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

Haoqing Tang ^{a, b, *}, Lingxing Zan ^c, Jiangtao Zhu ^b, Yiheng Ma ^b,

Naiqin Zhao ^a, Zhiyuan Tang ^{b, *}

^a School of Materials Science and Engineering, Tianjin University, Tianjin 300072,

PR China

^b Department of Applied Chemistry, School of Chemical Engineering and Technology,

Tianjin University, Tianjin 300072, PR China

^c Institute of Physical and Theoretical Chemistry, University of Bonn, 53117 Bonn,

Germany

* Corresponding author:

E-mail: tanghaoqing@tju.edu.cn (H.Q. Tang);

zytang46@163.com (Z.Y. Tang)

Abstract:

Lithium zinc titanate ($\text{Li}_2\text{ZnTi}_3\text{O}_8$) 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 $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ nanocomposite for lithium-ion battery anode is prepared by a facile strategy. Compared to unmodified $\text{Li}_2\text{ZnTi}_3\text{O}_8$, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ 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 $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$, which is much higher than un-coated $\text{Li}_2\text{ZnTi}_3\text{O}_8$. The superior lithium-storage performances of the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ 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.

Keywords: Lithium zinc titanate, Lanthanum oxide, Surface modification, Electrochemical performance

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 ($\text{Li}_2\text{ZnTi}_3\text{O}_8$) 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 $\text{Li}_2\text{ZnTi}_3\text{O}_8$ 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, $\text{Li}_2\text{ZnTi}_3\text{O}_8$ 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. 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 $\text{Li}_2\text{ZnTi}_3\text{O}_8$ [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 $\text{Li}_2\text{ZnTi}_3\text{O}_8$ 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 $\text{Li}_2\text{ZnTi}_3\text{O}_8$ 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 $\text{Li}_2\text{ZnTi}_3\text{O}_8$ 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], $\text{FePO}_4/\text{Li}_3\text{PO}_4$ [22], LaPO_4 [23], $\text{Co}_3(\text{PO}_4)_2$ [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 $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ 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 $\text{Li}_2\text{ZnTi}_3\text{O}_8$

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 $\text{Li}_2\text{ZnTi}_3\text{O}_8$

Pristine $\text{Li}_2\text{ZnTi}_3\text{O}_8$ 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 $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (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 $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite powders

For preparation of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite, a certain amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dispersed in deionized water followed by stirring. After that, the prepared $\text{Li}_2\text{ZnTi}_3\text{O}_8$ 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° (2 θ) equipped with Cu K α 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-pyrrolidone (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 LiPF₆ 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

Li₂ZnTi₃O₈/La₂O₃ composite was synthesized in a simple process using *ex-situ* coating, as described in the Experimental Section. XRD patterns for Li₂ZnTi₃O₈ and Li₂ZnTi₃O₈/La₂O₃ 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 P4₃32 (Li₂ZnTi₃O₈, JCPDS#44-1037). Moreover, except those of Li₂ZnTi₃O₈, no other peaks appeared such as La₂O₃, which is most likely due to the low content. Besides, there is no apparent shift of all peaks according to the standard patterns of Li₂ZnTi₃O₈. To be more specific, the lattice constants of all samples are shown in Table 1. The results show that the lattice constants of Li₂ZnTi₃O₈ are not changed after coating, which indicates that La₂O₃ do not diffused into lattice of spinel structure but are just coated on the outer surface of Li₂ZnTi₃O₈ 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 Li₂ZnTi₃O₈ and Li₂ZnTi₃O₈/La₂O₃ can be observed via SEM and the results are displayed in Fig. 2. Some intuitive characteristic information can be obtained from SEM images. First, the surface

morphology of bare $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (Fig. 2a) particles is the same as the coating sample, indicating that the pristine particles are not influenced by La_2O_3 coating layer. Second, the degree of particle agglomeration of coated sample (Fig. 2c) is apparently alleviated compared with un-coated sample. Third, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ is composed of more uniform particles with small size. The particle size of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite was smaller than pure sample due to the ex-situ coating process and the second calcinations process. The possible reason could be explained that the coating layer on the outer surface of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ could prevent the direct contact between primary particles and obtain the small particle size. At the same time, small particles could acquire large specific surface area which increases the contact area between active grains and organic electrolyte and lithium intercalation/de-intercalation sites. These are profitable to improve the electrochemical performance of electrodes. Moreover, the lower degree of particle agglomeration and smaller particle size are profitable to increase contact area between active material particles and electrolyte, and more active sites can be used, hence making the Li^+ intercalation/de-intercalation into/out electrode more efficient, which improve the electrochemical performance of lithium-ion batteries.

