



# In situ nickel/carbon coated lithium titanium oxide anode material with improved electrochemical properties



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## ABSTRACT

*In situ* nickel/carbon coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  has been synthesized successfully via a facile sol-gel method with chitosan serving as chelating agent and carbon source. The as-prepared samples are tested by different physical and electrochemical methods. The results of SEM and TEM indicate that the Ni/C layer was successfully coated on the surface of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  with the thickness of 2–3 nm. Furthermore, the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ @Ni/C composite shows excellent rate capability and cycling stability. A large charge capacity of  $237.3 \text{ mAh g}^{-1}$  can be remained after 100 cycles with the current of  $0.1 \text{ A g}^{-1}$  between 0.02–3.0 V, which is close to its theoretical capacity ( $\sim 262 \text{ mAh g}^{-1}$ ). Even at the current of  $4.0 \text{ A g}^{-1}$ , it still delivers a quite high charge capacity of  $186.5 \text{ mAh g}^{-1}$  after 100 cycles, with no significant capacity fading. Additionally, the results of EIS reveal that the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ @Ni/C electrode has faster lithium-ion diffusivity and less resistance compared with pure  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . The remarkable improvement of the electrochemical properties should be attributed to the Ni/C coating layer, which acts as an effective conductor and a protective material against side reactions with electrolyte.

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## 1. Introduction

Lithium-ion batteries (LIBs) are widely employed as the power sources for various portable devices nowadays. In the current LIBs, graphite is regarded as the standard anode material due to its high capacity of  $372 \text{ mAh g}^{-1}$ . Nevertheless, the graphite anodes are handicapped by several critical disadvantages for these power applications, including poor rate capability, disappointing cyclability and worrying safety hazards [1,2]. The limitation of the graphite anode comes from the safety concerns originated from lithium dendrite formation and growth on the anode surface at large operating current [3]. To improve the electrochemical performance of LIBs, many other alternative anodes have been developed. Recently, spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is put forward as a promising alternative anode material for lithium-ion batteries due to its high thermodynamic stability and excellent cycling performance [4]. Besides,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  exhibits a flat and relatively high lithium insertion/extraction voltage at around 1.55 V (vs. Li/Li<sup>+</sup>), which can ensure the safety of batteries by avoiding the formation of lithium dendrites. However, the higher working potential of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  compared with other anodes restricts its application for high energy density devices. On

the other hand, the electrochemical processes of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  down to  $\sim 0 \text{ V}$  can increase the specific capacity and energy density due to the lower discharge potential [5–7].

Although  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  has a high theoretical specific capacity of  $\sim 262 \text{ mAh g}^{-1}$  when cycled in the potential window of 0–3 V [3,6], its high charge/discharge rate capabilities are relatively low due to the poor electronic conductivity and ultra-slow lithium ion diffusion [8,9]. Many strategies have been explored to overcome these shortcomings and then improve the electrochemical performance. One effective way is to decrease the particle size which can shorten the lithium ion diffusion length and provide extended contact area between the electrode and electrolyte, consequently, improving lithium-ion intercalation kinetics [10–12]. For instance, M. Kalbác *et al.* [10] prepared phase-pure nanocrystalline  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  with BET surface areas between 183 and  $196 \text{ m}^2 \text{ g}^{-1}$ , which presented an excellent lithium-ion insertion behavior. N. Zhang *et al.* [12] synthesized nanocrystalline  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  via a sol-gel process and the obtained nanoparticles showed a high-rate capacity of  $108 \text{ mAh g}^{-1}$  at 40 C. The other way is to enhance the electronic conductivity by surface modification and metal cation doping [13–15]. L. Cheng *et al.* [13] synthesized nanostructured  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C material, which showed a significant improvement of the rate capability. X. Yang *et al.* [15] prepared core-shell  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ @ $\text{CeO}_2$  nanosphere with partial doping of  $\text{Ce}^{4+}$  into the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  structure, and it exhibited a high capacity of  $152 \text{ mAh g}^{-1}$  even after 180 cycles at 10 C,

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with no noticeable capacity fading. As a conductive additive, metal Cu deposited on the surface of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  showed a great potential in enhancing the electrochemical properties [16]. More recently, K. Wu *et al.* [17] synthesized core-shell  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}@\text{Cu}/\text{C}$  by a following coating process with Cu/C layer. As a result, it exhibited a lower electrochemical polarization and quicker kinetic behavior as compared to the pure  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$ . Thus, metal and conductive carbon coating layer can enhance the electrochemical performance effectively. It is well known that metal nickel (Ni) is widely employed as electrode material and surface protection material due to its high electrical conductivity and excellent corrosion resistance, respectively [18,19]. Herein, the nickel/carbon is an ideal coating material to enhance the electronic and ionic conductivity effectively, thus improving the rate capability and cyclability of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . To the best of our knowledge, however, there were little reports on Ni/C-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite as yet.

Generally, many electrode materials were mainly synthesized through a solid-state reaction method due to its simple operation and easy industrialization [20–26]. However, the solid-state method usually introduces some disadvantages, including low homogeneity, large particle size, high calcination temperature and long sintering time [4]. While, a sol-gel method, which could obtain decentralized and decreased particles in a relatively low calcination temperature and short time, has been widely developed for the preparation of electrode materials in lithium-ion battery field [27–30]. In this study, we present a sol-gel approach to synthesize  $\text{Li}_4\text{Ti}_5\text{O}_{12}@\text{Ni}/\text{C}$  composite as an advanced anode material for lithium-ion batteries. The morphology and electrochemical properties of the as-prepared samples were systematically investigated in detail. The results of electrochemical measurements indicate that the  $\text{Li}_4\text{Ti}_5\text{O}_{12}@\text{Ni}/\text{C}$  composite exhibits high rate capability and excellent cycling performance.

