**Long cycle life of carbon coated lithium zinc titanate using copper as conductive
additive for lithium ion batteries**

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Abstract

High conductivity pristine copper particles and carbon coated $\text{Li}_2\text{ZnTi}_3\text{O}_8$ composite ($\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$) is prepared by one-step sol-gel method followed by high temperature pyrolysis. Amorphous carbon coating layer reveals a thickness of 2.0-8.0 nm on the outer surface of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ active grains, which improves the electronic conductivity and charge transfer rate of primary and secondary particles. Moreover, copper particles between particles could enhance the electronic transmission at large current densities and decrease diffusion resistance. As a result, $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite shows lower electrochemical polarization and quicker kinetic behavior compared to $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$. Cycled at 1000 mA g^{-1} , 2000 mA g^{-1} , and 3000 mA g^{-1} , $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ can deliver a reversible capacity of 124.4 mAh g^{-1} , 90.8 mAh g^{-1} , and 79.1 mAh g^{-1} after 1000 cycles, which is much higher than the values of 70.7 mAh g^{-1} , 75.5 mAh g^{-1} , and 52.1 mAh g^{-1} obtained by $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$. In addition to higher specific capacity, electrode polarization and cycle stability have been improved after adding copper particles. The improved electrochemical properties of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite are attributed to the combination of copper additive and carbon layer.

Key words: Lithium-ion battery; Copper; Amorphous carbon; Electrochemical properties

1. Introduction

Rechargeable lithium ion batteries have already been achieving great success in mobile phones, power laptop computers and electric vehicles with high energy density and long cycling lifespan [1-3]. In the present commercialized lithium ion batteries, carbonaceous materials are widely employed as anode materials due to its low cost, acceptable storage capacity ($\sim 372 \text{ mAh g}^{-1}$), small volume expansion and good cycling stability. However, the low lithium ion storage potential of carbon-based materials raises serious safety problems: a dendritic structure can be formed on the surface of anode active material particles during the multiple lithium intercalation/de-intercalation at high current rate or overcharged, which cause a short circuit inside the battery and the short circuit of the battery to fire the flammable electrolyte [4-5]. To address the unsafe problem and meet the ever-increasing performance demands, searching for new anode active materials with high security and large capacity is urgent in developing the next-generation lithium ion batteries. Up to present, in addition to carbonaceous materials, different new types of anode materials such as metallic oxide [6-8], alloy compound [9-11] and titanium matrix composites [12-14] have been successful prepared and provided with good electrochemical performance.

As an alternative anode active material for lithium ion batteries, cubic spinel $\text{Li}_2\text{ZnTi}_3\text{O}_8$ has attracted considerable attention due to its low cost, non-toxicity, lower discharge voltage plateau (0.5-0.8 V vs. Li/Li^+) [15-16] and high discharge capacity. However, the prominent disadvantage of untreated pristine $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is inferior high

rate performance due to its intrinsic low electrical conductivity, which limits its application in rechargeable lithium ion batteries. In addition to this, compared with the graphite, the low energy density has also limited its widespread application. To solve this problem, various strategies have been exploited, i) synthesis of nanoparticles [17-19], ii) coating a thin carbon layer on the outer surface of active particles [20-22], and iii) doping guest metal or non-metal ions [23-25]. Among them, preparing nanoscale active particles could obtain high specific surface area which shorten the transmission distance of Li^+ , increase the contact area between active grains and electrolyte, and acquire more active sites; Coating a thickness of nanometer conductive carbon layer on the outer surface of active particles is an effective method which could improve the electron conductivity between particles and increase charge/discharge capacity at high current; Doping guest metal or nonmetal ions into crystal is propitious to improve the electron conductivity in active particles because vacancy of atomic site and dislocation are generated.

According to the Trendafilova *et al.* and Chen *et al.* reports [26, 27], the crystal structure of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ can be described as $(\text{Li}_{0.5}\text{Zn}_{0.5})^{\text{tet}}[\text{Li}_{0.5}\text{Ti}_{1.5}]^{\text{oct}}\text{O}_4$, which can form a stable frame built by LiO_6 and TiO_6 octahedrons during the repeated Li^+ insertion and de-insertion. Besides, all of Zn ions are located at 8c tetrahedral sites, and 12d and 4b octahedral sites are occupied by 1 : 3 cation ordering of Li : Ti. Thus, a three dimensional network is formed which can provide diffusion routes and be propitious to the Li^+ reversible intercalation and de-intercalation during the discharge and charge process. In the galvanostatic discharge process,

($\text{Li}_{0.5}\text{Zn}_{0.5}$)^{tet}[$\text{Li}_{0.5}\text{Ti}_{1.5}$]^{oct}O₄ has multiple interstitials to accommodate three Li⁺, in which the octahedral and the tetrahedral empty sites would be occupied by Li⁺ at high working potential and low working potential, respectively [28].

