anode material for lithium-ion batteries used in EV and HEV, because it has a very flat potential

plateau at approximately 1.5 V versus Li^+/Li and displays good reversibility and structural stability (zero-strain insertion material) in the charge/discharge process [3]. Unfortunately, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a poor electrical conductivity ($<10^{-13} \text{ S} \cdot \text{cm}^{-1}$), which accounts for its initial capacity loss and poor rate capability and retards its wide practical applications [4]. To improve the rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, researchers have made great efforts to reduce its ionic and electronic transportation distance by constructing nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$, incorporating second phase with high electronic conductivity [5,6], and doping active materials with heteroatoms [7–9]. Among these techniques, carbon coating is considered to be economic and feasible for improving the surface conductivity and electrical contact of electrode [10,11]. However, it usually requires high-temperature calcination to increase the graphitization degree of carbon coating so as to acquire desired electrical conductivity and electrochemical performance, which is unfavorable for constructing nanostructured electrode materials. Similarly, TiN has a far higher metallic conductivity ($1 \times 10^6 \sim 4 \times 10^6 \text{ S/m}$) than graphite carbon [12] and can be used to improve the electrochemical performance of electrode materials [13,14], but the formation of TiN also requires high-temperature calcination. Such a bottleneck, fortunately, could be broken by introducing carbon as a reducing agent

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in the reaction system thereby promoting the formation of TiN at a relatively low temperature [15,16], which makes it feasible to construct carbon-TiN composite structure with excellent conductivity at lowered temperature. Nevertheless, surface conductive coating can only improve the surface conductivity and electrical contact but cannot improve the intrinsic conductivity of electrodes. To overcome this drawback, researchers have adopted doping method to incorporate various metal ions so as to improve the intrinsic conductivity of electrodes [17–19].

It is not surprising that very few reports are currently available about improving the rate capacity of electrodes through doping non-metal anions [20–22], mainly because anion dopants with higher surface energy and lower solubility than the bulk tend to locate dominantly in the subsurface region of very limited depth but not be homogeneously distributed throughout the bulk particles [23]. This problem could be solved by adopting two possible routes: one is to decrease the particle size so as to reduce the diffusion length of dopants thereby realizing homogeneous doping, and the other is to introduce particles with layered structure so as to facilitate easy diffusion of dopants from the surface to the bulk through the interlayer galleries. As to the latter route, sodium titanate nanotubes (STN) are of particular significance, because they exhibit unique nanotubular and layered structure (interlayer distance about 0.8 nm, inner diameter about 4 nm) [24,25]. In the meantime, STN can readily exchange with Li^+ cation in aqueous solution, which provides an alternate to fabricate nanosized spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via calcination of the intermediates of lithium titanate at relatively lowered temperature and shortened time. Furthermore, because of spatial confinement effect of nanotubular and layered structure, organic substance of small molecules can be embedded into the interlayer spaces of STN; and resultant embedded small organic molecules can be converted into uniformly distributed carbon coating by pyrolysis. As-obtained carbon coating, in combination with nanosized TiN made from STN, should help to greatly improve the conductivity and rate capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes.

Viewing the aforementioned perspectives, here we report the construction of the composite conductive structure of N-doped carbon and TiN with homogeneous distributions on the surface and in the bulk of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles via a simple one-step chemical vapor deposition assisted solid-state reaction of STN as the titanium source and ethylenediamine as the carbon and nitrogen sources. The rate capability and long cycle stability of as-fabricated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites as anode materials for lithium-ion batteries are also reported.