The surface area of prepared samples is determined by the nitrogen adsorption-desorption isotherms at 77 K, and the isotherm curves are displayed in Fig. 2 (b, d). The specific surface area, total pore volume (such pores were formed mainly from the stacking of particles) and average pore diameter of both samples are presented in Table 2. It can be seen, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ has a BET surface area of

10.26 m² g⁻¹, which is larger than that of pure Li₂ZnTi₃O₈ (8.23 m² g⁻¹), confirming the contribution of nanoparticles to the specific surface area. As seen in the insert of Fig. 2 (b, d), the total pore volume of Li₂ZnTi₃O₈/La₂O₃ is 0.0861 mL g⁻¹ and the average pore diameter is 33.566 nm. The increased pore volume and diameter may be ascribed to the gaps among the nanoparticles which produced in the second sintering process. The larger BET surface area and bigger pore are greatly increased the contact area between active particles and electrolyte, and facilitated the penetration of electrolyte for the promotion of Li⁺ diffusion. Moreover, the large size and volume of pores may provide wider transmission channels which allowed more Li⁺ simultaneously diffusion, and is favor to increase the Li⁺ storage capacity at large current densities.

The particle size distribution curves of Li₂ZnTi₃O₈/La₂O₃ composite and bare Li₂ZnTi₃O₈ are depicted in Fig. S2 (Supporting materials). From this figure, some useful information can be summarized three aspects: First, the average diameters of Li₂ZnTi₃O₈/La₂O₃ composite grains is approximately 0.9 μm, which smaller than that of 1.3 μm of pristine Li₂ZnTi₃O₈. Second, the differential intensity and peak width of Li₂ZnTi₃O₈/La₂O₃ composite are significantly higher and smaller than that of Li₂ZnTi₃O₈, indicating that the particle size distribution of Li₂ZnTi₃O₈/La₂O₃ composite is relatively concentrated. Third, the main particle size distribution peak of Li₂ZnTi₃O₈/La₂O₃ is smaller (1.1 μm) than that of Li₂ZnTi₃O₈ (1.6 μm). This obtained results can be ascribed to the effect of La₂O₃ coating later which can prevent secondary particle growth and agglomeration in calcination process. Smaller primary

and secondary particles will be advantageous to improve the high rates charge-discharge performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ electrode.

For detecting the existing elements and prove the homogeneity of La_2O_3 , energy dispersive spectroscopy (EDS) analysis is performed and the results are presented in Fig. 3. The elements of O, Ti, Zn and La in the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite have been detected from the EDS spectra. Moreover, the elemental mappings that the elements of surface coating layer are dispersed uniformly. The obtained results indicated that La_2O_3 is dispersed on the outer surface of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ active particles. More information of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ is provided in TEM images (Fig. 4). Before testing, the powder was ultrasonically dispersed in ethanol, and a few drops were coated on a copper grid for TEM characterization. From Fig. 4a, the particles of tested sample are contact with each other and have certain aggregation phenomenon. This appearance is the result of high temperature calcination process. In addition to this, particle packing voids formed during the process of material forming can be clearly seen from the image, which is beneficial to better contact between electrolyte and active particles and improve the electrochemical performance. The image of Fig. 4d clearly shows that a thin homogeneous La_2O_3 layer is coated on the surface of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ grains and its thickness is estimated to be ca. 1-2.5 nm. As depicted in Fig. 4d, the lattice fringe was approximately 0.489 nm, suggesting that $\text{Li}_2\text{ZnTi}_3\text{O}_8$ nanoparticles grew along the (001) direction. Moreover, the bulk crystallographic structure of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is not changed after the surface modification with La_2O_3 nano layer. In order to obtain the specific content of La_2O_3 in the composite, energy

dispersion spectroscopy (EDS) was conducted, as shown in Fig. S1. The results from EDS can corroborate that $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite include the elements of La and the weight percentage is about 3.05%. Besides, the elements of Zn, Ti, and O are detected and the contents of them are apparently higher than that of La.

