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High rate capacity nanocomposite lanthanum oxide coated lithium zinc titanate anode for rechargeable lithium-ion battery

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ABSTRACT

Lithium zinc titanate ($Li_2ZnTi_3O_8$) is an important titanium material of promising candidates for anode materials with superior electrochemical performance and thus has attracted extensive attention. Herein, high capacity, stable $Li_2ZnTi_3O_8/La_2O_3$ nanocomposite for lithium-ion battery anode is prepared by a facile strategy. Compared to unmodified $Li_2ZnTi_3O_8$, the $Li_2ZnTi_3O_8/La_2O_3$ electrode display a high specific capacity of 188.6 mAh g^{-1} and remain as high as 147.7 mAh g^{-1} after 100 cycles at 2.0 A g^{-1}. Moreover, a reversible capacity of 76.3 mAh g^{-1} can be obtained after 1000 cycles at 2.0 A g^{-1} and the retention is 42.7% for $Li_2ZnTi_3O_8/La_2O_3$, which is much higher than un-coated $Li_2ZnTi_3O_8$. The superior lithium storage performances of the $Li_2ZnTi_3O_8/La_2O_3$ can be ascribed to the stable layer of protection, small particle size and large surface area. Cyclic voltammograms result reveals that the La_2O_3 coating layer reduces the polarization and improves the electrochemical activity of anode.

1. Introduction

Energy sources are of vital importance for the survival of mankind and the industrial production. With the rapid exhaustion of non-renewable fossil fuels (coal, crude oil) and aggravation of environment problems (greenhouse effect), the development of renewable and clean energy is become more and more important. However, some of kinds of natural resources could not continue to provide due to the weather conditions. For example, solar energy, wind energy and tidal energy. In order to make full use of energy from natural resources, a large-scale energy storage system which store unused electricity energy becomes extremely necessary to modulate intermittent renewable resources.

Lithium-ion battery first commercialization was achieved in 1991 and it has grown to become the dominant energy storage solution for portable information technology devices and industrial energy storage system [1–3]. As for energy storage performance of lithium-ion battery, electrochemical performance of cathode and anode electrode active material is of crucial importance. Graphite is mostly used as anode active material due to flat and low working potential, appropriate reversible capacity (372 mAh g^{-1}) and inexpensive. However, it still suffers from safety concerns that the growth of dendritic lithium on the surface of carbon anodes during reversible Li^+ intercalated and de-intercalated, which can pierce separator and cause explode [4]. To make breakthroughs in progress, a great deal of attention has been focused on developing new anode materials which provide high capacity, good cycling life and free from safety concerns.

Ti-based materials have been intensively investigated as alternative anode materials for lithium-ion batteries due to their high safety and excellent cycling performance. Spinel structure lithium zinc titanate ($Li_2ZnTi_3O_8$) anode material with a space group $P4_332$ has been studied manifesting a good cycle performance since the first used for lithium-ion batteries by Z. Hong etc. in 2010 [7]. The $Li_2ZnTi_3O_8$ has attracted much attention as an anode material for lithium-ion batteries due to low cost, non-toxicity, and lower discharge voltage plateau (0.5 V) [5,6]. However, $Li_2ZnTi_3O_8$ suffers from intrinsic drawbacks of low electronic conductivity and low ionic conductivity, which make it difficult for the Li^+ lithiation/delithiation processes, as well as electron transfer to active sites.

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The reason for this phenomenon is the 3d-states of Ti with a band-gap energy of 2–3 eV gives an insulating character to $Li_2ZnTi_3O_8$ [8]. On the other hand, the side reactions at the interface of electrode and electrolyte can change structure on the surface of active particles, which cause reversible capacities lose. Thus far, several effective ways, including carbon coating, particle size minimizing and guest ion doping, have already been proposed for improving the electronic conductivity and high rate electrochemical performance. Wang et al. [9] prepared carbon-coated $Li_2ZnTi_3O_8$ anodes using β-cyclodextrin as carbon source, and the optimal product has large capacities and presents good high rate capability. Li et al. [10] presented a facile one-step solution-combustion to prepared porous $Li_2ZnTi_3O_8$ flakes, which exhibited great cycling stability and high rate performance even at 2000 mA g^{-1}. Li et al. [11] doped Cu^{2+} into the Zn site in $Li_2ZnTi_3O_8$ via sol–gel method. The obtained products showed good cycle stability and rate capability, indicating doping guest ion is an effective modification method. Besides, synthetic products through different methods such as molten-salt method may be another way to improve the electrochemical performance [12].

Among different modification methods, surface modification has been proved to be a facile and effective approach to solve the above issues. Up to today, various oxides and phosphates have been used as coatings for different cathode and anode materials, such as TiO_2 [13], V_2O_5 [14], ZrO_2 [15,16], CeO_2 [17,18], La_2O_3 [19], ZnO [20], Y_2O_3 [21], $FePO_4/Li_3PO_4$ [22], $LaPO_4$ [23], $Co_3(PO_4)_2$ [24], YPO_4 [25], SiO_2 [26], Fe_2O_3 [27], $FePO_4$ [28], MgO [29], Al_2O_3 [30], $LiFePO_4$ [31] and $LiCoO_2$ [32]. These previous literatures have reported that the surface-modifications using inorganic materials are effective to enhance the cycling stability, high rate discharge capacity and thermal stability of electrodes system, confirming the several functions of nano coating layer such as the protection of active materials from HF attack, reduction of an increase in interfacial impedance, and pH environment control between the electrode and the electrolyte.