2. Experimental

2.1. Sample preparation

STN is used as Ti source, and its preparation is reported elsewhere [26]. The intermediate of lithium titanate is prepared by ion-exchange method. Briefly, the solution of 0.6 M LiOH containing STN with a Li:Ti molar ratio of 6:1 was repeatedly stirred at room temperature for three times (each cycle 24 h), followed by filtrating and drying at 60 °C for 12 h to obtain the intermediate of lithium titanate. The dried intermediate of lithium titanate was then heated at 600 °C for 2 h in air and cooled down to room temperature naturally, yielding spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ denoted as LTO. In the meantime, the intermediate of lithium titanate was loaded into a silica tube reactor that was placed in a furnace and connected to a gas-feeding system. After a flow of Ar gas (99.99%) was charged into the furnace to purge air within about 30 min, the furnace was heated from room temperature to 600 °C at the rate of 10 °C/min and held at 600 °C for 2 h, while ethylenediamine was added dropwise into the reactor with a peristaltic pump at a rate of about 0.75 mL/min. The dropping durations of ethylenediamine were selected as 10,

30, and 60 min, respectively; and corresponding samples collected after the furnace was cooled down to room temperature under flowing Ar gas are denoted as LTO-EDA-10, LTO-EDA-30 and LTO-EDA-60, respectively (the numeral suffixes refer to calcination time of ethylenediamine).

2.2. Characterization

Transmission electron microscopic (TEM) images were obtained with a JEM-2010 electron microscope. X-ray diffraction (XRD) patterns were measured with a Philips X'Pert Pro X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) analyses and Ar^+ ion sputtering analyses were conducted with a Shimadzu Axis Ultra multifunctional X-ray photoelectron spectroscope (Al- $K\alpha$ X-ray, $h\nu = 1486.6$ eV). The energy scale of the XPS spectra is corrected in relation to the binding energy of adventitious carbon ($\text{C}1s = 284.8$ eV). Ar^+ ion sputtering over a measurement area of 2×2 mm² was conducted at a voltage of 25 kV, current of 100 mA, power of 100 W and Ar^+ sputtering rate of $1 \text{ nm}\cdot\text{s}^{-1}$ with Al_2O_3 as the reference. An AVATAR360 Fourier transform infrared spectrometer (FTIR) was used to analyze the chemical components of the coated layers.

2.3. Electrochemical measurements

As-synthesized LTO, LTO-EDA-10, LTO-EDA-30 and LTO-EDA-60 samples were separately homogeneously mixed with acetylene black and polyvinylidene fluoride (PVDF) binder at a weight ratio of 80:10:10. Into resultant mixture were added several drops of N-methylpyrrolidinone (NMP) to afford a slurry. The slurry was coated uniformly onto a copper foil and dried at 120 °C for 24 h. Upon completion of drying, a circular electrode with a diameter of 15 mm was punched from the copper foil and used as the working electrode. Simulated batteries were assembled from as-fabricated working electrodes and lithium foil counter electrode in a glove box filled with high-purity argon; and the moisture content and oxygen level inside the glove box are less than 1×10^{-6} . A solution of 1 M LiPF₆ dissolved in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte (the volume ratio of EC to DEC is 1:1), and Celgard 2400 was used as the separator membrane. An IM6 impedance and electrochemical measurement system (Zahner, Germany) equipped with a conventional two-electrode cell was performed to record the electrochemical impedance spectra (EIS) at an alternating current amplitude of 5 mV and in the frequency range from 100 kHz to 0.01 Hz.

3. Results and discussion

Fig. 1 shows the XRD patterns of pristine LTO and LTO-EDA series samples. All XRD patterns can be indexed as lithium titanium oxide (cubic phase, space group Fd-3 m) in accordance with spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Ethylenediamine does not disrupt the crystal structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, but the crystal structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is destroyed at an extended ethylenediamine calcination time of 2 h, due to reductive ability of ethylenediamine (see supporting information Fig. S1). The mean crystallite sizes of pristine LTO and LTO-EDA-10, LTO-EDA-30, and LTO-EDA-60 series samples calculated by Scherrer's formula are about 30, 26, 24, and 23 nm, respectively. This indicates that the surface coated conductive layer can inhibit the growth and reduce the size of LTO grains, which is beneficial to improving the electrochemical performance.

Fig. 2 gives the TEM images of STN precursor, the intermediate of lithium titanate nanotube after ion-exchange, and LTO-EDA series samples. STN precursor, with multi-layered structure and an interlayer distance of about 0.8 nm (inset of Fig. 2a), has an outer diameter of about 10 nm and a length of several tens to hundreds

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