In order to prove the formation of lanthanum oxide on the outer surface of core material, X-ray photo-electron spectroscopy (XPS) technique is employed to analyze the surface composition and the oxidation state of the elements in $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite grains. The XPS wide-spectrum of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite and pristine $\text{Li}_2\text{ZnTi}_3\text{O}_8$ samples is given in Fig. 5. It is clear that the signals of Zn 2p, Ti 2p, O 1s appear on the both samples and La 3d can be detected only on the outer surface of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite, suggesting that La_2O_3 coating remained on the surface of the core material. In Fig. 5 (a), two separate peaks at about 852.8 eV and 835.9 eV, attributed to the two spin orbits of $\text{La}3d_{5/2}$ and $\text{La}3d_{3/2}$, respectively [35-36]. Typical high-resolution XPS spectra of La 3d for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite acquired under the same conditions are shown in Fig. 5 (b). For the coated sample, either peak can be defined as a superposition of two Gaussian components. The obtained results are in accordance with Huang *et al.* report [37]. As a result, these characterization results indicate that the La_2O_3 -deposited $\text{Li}_2\text{ZnTi}_3\text{O}_8$ active particles are achieved by *ex situ* coating process.

Fig. 6 (a, b) reveals the initial charge-discharge curves of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ half-cell at 0.1 A g^{-1} , 0.5 A g^{-1} , 1.0 A g^{-1} between 0.05 V and 3.0 V, respectively. Similar charge-discharge profiles have been observed in both

as-prepared electrodes, indicating electrochemical reaction process did not change after coating [38]. In addition, the first cycle discharge capacities, charge-discharge platform voltages, and platform voltage difference for both samples are presented in Table 3. The initial specific discharge capacities of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ are 211.4 mAh g^{-1} , 176.1 mAh g^{-1} , 171.5 mAh g^{-1} at 0.1 A g^{-1} , 0.5 A g^{-1} , 1.0 A g^{-1} , respectively, which are higher than that of bare $\text{Li}_2\text{ZnTi}_3\text{O}_8$ sample. Compared with the theoretic capacity of 227 mAh g^{-1} [6], the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite has larger capacity which very closed to the theoretic capacity compared with the bare $\text{Li}_2\text{ZnTi}_3\text{O}_8$. Furthermore, the difference voltage platform of coated sample are 0.81 V, 0.86 V, 1.03 V at 0.1 A g^{-1} , 0.5 A g^{-1} , 1.0 A g^{-1} respectively, which are lower compared with un-coated sample. The values of difference voltage platform of coated sample is decreased means electrode polarization become smaller, which is beneficial to minish interface resistance and Li^+ reversible intercalation/de-intercalation. This may be due to the more stable protecting layer resulting from the La_2O_3 coating. Moreover, from the charge-discharge curves, an obvious discharge plateau is observed at 0.5-0.7 V and the other discharge plateau is observed at 1.2-1.4 V. Different discharge platform potential might be due to the internal structure of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$, which the octahedral sites are ordered into two sets with full occupancy by Ti and Li, respectively, while the tetrahedral sites would be occupied stably by Li-ion at a low potential. According to Chen *et al.* reports [39, 40], $[\text{Li}_{0.5}\text{Zn}_{0.5}]^{\text{tet}}[\text{Ti}_{1.5}\text{Li}_{0.5}]^{\text{oct}}\text{O}_4$ has multiple interstitials to accommodate three lithium ions during the lithiation process, in which the octahedral empty sites would be occupied by lithium ions at high

working potential (equation (1)) and the tetrahedral empty sites would be occupied by lithium ions at low working potential (equation (2)). The Li insertion mechanism of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is proposed can be expressed as [38, 41]:

Fig. 6 (c, d) shows the results of cycling performance at 2.0 and 3.0 A g^{-1} between the range of 0.05 V and 3.0 V for $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$, respectively, up to 100 cycles. As shown in Fig. 6 (c), the initial specific discharge capacities are 144.9 mAh g^{-1} , 188.6 mAh g^{-1} at 2.0 A g^{-1} , and 71.3 mAh g^{-1} , 147.7 mAh g^{-1} can be obtained after 100 cycles with capacity retention are 49.2%, 78.3% for $\text{Li}_2\text{ZnTi}_3\text{O}_8$, $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$, respectively. In addition, at 3.0 A g^{-1} , the initial and 100th cycle discharge capacities reach 154.0, 104.0 mAh g^{-1} and 148.2, 41.5 mAh g^{-1} for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrodes, respectively. Besides, the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ exhibits rapid capacity loss as the cycling rate increase, whereas the cycling stability is apparently improved after coating a layer of oxide. The reasons for increased capacities and enhanced cycle stability can be summarized as follows: (1) The coating layer can improve the electrical contact between the active particles and minish the interfacial impedance [31]; (2) The $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ has larger surface area, which endows the composite with more lithium storage sites and large electrode-electrolyte contact area for Li^+ flux across the interface [42]; (3) The holes which formed by accumulation of particles can help the outer surface of active particles make contact with electrolyte and shorten the diffusion distances of lithium ions; (4) The lithium

salt LiPF_6 can be reacted with water and produce a certain amount of HF due to the commercial LiPF_6 -based lithium battery electrolyte solution always contains a trace amount of water [9]. The produced HF would cause the dissolution of transition metal in the electrode and/or the surface erosion of the active materials, therefore leading to capacity decay upon charge-discharge cycling. However, the compacted coating layer can prevent $\text{Li}_2\text{ZnTi}_3\text{O}_8$ contact with HF and electrolyte, which avoid capacity loss and other side reactions.