In this paper, for the first time, copper particles as conductive particles were used to modify the $\text{Li}_2\text{ZnTi}_3\text{O}_8$. According to the existing literatures, copper is one of the most widely used doping metals for electrode active materials due to its inherent high conductivity. It was reported that mixing copper with electrode active materials via diverse ways could greatly enhance the electronic conductivity as well as improve the high rates cycling performance [29-32]. In this article, the target product copper modified $\text{Li}_2\text{ZnTi}_3\text{O}_8$ ($\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$) is prepared via a facile sol-gel method followed by high temperature calcination in the vacuum tube furnace. The as-synthesized $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite has excellent electronic conductivity due to the carbon layer on the outer surface of active particles and the copper atoms between the particles of bulk, which can significantly facilitate the kinetics of electron transport and improve the charge-discharge capacities at high current densities.

2. Experimental

2.1 Materials preparation

$\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite was prepared by a facile sol-gel method. Stoichiometric amounts of $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ (1.4483 g) and $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ (0.6219 g) were dissolved in ethanol with continued magnetic stirring. Then 1.7862 g of citric acid was added above solution. Finally, 2.8931 g of tetrabutyl titanate

[Ti(OC₄H₉)₄] was added to the above solution drop wise. The mole ratio of Li:Zn:Ti:citric acid = 1:0.5:1.5:1. The white solution turned buff after stirring it for 5 min. After forming the light yellow mixing solution, 0.05 g of pure copper particles was added into the mixing solution and stirred for 2-3 hours at room temperature. The temperature of the solution was raised to 80 °C and stirred continuously to form the gel. Afterwards, the gel was dried at 80 °C for 12 h in air dry oven. The precursor was decomposed at high temperature calcination for some hours in pipe furnace (Argon atmosphere). Last, the obtained dry powders were ground in agate mortar.

2.2 Materials characterization

Structure characterization of Li₂ZnTi₃O₈/C@Cu composites and pure Li₂ZnTi₃O₈ samples was performed by X-ray diffraction (XRD) with a Rigaku D/max 2550 VB+/PC instrument equipped with Cu K α 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).

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 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 coin cells were assembled in an Argon-filled glove box and the water content in it was low than 1 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

The galvanostatic cycling performance of as-prepared $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composites electrodes have been investigated within the potential window 0.05-3.0 V. The content of the copper in composite has influence the electrochemical performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$. Fig. S1 (Supporting information) shows the cycling performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ at 1000 mA g^{-1} , 2000 mA g^{-1} , 3000 mA g^{-1} with different content of copper (0.5%, 1.0%, 1.5%, 2.0%) in composite. By comparison, the 1.0% copper in $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ material has the largest discharge capacities at different current densities, indicating the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ -1.0% has the highest electronic conductivity in all prepared samples. Therefore, this research article focuses on the 1.0% copper in $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ composite which includes different physical characterization and electrochemical testing.

The phase purity and crystal structure of the products were characterized by X-ray powder diffraction (XRD). Fig. 1 shows the XRD patterns of the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$. The diffraction peaks of both samples located at 15.1° , 18.2° , 23.8° , 26.1° , 30.2° , 34.0° , 35.6° , 43.3° , 49.9° , 53.7° , 57.2° , 62.9° and 74.4° can be attributed to the (110), (111), (210), (211), (220), (310), (113), (004), (421), (422), (115), (404) and (335) faces of cubic spinel $\text{Li}_2\text{ZnTi}_3\text{O}_8$ with a space group of $\text{P4}_3\text{32}$, which is in good agreement with JCPDS, no. 44-1037 [33]. The both as-prepared samples have a high crystallinity for the narrow diffraction peaks as shown in the XRD profiles. Moreover, except those of $\text{Li}_2\text{ZnTi}_3\text{O}_8$, no other peaks appeared such as copper and carbon can be seen in the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite, which is most likely due to the low content and amorphous state. Besides, there is no apparent shift of all peaks according to the standard patterns of $\text{Li}_2\text{ZnTi}_3\text{O}_8$. To be more specific, the lattice constant of a for $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ are $8.3739 \text{ \AA}$ and $8.3741 \text{ \AA}$. The results show that the lattice constants of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ are not changed after coating carbon layer and adding copper particles.

