Synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ Nanocomposites for Lithium-ion Batteries by a One-pot co-precipitation Method

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Abstract

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ nanocomposites were synthesized by a one-pot co-precipitation method. The structure and morphology of the as-prepared materials were analyzed by X-ray diffraction and transmission electron microscopy. The results show that $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ composites with different nano size were successfully synthesized. The $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ sample (2 wt.% V_2O_5 addition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$) keep at a high discharge capacity of 169.9 mAh g^{-1} after 150 cycles at 1 C. The existence of the V_2O_5 reduces the size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which improve the electrochemical activity of the sample.

1. Introduction

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ is an attractive candidate anode material for lithium-ion batteries (LIBs) since its structural stability, safety and long life [1]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has good Li^+ ions intercalation and de-intercalation reversibility, high working voltage (over 1.5V vs. Li^+/Li) and almost none structural change (less than 0.2 %) during charge-discharge cycling[2, 3]. However, the low electrical and ionic conductivity combined with the inadequate transport properties of Li^+ ions in microcrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can lead to poor rate performance, which hinders its development [4].

Transition to the nanoscale is an effective way to improve the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. [5, 6] The respective $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles with small size were prepared via various routes, including solid-state, hydrothermal, microwave, sol-gel, molten salt, combustion, and rheological phase methods[4, 7, 8]. Although $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles can deliver good electrochemical performance, complex synthesis processes limit its applications[9]. The synthesis of nanomaterials by chemical co-precipitation has the advantages of a simple process, low cost, easy control of synthesis conditions, and short synthesis time[10]. However, in order to synthesize materials with a smaller nano size, it is often necessary to add various types of surfactants to regulate the morphology of materials during the co-precipitation process[11, 12]. So it is expected to synthesize nanomaterials by this method without adding surfactants.

In this paper, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ composites were synthesized with no surfactant by a simple one-pot co-precipitation method. VO_3^- ion formation with the dissolve of the added V_2O_5 dramatically reduced the particle size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and V_2O_5 obtained again and composite with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the calcination process. The sample exhibits a capacity of 169 mAh g^{-1} after 150 cycles at 1C. This simple synthesis route with low synthesis cost is expected to show a potential commercial application

2. Experimental

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ was synthesized by a one-pot co-precipitation method. In a typical process, Tetrabutyl Titanate (TBT) and $\text{LiOH}\cdot\text{H}_2\text{O}$ were dissolved with ethanol and deionized water (at the molar ratio of $\text{Li}:\text{Ti} = 4.1:5$), respectively. Adding different ratios of V_2O_5 (0, 2, 5, 8 wt.% of $\text{Li}_4\text{Ti}_5\text{O}_{12}$) into $\text{LiOH}\cdot\text{H}_2\text{O}$ solution and stirred for 4 hours, then the mixture dropped into the TBT ethanol solution slowly. The mixture was

stirred for 24 h, and then dried at 100 °C to remove the solvent fully, with subsequent heating in a muffle furnace at 600 °C for 10 h in air and cooled down to room temperature naturally. The products were denoted as LTO-0, LTO-0.02, LTO-0.05, LTO-0.08 according to different V_2O_5 addition (0, 2, 5, 8 wt.% of $Li_4Ti_5O_{12}$), respectively.

Phase analysis and morphologies of $Li_4Ti_5O_{12}/V_2O_5$ composites were characterized by X-ray diffraction (XRD: Bruker D8 Advance equipped with Cu K α radiation source), scanning electron microscope (SEM: S-4800, Hitachi, Japan) and transmission electron microscopy (TEM: H-600, Hitachi, Japan).

$Li_4Ti_5O_{12}/V_2O_5$ was thoroughly mixed with 10% polyvinylidene fluoride and 10% acetylene black in N-methyl pyrrolidone. The slurry of the mixture was coated uniformly on copper foil and dried under vacuum at 100°C for 10 h. Coin-type cells (2032) were assembled with a solution of 1 M $LiPF_6$, ethylene carbonate: dimethyl carbonate = 1:1 in volume ratio as the electrolyte, a Celgard 2300 microporous polyethylene membrane as the separator, and a lithium disk as the counter electrode. All the cells were assembled in an argon-filled glove box, where the water and oxygen concentrations were kept at less than 5 ppm. Charge and discharge tests were carried out using a battery test system (CT2001A, Land, China) in the voltage range of 1.0–3.0 V (vs. Li^+/Li). All the electrochemical tests were carried out at room temperature.