Fig. 6 (e) reveals the long lifespan properties at a higher current density of 2.0 A g^{-1} . Obviously, the reversible discharge capacity began to decay from the 135th and the 39th cycle for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8$, respectively. After 1000 cycles, 76.3 mAh g^{-1} can be obtained for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$, much higher than that of pristine $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (37.9 mAh g^{-1}), and the retention rate is 42.7 % for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ but only 22.8 % for pristine $\text{Li}_2\text{ZnTi}_3\text{O}_8$ after 1000 cycles.

Cyclic voltammograms (CV) was carried out in order to investigate the effect of La_2O_3 coating in the electrochemical properties of $\text{Li}_2\text{ZnTi}_3\text{O}_8$. The CV profiles of coated and un-coated samples for the first three cycles at a scan rate of 0.5 mV s^{-1} in the voltage range of 0.05 V-3.0 V are shown in Fig. 7. All the as-prepared samples show that similar CV curves. The value of cathodic peak, anodic peak and difference between cathodic and anodic peaks are listed in Table 4. From charts, one pair of redox peaks appears between 1.0 V and 2.0 V in the first cycle for three samples, and the redox peaks shifts to high voltage from the second cycle. This might be related to the phase transition between spinel and rock salts [7]. Furthermore, it can be seen that

there is a pair of redox peaks for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ anode material in the second and the third cycles located at ca. 1.66/1.38 V and 1.67/1.41 V, which is related to $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple. Compared with the redox peaks of un-coated sample, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ electrode has lower polarization and this result indicating that Li^+ intercalation/de-intercalation into/out is highly reversible. On the other hand, a reduction peak lower 0.5 V is detected in both samples. This might be attributed to multiple restoration of Ti^{4+} , which is in good agreement with the previous reports by Borghols et al. and Ge et al. [43-44]. Furthermore, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ electrode has the highest peak current compared with others. It suggests that the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ electrode with has better kinetic characteristics.

Electrochemical impedance spectroscopy (EIS) of pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ electrodes were measured in the frequency range of 100 kHz to 10 mHz, and the results are shown in Fig. 8. Both samples present the similar EIS plots, which are consisted with a semicircle in the high frequency region and a straight line in the low frequency region. The semicircle in the high frequency region is mainly related to the complex reaction process over the electrolyte/electrode interface (e.g. charge transfer resistance and particle to particle contact resistance), while the straight line in the low frequency region is attributed to the diffusion of Li^+ into the bulk of electrode, namely the Warburg resistance [45]. In the equivalent circuit, R_s is solution and contact resistance, R_c is charge transfer resistance, CPE is constant phase element, and W means Warburg diffusion impedance. As reckoned from the impedance spectra data, the size of high frequency region semicircle of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ is

improvement. Such improvement may be associated with the improvement of the charge transfer process over the electrode surface, which can be contributed to smaller particle size and larger specific surface area of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ arising from La_2O_3 . In other words, smaller particle size and larger specific surface area result in shorter diffusion length for Li^+ and sufficient contact between the active materials and electrolyte, which is beneficial for the charge transfer process. Moreover, the slope in the low frequency region for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ is slightly greater than that of bare one, which is ascribed to the coating layer that can improve lithium ions migration in $\text{Li}_2\text{ZnTi}_3\text{O}_8$. The EIS data of both samples after discharge-charge cycling are shown in Fig. S3. The Nyquist plots are composed of two depressed semicircles in the high-frequency region and middle frequency region, which can be attributed to the resistance of SEI film and charge-transfer resistance at the interface between electrolyte and electrode. The $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite electrode not only shows lower solution/contact resistance but also exhibits lower charge transfer resistance than those of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode. Compared with the EIS data of fresh cells, the decrease of electrode impedance may be ascribed to the more ion transport and charge transfer sites created at the electrode and electrolyte interface during the long cycle process.