The low magnification SEM images of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite are presented in Fig. 2. From image (a) it can be seen that the secondary particles size of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ particles are 100-200 nm, and some of them aggregated together. Compared with $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ grains, the surface topography and particle size of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite (image (b)) have not been changed after adding object substances. For further studying the micromorphology and microstructure of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite, TEM images are characterized and shown in Fig. 2

(c-d). The sample was ultrasonically dispersed in ethanol, and a few drops were coated on a copper grid for TEM characterization. As seen, these accumulation nanoparticles are composed of a large number of small particles with a mean size of about 15-20 nm. From image of Fig. 2 (c), around each particle is surrounded with amorphous carbon which comes from high temperature carbonization of organic compounds. The obtained amorphous carbon coated electroactive material could improve electron conductivity between nanoparticles in agglomeration particles, which is advantageous to improve high rate performance. In addition, the thickness of the carbon layer on the outer surface of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is estimated to be ca. 2.0-8.0 nm. Moreover, the lattice fringe of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ can be clearly seen from images (d), which demonstrate the composite is crystalline state. The carbon coating layer could provide faster pathways for electron transfer, facilitating the electronic connection among $\text{Li}_2\text{ZnTi}_3\text{O}_8$ particles; this is favor to the rate capability improvement.

Fig. 2 (e) and Fig. 2 (f) display the N_2 adsorption-desorption isotherm curves of the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite and carbon coated $\text{Li}_2\text{ZnTi}_3\text{O}_8$. The Brunauer-Emmett-Teller (BET) surface area of the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite is calculated to be $44.01 \text{ m}^2 \text{ g}^{-1}$, which is larger than that of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ ($38.07 \text{ m}^2 \text{ g}^{-1}$). It indicates that the copper particles in composite with a high specific surface area. The Barrett-Joyner-Halenda (BJH) pore size distribution curves reveal the average particle size of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ are 8.43 nm and 7.36 nm, respectively. In addition, the pore volume of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ is calculated to be $0.082 \text{ cm}^3 \text{ g}^{-1}$, which slightly larger than that of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ ($0.080 \text{ cm}^3 \text{ g}^{-1}$). The

1 relatively high surface area, small secondary particles and porous structure of
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3 $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ have advantages for electrolyte diffusion and provide more active
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5 sites for redox reactions, hence leading to the enhance electrochemical performance at
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7 high charge-discharge rates.
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11 The EDX image of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite is presented in Fig. 3. The
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13 elements of Ti, Zn, O, and Cu have been detected, indicating that the Cu particles and
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15 carbon layer have been successfully combined with bare $\text{Li}_2\text{ZnTi}_3\text{O}_8$. Meanwhile,
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17 EDS elemental mapping demonstrates clearly the presence of Zn, O, Ti and Cu
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19 elements in the product, suggesting the successful preparation of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$
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21 composite.
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28 The galvanostatic charge-discharge curves of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$
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30 at the current density of 100 mA g^{-1} between 0.05 and 3.0 V (vs. Li/Li^+) are shown in
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32 Fig. 4 (a). Two samples show similar discharge and charge plateaus, indicating the
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34 mechanism of lithium intercalation/de-intercalation is not affected. The
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36 $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ sample delivers the first discharge capacity of 526.6 mAh g^{-1} ,
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38 higher than 373.8 mAh g^{-1} for the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ sample. The possible reasons for the
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40 higher initial capacity of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ sample can be summarized as the
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42 following: the copper particles in the active particles could increase the electronic
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44 contact area and improve the transmission speed of the electron; copper oxide being
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46 reduced at the first reduction; larger interface contact area and smaller particle size
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48 which could provide more lithium-intercalation active sites. Moreover, the difference
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50 voltage between charge and discharge platform are 0.80 V and 0.68 V for
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1 $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$, indicating the latter specimen has smaller
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3 polarization.
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6 The charge-discharge profiles of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ between
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8 0.05 and 3.0 V and the corresponding differential capacities vs. voltage plots are
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10 shown in Fig. 4 (b). During the first charge-discharge cycle, both the working
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12 electrodes exhibit one couple of dQ/dV peak and one more peak below 0.8 V (vs.
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14 Li/Li^+). The peak at 1.41 V is ascribed to the extraction of Li^+ , while the peak at 1.17
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16 V is intercalation of Li^+ . ΔV is representative of the kinetic process, especially
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18 considering that the electrochemical process involves lithium diffusion in a solid
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20 phase and electron jumping across the electrode materials [34]. According to the first
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22 charge and discharge curves, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ working electrode shows smaller
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24 value of ΔV compared with $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ electrode can be attributed to the copper
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26 particles in electrode. The reasons can be summarized as the following [35-41]: (i)
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28 decrease resistance of the electrode, electrolyte, and separator; (ii) enhance the
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30 electronic conductivity because the insertion and extraction of Li^+ must occur
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32 simultaneously with the electron conduction; (iii) improve the charge-transfer
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34 kinetics.
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47 Plots of specific capacity against cycle number can be seen in Fig. 5. In Fig. 5a, the
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49 long-term capacity and stability were evaluated at a modest current rate of 1000 mA
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51 g^{-1} . The $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ samples showed high capacity of 222.7
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53 mAh g^{-1} and 221.2 mAh g^{-1} during the first discharge process. After 1000
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55 charge-discharge cycles, 124.4 mAh g^{-1} and 70.7 mAh g^{-1} discharge capacities were
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obtained. The $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ sample shows good capacity retention and better cycle stability compared with no copper particles. At a current density of 2000 mA g^{-1} , a high discharge capacity of 210.9 mAh g^{-1} can be delivered after 1000 charge-discharge cycles. Even at high current density of 3000 mA g^{-1} , the 1000th discharge capacity reached 79.1 mAh g^{-1} , while $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ has only 52.1 mAh g^{-1} . According to the obtained information, the lithium intercalation capacity of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ is decreased with the discharge current density increasing, which is due to the severe electrode polarization at high rates. Based on the obtained results, the reasons of the enhanced electrochemical performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite can be mainly attributed to the following four reasons: (1) the electronic conductivity of copper is much higher than that of pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$, which can apparently enhance the electronic conductivity of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ after recombination and increase the high rates discharge capacities. (2) Thin carbon coating layer on the outer surface of active particles could improve the electrical contact between the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ particles and minish the interfacial impedance [42]. (3) Adding copper into the bulk $\text{Li}_2\text{ZnTi}_3\text{O}_8$ could reduce the direct contact between primary particles and acquire large contact area, providing high interfacial contact area with electrolyte to increase amount of reactive sites and facilitating ion transport within interior of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ [43]. (4) Lithium salt LiPF_6 is inclined to react with water resulting in the formation of HF because the commercial LiPF_6 -based lithium battery electrolyte solution always contains a trace amount of water [44]. The function of carbon layer on the outer surface of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is to insulate active material in the