## 2. Experimental

### 2.1. Materials preparation

All of the reactants and solvents were analytical grade and used without further purification. The  $\text{Li}_4\text{Ti}_5\text{O}_{12}@\text{Ni}/\text{C}$  composite was prepared by a facile sol-gel method using  $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ , and tetrabutyl titanate (TBT) as raw materials, and chitosan was employed as the chelating agent and carbon source. The schematic of the formation process is shown in Fig. 1. At first, stoichiometric amounts of  $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$  and  $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ : Ni = 95:5 in mass) were dissolved into deionized water under stirring at room temperature to form solution A. Second, a suitable amount of chitosan (10 wt. % to the final product) was dissolved in ice acetic acid solution which with the volume fraction of 5% and then ultrasonically treated for 0.5 h to form solution B. Third, a stoichiometric amount of tetrabutyl titanate (TBT) was dissolved in anhydrous ethanol to form solution C. Afterwards, the as-prepared solution A and B were added gradually into the solution C with vigorous stirring at room temperature. The resultant solution was heated at 70 °C in a water bath under stirring to vaporize the contained water and ethanol completely, which was followed by a heat treatment at 400 °C for 4 h in nitrogen atmosphere to allow a pyrolysis process, thus yielding the precursor. The obtained powders were ground and calcined at 800 °C for 5 h in nitrogen atmosphere to obtain the nickel/carbon coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase (LTO@Ni/C). As a reference sample,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) was also synthesized by the same route without the addition of  $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  and calcined under air atmosphere.

### 2.2. Materials characterization

X-ray diffraction patterns (XRD) were obtained using an X-ray diffractometer (Rigaku RINT2000) with Cu K $\alpha$  radiation and recorded between 10° and 80° with a step count of 0.02° and scanning speed of 3° min<sup>-1</sup>. The morphology of the samples was observed using a scanning electron microscope (Hitachi S4800) (SEM). Transmission electron microscopy (TEM) studies of the samples were conducted using a JEM-2100F transmission electron microscope operated at 200 kV.

### 2.3. Electrochemical measurements

For the electrochemical measurements, 80 wt.% active materials were mixed and grounded with 10 wt.% polyvinylidene fluoride (PVDF) powders as binder and 10 wt.% super-P as the conductive assistant materials. The mixture was added to N-methyl-2-pyrrolidinone (NMP) solvent to form a homogeneous slurry and coated on a copper foil as the working electrode, and dried at 120 °C in a vacuum oven for 12 h. Metallic lithium foils were used as the counter electrodes. 1 M  $\text{LiPF}_6$  in ethylene carbonate and dimethyl carbonate (1:1 in volume) served as electrolyte, and polypropylene was used as the separator. The cells were assembled in a glove box filled with high purity argon gas ( $\text{O}_2$  and  $\text{H}_2\text{O}$  levels <5 ppm).

The cyclic voltammetry (CV) tests were conducted on an electrochemical workstation (CHI1040B, ChenHua, China) at a scanning rate of 0.3 mV s<sup>-1</sup> in the voltage range of 0.02–3.0 V (vs.  $\text{Li}/\text{Li}^+$ ). And the charge/discharge tests were performed in the voltage range of 0.02–3 V (vs.  $\text{Li}/\text{Li}^+$ ) at different current densities on an automatic batteries tester (Land CT 2001A, Wuhan, China). The electrochemical impedance spectroscopy (EIS) was measured by an electrochemical workstation (GAMRY PC14-750) in the frequency range from 100 kHz to 10 mHz. All the electrochemical performances were tested at room temperature of 25 °C.

## 3. Results and discussion

### 3.1. Carbon content determination

The carbon in the LTO@Ni/C composite was resulted from the pyrolysis of tetrabutyl titanate and chitosan under high temperature treatment. A methodology previously reported [31] was adopted to evaluate the carbon content in the LTO@Ni/C composite. The as-prepared LTO@Ni/C sample was fired at 600 °C in air for 2 h to burn off the residual carbon and the mass loss fraction (*y* wt.%) was noted down. As metal nickel is hard to be oxidized into trivalent nickel ion at 600 °C in air atmosphere, the final fired products of LTO and NiO were obtained. Additionally, the fired products were dissolved in a hydrochloric acid solution, and the resulted solution displayed a color of light green, which indicated the existence of  $\text{Ni}^{2+}$ . Hence, the possible chemical reactions can be given as following:



According to the above equations, the mass gain of the sample was ascribed to the oxidation of metal Ni and the mass loss corresponded to the driven out carbon. Thus, the amount of residual carbon can be calculated as following:

$$\begin{aligned} x \text{ wt.}\% &= (1 - x \text{ wt.}\%) \frac{16 \times 5\%}{58.6934} + y \text{ wt.}\% \\ &= \frac{1.36 \text{ wt.}\% + y \text{ wt.}\%}{1 + 1.36 \text{ wt.}\%} \quad (3) \end{aligned}$$

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