To study the rate capability of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite and bare $\text{Li}_2\text{ZnTi}_3\text{O}_8$, the assembled coin half-cells were discharged and charged at different scan rates, with the results shown in Fig. 8. As can be seen, a specific discharge capacity of 222.9 mAh g^{-1} and 207.9 mAh g^{-1} are obtained for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite and bare

$\text{Li}_2\text{ZnTi}_3\text{O}_8$ at 0.1 A g^{-1} after 10 charge/discharge cycles. Moreover, at higher current density of 3.0 A g^{-1} , 149.3 mAh g^{-1} and 116.9 mAh g^{-1} can be obtained at the 10th cycle for both samples, respectively. When the current rate goes down again to 0.1 A g^{-1} , the capacity of 203.3 mAh g^{-1} and 190.2 mAh g^{-1} could be regained for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite and bare $\text{Li}_2\text{ZnTi}_3\text{O}_8$ at the first cycle. From what has been obtained above, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite has good lithium intercalation and lithium de-intercalation performance. Besides, the cycling performance indicates that modified $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode has excellent cycling stability even after rather harsh loading and de-loading rates. In addition, the Coulombic efficiency of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite is higher than 99.0 % from 0.1 A g^{-1} to 3.0 A g^{-1} , and is higher than 97.0 % when back to 0.1 A g^{-1} , which shows the coating sample has little capacity loss in all different rates. This phenomenon is owing to the intrinsic characteristic of a three dimensional pathway for Li^+ intercalation and de-intercalation in the crystal structure of $\text{Li}_2\text{ZnTi}_3\text{O}_8$, which is beneficial to high rate performance. In a word, all the evidences demonstrate that the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite could be a promising anode material with high rate capability, good cycling stability and long lifespan performance.

4. Conclusions

In this paper, $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite was successful prepared. Coating a thin layer of inactive oxide on the surface of pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is regarded a facile method for improving the high rate performance. The as-prepared composites are

characterized by XRD, SEM, TEM, EDS and BET techniques. At high current densities of 2.0 and 3.0 A g⁻¹, the Li₂ZnTi₃O₈/La₂O₃ delivers larger initial specific discharge capacity of 188.6 and 154.0 mAh g⁻¹, 147.7 and 104.0 mAh g⁻¹ can be obtained after 100 cycles between 0.05 V and 3.0 V at room temperature, which are higher than that un-coated sample. CV and EIS show that the coated sample have superior electrochemical performance compared with un-coated sample. These properties make Li₂ZnTi₃O₈/La₂O₃ composite to be a promising anode material, and this technique provides an effective and convenient way for improving the high rates capacities.

Acknowledgments

This work was supported by National Science Foundation of China (Grant No. 20973124).

References

- [1] M. Armand, J.M. Tarascon, Building better batteries, Nature 451 (2008) 652-657.
- [2] B. Dunn, H. Kamath, J.M. Tarascon, Electrical energy storage for the grid: a battery of choices, Science 334 (2011) 928-935.
- [3] H. Li, Z.X. Wang, L.Q. Chen, X.J. Huang, Research on advanced materials for Li-ion batteries, Adv. Mater. 21(2009) 4593-4607.
- [4] Q.Y. Zhang, C.L. Zhang, B. Li, D.D. Jiang, S.F. Kang, Preparation and characterization of W-doped Li₄Ti₅O₁₂ anode material for enhancing the high rate

performance, *Electrochim. Acta* 107 (2013) 139-146.

[5] Z.S. Hong, X.Z. Zheng, X.K. Ding, L.L. Jiang, M.D. Wei, K.M. Wei, *Complex spinel titanate nanowires for a high rate lithium-ion batteries*, *Energy Environ. Sci.* 4 (2011) 1886-1891.

[6] L. Wang, L.J. Wu, Z.H. Li, G.T. Lei, Q.Z. Xiao, P. Zhang, *Synthesis and electrochemical properties of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ fibers as an anode material for lithium-ion batteries*, *Electrochim. Acta* 56 (2011) 5343-5346.

[7] Z.S. Hong, M. D. Wei, X.K. Ding, L.L. Jiang, K.M. Wei, *$\text{Li}_2\text{ZnTi}_3\text{O}_8$ nanorods: A new anode material for lithium-ion battery*, *Electrochem. Commun.* 12 (2010) 720-723.

[8] T.F. Yi, J. Shu, Y.R. Zhu, X.D. Zhu, C.B. Yue, *High-performance $\text{Li}_4\text{Ti}_{5-x}\text{V}_x\text{O}_{12}$ ($0 \leq x \leq 0.3$) as an anode material for secondary lithium-ion battery*, *Electrochim. Acta* 54 (2009) 7464-7470.