electrolyte, which can prevent the active material particles from HF attack and prevent side reactions at the interface of electrode and electrolyte [45, 46]. Considering its low cost and simple preparation process, $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ has been proven to be a new promising candidate as the anode material for lithium ion battery.

Cyclic voltammograms (CV) experiments were carried out in order to investigate the effect of copper particles in the electrochemical properties of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$. Fig. 6 (a-b) shows the CV profiles of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ in the voltage range of 0.05 V-3.0 V (vs. Li/Li^+), with a scan rate of 0.5 mV s^{-1} . Both samples show that similar CV curves. From charts, one pair of redox peaks appears between 1.0 V and 2.0 V in the first five cycles for both 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 [47]. Furthermore, it can be seen that there is a pair of redox peaks for both anode material from the first to five cycles located at between 1.70 V and 1.30 V, which is related to $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple. Compared with the redox peaks of un-coated sample, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ 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 0.6 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. [48-49]. Furthermore, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ electrode has the highest peak current compared with others. It suggests that the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ electrode with has better kinetic characteristics which means it has faster electronic transmission speed in active particles.

To get further insight into the interface charge-transfer resistance, electrochemical impedance spectroscopy (EIS) of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ electrodes were measured in the frequency range of 100 kHz to 10 mHz, and presented in Fig. 6 (c). Two electrodes 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 related to the complex reaction process over the electrolyte/electrode interface, 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 [50]. 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 $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ is improvement. Such improvement may be associated with the improvement of the charge transfer process over the electrode surface, which can be contributed to copper among bulk particles and nanometer carbon layer on the outer surface of $\text{Li}_2\text{ZnTi}_3\text{O}_8$. 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.

As anticipated, the $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite represents an excellent cycle performance at different current densities as shown in Fig. 6 (d). The reversible capacity decreases gradually as the current rate increases. From the Figure, a specific discharge capacity of 326 mAh g^{-1} is obtained at 100 mA g^{-1} after 10 charge/discharge

cycles. Moreover, at higher current density of 1600 mA g⁻¹, 220 mAh g⁻¹ can be obtained at the 10th cycle. When the current density finally backs to 100 mA g⁻¹, a capacity of 310 mAh g⁻¹ can be restored. The cycling performance indicates that Li₂ZnTi₃O₈/C@Cu electrode has good rate performance and cycling stability even after rather harsh loading and de-loading rates. In addition, the average coulombic efficiency is around 98.7% at different charge-discharge rates from the third cycle to the end. In a word, all the evidences demonstrate that the Li₂ZnTi₃O₈/C@Cu composite could be a promising anode material with high rate capability, good cycling stability and long lifespan performance.