In this present work, the rare earth oxide La_2O_3 chosen as a protective layer because it can restrict the dissolution of the surface metal ions come from the active materials and suppress the side reaction. The $Li_2ZnTi_3O_8/La_2O_3$ composite anode material is prepared via a suspension mixing process followed by a solid-state reaction. To identify and understand the physical and electrochemical properties of as-prepared samples, various analytical techniques are employed. Electrochemical performance results show that the coating layer on the outer surface of $Li_2ZnTi_3O_8$ could reduce the reversible specific capacity loss and improve the cycling stability, cycling calendar life and high rate performance.

2. Experimental

2.1. Preparation of pristine $Li_2ZnTi_3O_8$

Pristine $Li_2ZnTi_3O_8$ anode material was prepared via a high-temperature solid-state reaction [33]. The stoichiometric amount of TiO_2 (99.5%, Aladdin Chemistry), Li_2CO_3 (99.0%, Aladdin Chemistry) and $Zn(CH_3COO)_2\cdot 2H_2O$ (99.0%, Aladdin Chemistry) were dispersed in anhydrous ethanol and ball-milled for 4 h in planetary ball mill, followed by drying at 80 °C for 12 h. The mash was then dried at 80 °C for 12 h in a medium vacuum atmosphere. Then the white powders were ground and heated in a muffle furnace at 800 °C for 5 h at a heating rate of 3 °C min^{-1} from room temperature in air.

2.2. Preparation of $Li_2ZnTi_3O_8/La_2O_3$ composite powders

For preparation of $Li_2ZnTi_3O_8/La_2O_3$ composite, a certain amount of $La(NO_3)_3\cdot 6H_2O$ was dispersed in deionized water followed by stirring. After that, the prepared $Li_2ZnTi_3O_8$ particles were added into above solution and thoroughly mixed well by a 1 h sonication followed by 12 h stirring. Then the mixture solution was dried at 80 °C for 12 h. Subsequently, the dry powder was heat treated at 600 °C for 5 h at a heating ramp of 3 °C min^{-1} in air.

2.3. Materials characterization

The crystalline phase of the prepared samples were studied by Powder X-ray diffraction (XRD, Rigaku D/max 2550 VB+/PC) was recorded in the range of 5–85° (2θ) equipped with Cu Kα radiation (λ = 0.154 nm, voltage 30 kV, current 40 mA). The microstructure characterization of the samples was analyzed using scanning electron microscope (SEM, Philips Quanta 200) and high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100F). The Brunauer–Emmett–Teller (BET) surface area measurements were carried out on a Bel Japan Belsorp-Max. Surface chemical composition and binding energy were analyzed by X-ray photo-electron spectroscopic (XPS, AXIS Ultra DLD, Kratos) employing a Al Ka excitation source.

2.4. Electrochemical measurements

Electrochemical performances of samples were studied employing 2032 coin type cells. Electrodes were prepared by mixing the as-synthesized anode active materials (80 wt%) with acetylene black (10 wt%) and polyvinylidene fluoride (PVDF) (10 wt %) in N-methyl-2-pyrrolidine (NMP) for electrochemical characterization. The obtained uniform slurry was daubed on copper foil. The electrodes were dried at 120 °C for 12 h. Metallic lithium foil was employed as the anode. 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 half-cells were assembled in an argon filled glove box. The electrochemical property was investigated using a LISUN-CBT-138-32 multichannel battery test system in the voltage range of 0.05–3.0 V (vs. Li/Li^+). Cyclic voltammetry (CV) tests were conducted on a GAMRY PC14-750 electrochemical workstation at a scanning rate of 0.5 mV s^{-1} in the voltage range of 0.05–3.0 V. The electrochemical impedance spectroscopy (EIS) was measured by GAMRY PC14-750 in the frequency range from 10 mHz to 10 kHz. All electrochemical performances were tested at constant temperature of 25 °C.

3. Results and discussion

$Li_2ZnTi_3O_8/La_2O_3$ composite was synthesized in a simple process using ex-situ coating, as described in the Experimental Section. XRD patterns for $Li_2ZnTi_3O_8$ and $Li_2ZnTi_3O_8/La_2O_3$ materials are presented in Fig. 1. The both as-prepared samples have a high crystallinity for the narrow diffraction peaks as shown in the XRD profiles. The two samples are well-defined cubic spinel structure with a space group of $P4_332$ ($Li_2ZnTi_3O_8$, JCPDS#44-1037). Moreover, except those of $Li_2ZnTi_3O_8$, no other peaks appeared such as La_2O_3, which is most likely due to the low content. Besides, there is no apparent shift of all peaks according to the standard patterns of $Li_2ZnTi_3O_8$. To be more specific, the lattice constants of all samples are shown in Table 1. The results show that the lattice constants of $Li_2ZnTi_3O_8$ are not changed after coating, which indicates that La_2O_3 do not diffused into lattice of spinel structure but are just coated on the outer surface of $Li_2ZnTi_3O_8$ particles. Furthermore, it also indicates that the subsequent annealing process has no influence on the basic spinel structure [26,34].

The microscopic particles surface topography of $Li_2ZnTi_3O_8$ and