[9] L.J. Wang, B.K. Chen, Z.H. Meng, B.M. Luo, X.J. Wang, Y.Y. Zhao, *High performance carbon-coated lithium zinc titanate as an anode material for lithium-ion batteries*, *Electrochim. Acta* 188 (2016) 135-144.

[10] X. Li, Q. Xiao, B. Liu, H.C. Lin, J.B. Zhao, *One-step solution-combustion synthesis of complex spinel titanate flake particles with enhanced lithium-storage properties*, *J. Power Sources* 273 (2015) 128-135.

[11] Y.Y. Li, C.Q. Du, J. Liu, F. Zhang, Q. Xu, D.Y. Qu, X.H. Zhang, Z.Y. Tang, *Synthesis and characterization of $\text{Li}_2\text{Zn}_{0.6}\text{Cu}_{0.4}\text{Ti}_3\text{O}_8$ anode material via a sol-gel method*, *Electrochim. Acta* 167 (2015) 201-206.

- [12] B.K. Chen, C.J. Du, Y.Z. Zhang, R.X. Sun, L. Zhou, L.J. Wang, A new strategy for synthesis of lithium zinc titanate as an anode material for lithium ion batteries, *Electrochim. Acta* 159 (2015) 102-110.
- [13] S.J. Kim, M.C. Kim, D.H. Kwak, D.M. Kim, G.H. Lee, H.S. Choe, K.W. Park, Highly stable TiO_2 coated Li_2MnO_3 cathode materials for lithium-ion batteries, *J. Power Sources* 304 (2016) 119-127.
- [14] J. Wang, S.Z. Yao, W.Q. Lin, B.H. Wu, X.Y. He, J.Y. Li, J.B. Zhao, Improving the electrochemical properties of high-voltage lithium nickel manganese oxide by surface coating with vanadium oxides for lithium ion batteries, *J. Power Sources* 280 (2015) 114-124.
- [15] J.Z. Kong, S.S. Wang, G.A. Tai, L. Zhu, L.G. Wang, H.F. Zhai, D. Wu, A.D. Li, H. Li, Enhanced electrochemical performance of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode material by ultrathin ZrO_2 coating, *J. Alloys Compd.* 657 (2016) 593-600.
- [16] S.K. Hu, G.H. Cheng, M.Y. Cheng, B.J. Hwang, R. Santhanam, Cycle life improvement of ZrO_2 -coated spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material for lithium ion batteries, *J. Power Sources* 188 (2009) 564-569.
- [17] T.F. Yi, J.Z. Wu, M. Li, Y.R. Zhu, Y. Xie, R.S. Zhu, Enhanced fast charge-discharge performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode materials for lithium-ion batteries by Ce and CeO_2 modification using a facile method, *RSC Adv.* 5 (2015) 37367-37376.

- [18] M. Sivakumar, R. Muruganantham, R. Subadevi, Investigations on the rate performance of $\text{LiFePO}_4/\text{CeO}_2$ composite materials via polyol technique for rechargeable lithium batteries, *RSC Adv.* 5 (2015) 86126-86136.
- [19] L.J. Feng, S.P. Wang, L. Han, X.Y. Qin, H.Y. Wei, Y.Z. Yang, Enhanced electrochemical properties of LiMn_2O_4 cathode material coated by 5 wt.% of nano- La_2O_3 , *Mater. Lett.* 78 (2012) 116-119.
- [20] Y.K. S, K.J. Hong, J. Prakash, K. Amine, Electrochemical performance of nano-sized ZnO-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel as 5 V materials at elevated temperatures, *Electrochem. Commun.* 4 (2002) 344-348.
- [21] F. Wu, M. Wang, Y.F. Su, S. Chen, Surface modification of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with Y_2O_3 for lithium-ion battery, *J. Power Sources* 189 (2009) 743-747.
- [22] F. Wu, X.X. Zhang, T.L. Zhao, L. Li, M. Xie, R.J. Chen, Surface modification of a cobalt-free layered $\text{Li}[\text{Li}_{0.2}\text{Fe}_{0.1}\text{Ni}_{0.15}\text{Mn}_{0.55}]\text{O}_2$ oxide with the $\text{FePO}_4/\text{Li}_3\text{PO}_4$ composite as the cathode for lithium-ion batteries, *J. Mater. Chem. A* 3 (2015) 9528-9537.
- [23] Q.L. Xie, C.H. Zhao, Z.B. Hu, Q. Huang, C. Chen, K.Y. Liu, LaPO_4 -coated $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$ as a cathode material with enhanced coulombic efficiency and rate capability for lithium ion batteries, *RSC Adv.* 5 (2015) 77324-77331.
- [24] X.Y. Feng, J.X. Zhang, L.W. Yin, Enhanced cycling stability of $\text{Co}_3(\text{PO}_4)_2$ -coated LiMn_2O_4 cathode materials for lithium ion batteries, *Powder Technology* 287 (2016) 77-81.