As a kind of good electrode active material, in addition to possessing good rate capabilities, it must meet the requirements for real life battery operation that withstand fast charge and slow discharge or slow charge and fast discharge. Fig. 6 (e-f) shows cyclic performance of Li₂ZnTi₃O₈/C@Cu composite in the voltage range of 0.05-3.0 V (vs. Li/Li⁺). As shown in Fig. 6 (e), the initial charge-discharge capacities are 208.5 and 216.7 mAh g⁻¹ for Li₂ZnTi₃O₈/C@Cu composite at 0.5 A g⁻¹ charge and 2.0 A g⁻¹ discharge, and coulombic efficiency more than 99% from second cycle to the 100th cycle. Besides, at 2.0 A g⁻¹ charge and 0.5 A g⁻¹ discharge, the initial charge and discharge capacities are 208.8 mAh g⁻¹ and 234.9 mAh g⁻¹ for Li₂ZnTi₃O₈/C@Cu (Fig. 6 (f)), respectively. After 100 charge-discharge cycles, 198.8 mAh g⁻¹ charge capacity and 199.8 mAh g⁻¹ discharge capacity are obtained, respectively, which exhibits good cycling stability at irregular current density. Moreover, the composite sample exhibits high coulombic efficiency and good cyclic performance at irregular charge discharge

1 tests. The good performance could be ascribed to the copper and carbon layer with
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3 high electronic conductivity. High rate charge or high rate discharge electrochemical
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5 performance is very beneficial to its application in portable electronic device and
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7 large storage equipment which need to be charged or discharged quickly with large
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9 current densities.
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17 **4. Conclusions**

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19 In conclusion, cubic spinel $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite was successfully
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21 synthesized by a sol-gel method with good crystallinity and was then used for the first
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23 time as the anode material in lithium ion battery. XRD measurements prove the
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25 existence of carbon and copper in the composite have not effect on the crystal
26
27 structure of bare $\text{Li}_2\text{ZnTi}_3\text{O}_8$ active material. TEM images and EDS demonstrate an
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29 amorphous carbon layer with a thickness of 2.0-8.0 nm coating on the surface of the
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31 $\text{Li}_2\text{ZnTi}_3\text{O}_8$, and metal copper uniform distribution between primary particles. The
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33 combination of carbon layer and electrical conductivity of copper effectively
34
35 improves the electronic conductivity and charge transfer rate of $\text{Li}_2\text{ZnTi}_3\text{O}_8$. As a
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37 result, $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ shows greatly improved cycling stability and rate capability.
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39 Charge-discharge results show that $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ reveals the reversible
40
41 capacities of 124.4 mAh g^{-1} at 1000 mA g^{-1} , 90.8 mAh g^{-1} at 2000 mA g^{-1} , and 79.1
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43 mAh g^{-1} at 3000 mA g^{-1} after 1000 cycles, which higher than that $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$
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45 sample. Moreover, $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ shows lower electrochemical polarization and
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47 higher peak current than those of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ in the cyclic voltammograms.
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1 Electrochemical impedance spectroscopy measurement shows that the smaller R_{ct}
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3 value in $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ electrode is the main reason for the improved
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5 electrochemical property. This outstanding $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ nonocomposite
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7 prepared by one step sol-gel method from low-cost raw materials is promising for
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9 application in rapid charge-discharge lithium ion battery.
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22 20973124).
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List of Figures:

Fig. 1 XRD patterns of sample $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite.

Fig. 2 SEM image of (a) $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ and (b) $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite. TEM image of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite (c-d). Nitrogen adsorption-desorption isotherms and the corresponding BJH pore-size distribution: (e) $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite; (f) $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$.

Fig. 3 EDX image of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite.

Fig. 4 The voltage profiles of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ at the 1st cycle, and the corresponding differential capacities vs. voltage plots.

Fig. 5 Cycling performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ at different current densities.

Fig. 6 CV profiles of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ (a) and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ (b) in the voltage range of 0.05 V-3.0 V (vs. Li/Li^+). EIS of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ and $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ electrodes (c). Cycling performance at different current densities of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ (d). Cycling performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}@\text{Cu}$ composite at various charge-discharge rates (e-f).

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