3. Results And Discussion

Figure 1 (a) shows the XRD patterns of $Li_4Ti_5O_{12}/V_2O_5$ composites. It was not found that the characteristic patterns of V_2O_5 , all the peaks were identical to pattern of $Li_4Ti_5O_{12}$ (JCPDS Card No. 49–0207). The V_2O_5 could not give rise to the change in spinel structure of $Li_4Ti_5O_{12}$. In addition, (111) peak move to the direction of small-angle with the increase in the amount of V_2O_5 (Fig. 1(b)). And the more amount of V_2O_5 , the more offset to the left. The strength of the XRD peak of $Li_4Ti_5O_{12}$ is weak with the increase in the amount of V_2O_5 . Lattice disorder is noticeable when the V_2O_5 content is 8wt.%.

Figure 2 shows the TEM and SEM images of LTO-0 and LTO-0.02. It can be seen from Fig. 2b, c, and e that LTO-0.02 has a thickness of V_2O_5 layer, and the layer structure was clearly detected, suggesting that V_2O_5 coats on the surface of $Li_4Ti_5O_{12}$, while there is no coating on LTO-0 (Fig. 2a, c). The particle size of LTO-0 is 500 nm, and the size of LTO-0.02 is less than 100 nm. The results show that V_2O_5 restrains aggregation of $Li_4Ti_5O_{12}$, and facilitate the formation of $Li_4Ti_5O_{12}/V_2O_5$ nanocomposites. The V_2O_5 addition limits the growth of $Li_4Ti_5O_{12}$ particles.

Figure 3 (a) shows the first charge-discharge curves for $Li_4Ti_5O_{12}/V_2O_5$ composites. The discharge capacity of the first cycle is 185.8, 182.2, 164.5 and 134.7 mAh g^{-1} for LTO-0, LTO-0.02, LTO-0.05, LTO-0.08, respectively. Moreover, the discharge capacity is almost equal to the charge capacity, suggesting that the charge-discharge process is reversible. Furthermore, the inset of Fig. 3 (a) presents the ΔV of LTO-0.02 (38 mV) is smaller than that of LTO-0 (48 mV), indicating that LTO-0.02 shows lower polarization than LTO-0.

The discharge capacity vs. cycle number for $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ composites is shown in Fig. 3 (b). The discharge capacity is 163.4, 169.9, 157.9 and 128.9 mAh g^{-1} for LTO-0, LTO-0.02, LTO-0.05, LTO-0.08 after 150 cycle, respectively. LTO-0.02 displays the highest discharge capacity. However, with the content of V_2O_5 increased to 8 wt.%, the discharge capacity deteriorate. It is obvious that the content of V_2O_5 plays a key role in improving the electrochemical performance of the composites. LTO-0.02 has an optimal amount of V_2O_5 .

The improved electrochemical performance of LTO-0.02 originates from the following factors. On the one hand, good electrical conductivity of V_2O_5 enhances the total electrical conductivity of LTO-0.02. On the other hand, the nanostructure can improve the capacity to some extent and restrain the resistance increase during the charge-discharge process. It is helpful to improve the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [13, 14].

4. Conclusions

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ samples were synthesized by a sample one-pot co-precipitation method. LTO-0.02 shows the discharge capacity of 182 mAh g^{-1} and maintains around 169.9 mAh g^{-1} after 150 cycles at 1C. The existence of V_2O_5 significantly reduces the nanoparticle size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It shows a new idea from achieving nano-size control to surface cladding by one step.

Declarations

Conflicts of interest

There are no conflicts to declare.

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Figures

Figure 1

(a) XRD patterns, and (b) magnified (111) peak of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ composites.

Figure 2

TEM (a) and SEM (d) images of LTO-0, and TEM (b, c) and SEM (e) images of LTO-0.02. Fig.2 shows the TEM and SEM images of LTO-0 and LTO-0.02. It can be seen from Fig. 2 b, c, and e that LTO-0.02 has a thickness of V2O5 layer, and the layer structure was clearly detected, suggesting that V2O5 coats on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, while there is no coating on LTO-0 (Fig. 2a, c). The particle size of LTO-0 is 500 nm, and the size of LTO-0.02 is less than 100 nm. The results show that V2O5 restrains aggregation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and facilitates the formation of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ nanocomposites. The V2O5 addition limits the growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles.

Figure 3

(a) The first charge-discharge curves, and (b) cycling performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{V}_2\text{O}_5$ composites.