- [25] Y. Bai, Q.J. Chang, Q. Yu, S. Zhao, K. Jiang, A novel approach to improve the electrochemical performances of layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode by YPO_4 surface coating, *Electrochim. Acta* 112 (2009) 414-421.
- [26] Y.D. Li, S.X. Zhao, C.W. Nan, B.H. Li, Electrochemical performance of SiO_2 -coated LiFePO_4 cathode materials for lithium ion battery, *J. Alloys Compd.* 509 (2011) 957-960.
- [27] Q. Hao, C.X. Xu, S.Z. Jia, X.Y. Zhao, Improving the cycling stability of LiCoO_2 at 4.5 V through surface modification by Fe_2O_3 coating, *Electrochim. Acta* 113 (2013) 439-445.
- [28] Y.S. Shang, J.L. Liu, T. Huang, A.S. Yu, Effect of heat treatment on the structure and electrochemical performance of FePO_4 coated spinel LiMn_2O_4 , *Electrochim. Acta* 113 (2013) 248-255.
- [29] S.J. Shi, J.P. Tu, Y.Y. Tang, X.Y. Liu, Y.Q. Zhang, X.L. Wang, C.D. Gu, Enhanced cycling stability of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ by surface modification of MgO with melting impregnation method, *Electrochim. Acta* 88 (2013) 671-679.
- [30] B. Huang, X.H. Li, Z.X. Wang, H.J. Guo, X.H. Xiong, J.X. Wang, A novel carbamide-assistant hydrothermal process for coating Al_2O_3 onto $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles used for cathode material of lithium-ion batteries, *J. Alloys Compd.* 583 (2014) 313-319.
- [31] I.C. Jang, H.H. Lim, S.B. Lee, K. Karthikeyan, V. Aravindan, K.S. Kang, W.S. Yoon, W.I. Cho, Y.S. Lee, Preparation of LiCoPO_4 and LiFePO_4 coated LiCoPO_4 materials with improved battery performance, *J. Alloys Compd.* 497 (2014) 321-324.

- [32] W.M. Liu, G.R. Hu, K. Du, Z.D. Peng, Y.B. Cao, Surface coating of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ with LiCoO_2 by a molten salt method, *Surf. Coat. Technol.* 216 (2013) 267-272.
- [33] H.Q. Tang, Z.Y. Tang, C.Q. Du, F.C. Qie, J.T. Zhu, Ag-doped $\text{Li}_2\text{ZnTi}_3\text{O}_8$ as a high rate anode material for rechargeable lithium-ion batteries, *Electrochim. Acta* 120 (2014) 187-192.
- [34] B.W. Ju, X.Y. Wang, C. Wu, X.K. Yang, H.B. Shu, Y.S. Bai, W.C. Wen, X. Yi, Electrochemical performance of the graphene/ Y_2O_3 / LiMn_2O_4 hybrid as cathode for lithium-ion battery, *J. Alloys Compd.* 584 (2014) 454-460.
- [35] G.T.K. Fey, P. Muralidharan, C.Zh Lu, Y.Da Cho, Enhanced electrochemical performance and thermal stability of La_2O_3 -coated LiCoO_2 , *Electrochim. Acta* 51 (2006) 4850-4858.
- [36] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Mullenberg, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie 1979, MN55344.
- [37] Y.L. Huang, W.L. Zhu, X.Q. Feng, Z.Y. Man, The effects of La^{3+} doping on luminescence properties of PbWO_4 single crystal, *J. Solid State Chem.* 172 (2003) 188-193.
- [38] Y. Huang, F.M. Jin, F.J. Chen, L. Chen, Improved cycle stability and high-rate capability of Li_3VO_4 -coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cathode material under different voltages, *J. Power Sources* 256 (2014) 1-7.
- [39] W. Chen, Z.R. Zhou, R.R. Wang, Z.T. Wu, H.F. Liang, L.Y. Shao, J. Shu, Z.C.

Wang, High performance Na-doped lithium zinc titanate as anode material for Li-ion batteries, *RSC Adv.* 5 (2015) 49890-49898.

