Improved rate performance of amorphous carbon coated lithium zinc titanate anode material with alginic acid as carbon precursor and particle size controller

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ARTICLE INFO

ABSTRACT

Carbon-coated $Li_2ZnTi_3O_8$ composites with nano particle size and excellent rate performance are synthesized via a facile solid-state reaction route using alginic acid as carbon precursor. The results of characterization indicate that amorphous carbon layer is homogeneously coated on the surface of $Li_2ZnTi_3O_8$ particles without any crystal structure change. The carbon-coated $Li_2ZnTi_3O_8$ composite with 10 wt.% alginic acid ($Li_2ZnTi_3O_8$/C-10) shows the largest initial discharge specific capacity of 242.5, 190.0, 165.2 and 91.2 mA h g^{-1} can be obtained after 100 cycles at 0.1, 0.5, 1.0 and 2.0 A g^{-1}, respectively. EIS reveals that $Li_2ZnTi_3O_8$/C-10 exhibits higher electronic conductivity and faster lithium ion diffusivity. The significant improvements of electrochemical performance are attributed to the carbon layer on the outer surface of $Li_2ZnTi_3O_8$ active particles, which can restrain the growth of particles, enhance electronic conductivity and suppress electrolyte decomposition.

1. Introduction

Rechargeable lithium-ion batteries are considered to be a promising power source for electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to high energy storage density, long cycle life and environment benign [1–3]. In conventional lithium-ion batteries, graphite is a widely used anode material, but the dendritic lithium growth during over charge or over discharge is still a serious safety problem [4]. An effective way to solve this issue is substitute the graphite by other anode materials with higher safety and better electrochemical performance. Titanium-based oxides, including the commercially available spinel $Li_4Ti_5O_{12}$, are suitable anodes because its negligible change in the unit cell, long-term cycling stability, a wide charge–discharge voltage plateau and high safety [5]. However, the low theoretic capacity of $Li_4Ti_5O_{12}$ (175 mA h g^{-1}) may prevent it from being widely used in large scale energy storage devices [6]. What's more, the intercalation potential of $Li_4Ti_5O_{12}$ is as high as 1.5 V, resulted in reduction of energy density. Thus, it is necessary to choose a new anode material with large capacity and high energy density instead of $Li_4Ti_5O_{12}$.

Recently, cubic spinel structure $Li_2ZnTi_3O_8$ with a space group P4$_3$32 exhibits favorable cycling stability. $Li_2ZnTi_3O_8$ has the advantages with larger lithium storage capacity and lower discharge voltage plateau, which can increase specific capacity and enhance energy density [7,8]. Nonetheless, its electronic conductivity and high rate performance are still not much too perfect. Therefore, our work is to improve the intrinsic poor electronic conductivity of $Li_2ZnTi_3O_8$ via different ways, such as synthesizing nano-sized particles, coating conductive materials (e.g. carbon and other high conductivity materials) and doping a small quantity of diverse valence-state ions [9–11]. Among the above mentioned methods, carbon coating is a common and effective approach in virtue of many advantages: (1) Carbon can be widely used as conductive material due to many kinds of carbon sources, low cost and less consumption. (2) Carbon has superior electrical conductivity, excellent thermal properties and chemical stability. According to published literatures, sucrose [12], pitch [13], citric acid [14], PAN [15] and other carbon sources [16–19] have been widely used as carbon source for $Li_4Ti_5O_8$ [20], $LiFePO_4$ [21] and $Li_3V_2(PO_4)_3$ [22], which could enhance the electronic conductivity and significant improve electrochemical performance.

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Alginic acid $((C_6H_8O_6)_n)$ is a polysaccharide refined from brown seaweed such as kelp, gulfweed, giant kelp and so on, and the amount of storage on the earth is extremely high. Besides, it possesses many ecofriendly properties including biocompatibility, non-toxic, non-pollution, hygroscopicity and viscosity, and thus has historically been widely used in food industry, medicine filed, tissue engineering and so on [23]. Moreover, porous carbon can be obtained from alginic acid carbonization during calcination process which shows a superior electrical conductivity [24]. In addition to above mentioned, percent content of carbon in molecule is higher than others organic carbon source such as glucose, oxalic acid, which is also an advantage to obtain high pure carbon. Thus, it is expected to present a great potential in electrochemistry. However, introducing alginic acid into $Li_2ZnTi_3O_8$ material is still no reports.

From a commercial viewpoint, solid-state reaction method exhibits a potential commercial application due to low synthesis cost and simple synthesis route. Therefore, in this paper, $Li_2ZnTi_3O_8$/C composites have been prepared using alginic acid as carbon source through high-energy ball-milling assisted solid-state reaction route, which features advantages of low energy consumption, convenient operation, and environment friendliness. All as-prepared samples of crystal structure, morphology and electrochemical property were systematically investigated. The results are very clearly demonstrated that the thin carbon layer on the outer-surface of $Li_2ZnTi_3O_8$ particles can improve rate performance effectively.