[40] W. Chen, R.H. Du, H.F. Liang, Z.R. Zhou, L.Y. Shao, J. Shu, Z.C. Wang, Lithium storage behavior of manganese based complex spinel titanate as anode material for Li-ion batteries, *J. Power Sources* 272 (2014) 622-628.

[41] Y.X. Xu, Z.S. Hong, L.C. Xia, J. Yang, M.D. Wei, One step sol-gel synthesis of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ nanocomposite with enhanced lithium-ion storage properties, *Electrochim. Acta* 88 (2013) 74-78.

[42] Z.Y. Wang, L. Zhou, X.W. Lou, Metal oxide hollow nanostructures for Lithium-ion batteries, *Adv. Mater.* 24 (2012) 1903-1911.

[43] X.Z. Liu, P. He, H.Q. Li, M. Ishida, H.S. Zhou, Improvement of electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ by coating with V_2O_5 layer, *J. Alloys Compd.* 552 (2013) 76-82.

[44] W.J.H. Borghols, M. Wagemaker, U. Lafont, E.M. Kelde, F.M. Mulder, Size Effects in the $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ Spinel, *J. Am. Chem. Soc.* 131 (2009) 17786-17792.

[45] H. Ge, N. Li, D. Li, C. Dai, D. Wang, Electrochemical characteristics of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ discharged to 0.01 V, *Electrochem. Commun.* 10 (2008) 719-722.

Table 1 Lattice parameters for $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$, respectively.

Sample	Lattice constant ($\text{\AA}$) a	Volume of unit ($\text{\AA}^3$)	Space group	R_w (%)
$\text{Li}_2\text{ZnTi}_3\text{O}_8$	8.3737	587.154	$P4_332$	5.97
$\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$	8.3731	587.028	$P4_332$	5.23

Table 2 Specific surface areas, total pore volumes and average pore diameter of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ powders.

Samples	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume (mL g^{-1})	Average pore diameter (nm)	Correlation coefficient
$\text{Li}_2\text{ZnTi}_3\text{O}_8$	8.23	0.0635	30.525	0.9995
$\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$	10.26	0.0861	33.566	0.9997

Table 3 The initial discharge capacities and platform voltages for $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$, respectively.

Samples	$\text{Li}_2\text{ZnTi}_3\text{O}_8$			$\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$		
Current densities (A/g)	0.1	0.5	1.0	0.1	0.5	1.0
Charge platform voltage (V)	1.39	1.47	1.61	1.38	1.43	1.50
Discharge platform voltage (V)	0.49	0.59	0.51	0.57	0.57	0.47
Difference platform voltage (V)	0.90	0.88	1.10	0.81	0.86	1.03
Initial discharge capacities (mAh/g)	200.4	162.5	145.2	211.4	176.1	171.5

Table 4 The value of cathodic peak and anodic peak for $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$.

	$\text{Li}_2\text{ZnTi}_3\text{O}_8$			$\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$		
	1st	2nd	3rd	1st	2nd	3rd
φ_{pa} (V)	1.59	1.67	1.67	1.58	1.66	1.67
φ_{pc} (V)	1.09	1.36	1.37	1.24	1.38	1.41
φ_p (V) = $\varphi_{pa} - \varphi_{pc}$	0.50	0.31	0.30	0.34	0.28	0.26

List of Figures:

Fig. 1 XRD patterns of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$, respectively.

Fig. 2 SEM images of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ (a, c). BET curves and pore size of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ (b, d).

Fig. 3 EDS spectrum and EDS element maps of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ particles.

Fig. 4 TEM images of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ at different amplifications.

Fig. 5 (a) XPS wide-scan spectra of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$. (b) High-resolution XPS spectra of La 3d in $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$.

Fig. 6 Initial charge-discharge curves of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (a) and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ (b) at 0.1, 0.5, and 1.0 A g^{-1} , respectively. Discharge capacities of pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ between the range of 0.05 V and 3.0 V at rates of 2.0 and 3.0 A g^{-1} (c-d), respectively. The long cycle life performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ at 2.0 A g^{-1} (e).

Fig. 7 CV curves of pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (a) and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ (b) in half cell assembly recorded between 0.05 and 3.0 V vs Li at scan rate of 0.5 mV s^{-1} , in which metallic lithium acts as both counter and reference electrode.

Fig. 8 EIS curves of pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ electrodes, respectively. Charge/discharge capacity and coulombic efficiency of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{La}_2\text{O}_3$ composite and pristine $\text{Li}_2\text{ZnTi}_3\text{O}_8$ at different current densities (0.1, 1.0, 2.0, 3.0 A g^{-1} and back to 0.1 A g^{-1}).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8