2. Experimental

2.1. Materials preparation

$Li_2ZnTi_3O_8$/C composites were prepared using TiO_2 (anatase, 20 nm), Li_2CO_3, $Zn(CH_3COO)_2·2H_2O$ and alginic acid (5, 10, 15 and 20 wt.%, which is weight ration of alginic acid to $Li_2ZnTi_3O_8$) as reagents (all reagents without further purification). All precursors were dispersed in anhydrous ethanol and ball-milled for 4 h in planetary ball mill, then transferred to a beaker and dried at 80 °C to evaporate ethanol. The obtained precursors were ground to powders at agate mortar and heated at 700 °C for 1 h and 800 °C for another 3 h in N_2 atmosphere, then cooled down to room temperature naturally, and the final black powders were obtained. As comparison, un-coated $Li_2ZnTi_3O_8$ was prepared without alginic acid by the same method in air.

2.2. Materials characterization

Structure characterization of carbon coated and un-coated $Li_2ZnTi_3O_8$ samples was performed by X-ray diffraction (XRD) with a Rigaku D/max 2550 VB+/PC instrument equipped with Cu Kα radiation in the range of 5–85° at a scan speed of 4° min^{-1}. The morphology of samples was observed by scanning electron microscope (SEM, Philips Quanta 200 instrument) and high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100F). The content of carbon was characterized by thermogravimetry (TG, TA instruments, Q1000DSC + LNCS + FACS Q600SDT). The powders' particle size and particle size distribution were identified by laser particle size analyzer (Beckman, Delsa Nano C).

2.3. Preparation of lithium-ion batteries

2032 coin-type cells were assembled to evaluate the electrochemical performance of samples. The cell was composed of working electrode, lithium metal electrode, separator and electrolyte. The working electrodes were prepared by mixing 80 wt.% the as-synthesized anode materials, 10 wt.% acetylene black and 10 wt.% polyvinylidene difluoride (PVDF). Metallic lithium foil was employed as the counter electrode. 1 mol L^{-1} $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1:1 in volume) was used as electrolyte, and polypropylene (Celgard 2300, Celgard Inc., USA) was used as the separator. The coin cells were assembled in an Argon-filled glove box and the water content in it was low than 10 ppm.

The galvanostatic charge/discharge experiments were operated on a LISUN-CBT-138-32 multichannel battery test system in the voltage range of 0.05–3.0 V at different current densities. Cyclic voltammetry (CV) tests were conducted on a GAMRY PC14-750 electrochemical workstation at a scanning rate of 0.5 mV s^{-1} from 0.05 to 3.0 V (vs. Li/Li^+). The electrochemical impedance spectroscopy (EIS) was measured by GAMRY PC14-750 in the frequency range from 10 mHz to 10 kHz. All the electrochemical performances were tested at constant temperature of 25 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of pristine $Li_2ZnTi_3O_8$ and carbon coated $Li_2ZnTi_3O_8$ composites. The diffraction peaks of all samples are indexed to cubic spinel structure of $Li_2ZnTi_3O_8$ (JCPDS#44-1037), demonstrating that the presence of carbon does not influence the structure of $Li_2ZnTi_3O_8$. It is clearly shown that no significant impurities peaks can be figured out through the XRD patterns. The absence of the peak of carbon is most likely due to the low content amorphous carbon. The absence of a new lithium titanium phase even at the high temperature of 800 °C suggests that the parent $Li_2ZnTi_3O_8$ is very stable under an inert atmosphere [7]. On the other hand, the intensity of diffraction peaks of $Li_2ZnTi_3O_8$/C composites is much lower than that of pure $Li_2ZnTi_3O_8$. As regards to this difference, it can be attributed to the carbon layer on the surface of active particles that can prevent the growth of $Li_2ZnTi_3O_8$ grains, consequently, which leads to poor crystallinity [15].

Fig. 2(a) shows the initial charge and discharge curves of $Li_2ZnTi_3O_8$ and $Li_2ZnTi_3O_8$/C electrodes which were measured ranging from 0.05 V to 3.0 V at a current density of 0.1 A g^{-1}. It can be clearly seen that the charge and discharge curves are similar in shape for the carbon coated and un-coated specimens, indicating that carbon does not change the electrochemical reaction process.
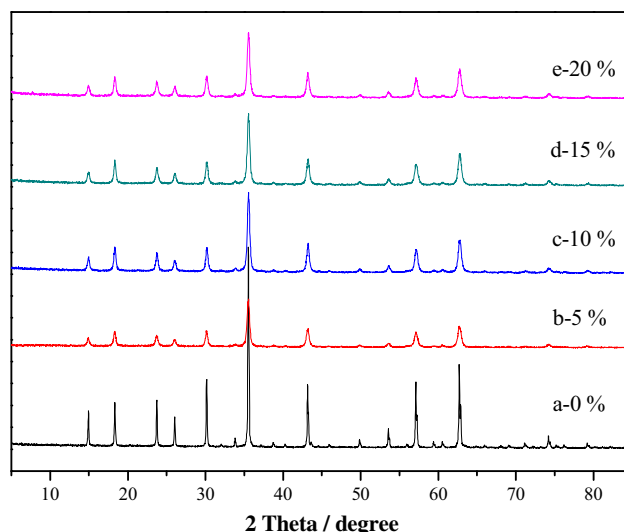

Fig. 1. XRD patterns of $Li_2ZnTi_3O_8$ and carbon-coated $Li_2ZnTi_3O_8$. (a) pristine; (b) 5 wt.%; (c) 10 wt.%; (d) 15 wt.%; (e) 20 wt.%.