Comparative study of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ anode material with good high rate capacities

prepared by solid state, molten salt and sol-gel methods

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Abstract:

Cubic spinel $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is a promising lithium ion battery electrode anode material with high specific lithium-intercalation capacity and low discharge voltage platform. Herein, $\text{Li}_2\text{ZnTi}_3\text{O}_8$ anode materials are synthesized through solid state reaction, molten salt route, and sol-gel method, respectively. Sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ exhibits good crystallinity from XRD and agglomeration is alleviated with uniform particle size and more stack holes from SEM images compared with other methods. Cyclic voltammograms (CV) results show that the sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode has the lowest polarization, indicating better kinetic process. Electrochemical impedance spectroscopy (EIS) reveals that the sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ sample exhibits highest electronic conductivity and faster lithium ion diffusivity in all three samples. The sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode has excellent long-term cycling performance and high discharge capacities of 71.2, 90.9, and 150.0 mAh g^{-1} after 1000 charge-discharge cycles with low capacity fadings of only 0.058%, 0.051%, and 0.028% per cycle, at 3000, 2000, and 1000 mA g^{-1} , respectively. These results show that sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is a promising anode electrode material for high performance lithium ion batteries.

Keywords: $\text{Li}_2\text{ZnTi}_3\text{O}_8$, Solid state, Molten salt, Sol-gel, Lithium-ion battery

1. Introduction

Owing to high energy density, long cyclic life and environmental friendliness, rechargeable lithium-ion batteries have been widely used as the power sources of personal electronic devices and large energy storage systems [1-3]. Carbon materials like graphite, which popularly used as anode materials in the commercial lithium-ion batteries. The graphite electrode, however, suffers from poor safety thus making it unsuitable for widely application. The safety issues arise from the dendritic deposition of metal lithium on the anode surface at this relatively low lithium insertion potential of graphite anode [4]. To make breakthroughs in progress, developing alternative anode materials which provide good electrochemical performances and free from safety concerns are necessary.

In recent years, in many of the anode materials, Ti-based materials have become a research hotspot owing to their high safety and excellent cycling stability. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material has been studied and presented many good features [5-9]. However, due to low theoretical capacity, poor electronic conductivity and high intercalation potential, it is difficult for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to be widely employed. Hence, find out a new Ti-based anode material is necessary. Cubic spinel $\text{Li}_2\text{ZnTi}_3\text{O}_8$ with a space group P4_332 has been studied manifesting good high discharge capacity and cycle stability [10]. Based on the crystal structure [11-13], $\text{Li}_2\text{ZnTi}_3\text{O}_8$ can be described as $(\text{Li}_{0.5}\text{Zn}_{0.5})^{\text{tet}}[\text{Li}_{0.5}\text{Ti}_{1.5}]^{\text{oct}}\text{O}_4$, and all of Zn in the tetrahedral sites and 1:3 cation ordering of Li:Ti occurs in the octahedral sites. Thus, a three dimensional network is formed in such a structure, where Li and Zn atoms are located in tetrahedral sites

forming tunnels. This is propitious to the Li^+ reversible intercalation/de-intercalation during repeated charge/discharge. Compared with $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_2\text{ZnTi}_3\text{O}_8$ has its own merits: high capacity of more than 227 mAh g^{-1} and lower discharge voltage plateau around 0.5 V (vs. Li/Li^+) [14-16]. To the best of our knowledge, the scientific studies about naked $\text{Li}_2\text{ZnTi}_3\text{O}_8$ as anode material have been rarely reported in the past years.

Herein, without any modification of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ materials were synthesized by using three different methods, including solid state reaction, molten salt, and sol-gel method. Physical characteristics and electrochemical performances of prepared samples are examined and compared. The results show that the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared via sol-gel technique displays the uniform dispersion of particles and the best lithium storage capability in all prepared samples with different routes.

2. Experimental

2.1 Materials preparation

In this paper, $\text{Li}_2\text{ZnTi}_3\text{O}_8$ anode material was prepared by three different methods: solid-state reaction, molten salt route and sol-gel method.

For solid-state reaction, TiO_2 , Li_2CO_3 , and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were dispersed in anhydrous ethanol and ball-milled for 4 h in planetary ball mill. The white mixtures were dried at 80°C to evaporate ethanol. Then ground to powders at agate mortar and heated in a muffle furnace at 700°C for 1 h and 800°C for another 3 h in air, and then cooled down to ambient temperature naturally.

For molten salt route, TiO_2 , Li_2CO_3 , $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, NaCl and KCl were

mixed and ground in a mortar with a pestle. The molar ratio of the starting materials Ti:NaCl-KCl is fixed to 1:4. The mixed powders were calcined at 800 °C for 5 h in air, and then naturally cooled to room temperature. The resulting powders were thoroughly washed with distilled water to remove the residual molten salt. The final products were obtained after vacuum-drying at 120 °C to remove the residual liquids.

The $\text{Li}_2\text{ZnTi}_3\text{O}_8$ was prepared by sol-gel method as follows. In a typical process, $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were dissolved in ethanol with continued magnetic stirring. Then a certain amount of citric acid was added above solution. Finally, tetrabutyl titanate $[\text{Ti}(\text{OC}_4\text{H}_9)_4]$ 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. 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 air.

2.2 Materials characterization °C

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).

2.3 Electrochemical measurements

The electrochemical performances of samples were studied employing 2032 coin type cells. Typically, the as-synthesized anode materials, acetylene black and polyvinylidene fluoride with a ratio of 8:1:1 were dissolved in N-methyl-2-pyrrolidone to form uniform slurry and daubed on copper foil. 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 coin 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

Powder X-ray diffraction patterns of naked Li₂ZnTi₃O₈ using different synthetic routes are presented in Fig. 1. It can be observed that the main phase of all tested samples is Li₂ZnTi₃O₈ with cubic spinel structure, which is well matched with the standard powder diffraction (JCPDS#44-1037) [17]. Moreover, it is clearly shown that no other impurities peaks such as TiO₂ and Li₄Ti₅O₁₂ can be figured out through all XRD patterns. Furthermore, the relative intensities of Li₂ZnTi₃O₈ prepared by sol-gel method are stronger than other two, which indicating it has good crystallinity. The

unit cell parameters of different $\text{Li}_2\text{ZnTi}_3\text{O}_8$ samples are calculated and shown in Table 1. All the as-prepared samples have the same space group of $P4_332$. The sample prepared by sol-gel method reveals bigger unit cell parameters than those derived from $\text{Li}_2\text{ZnTi}_3\text{O}_8$ formed at solid-state reaction and molten salt route, which makes the sol-gel formed structure is more suitable for rapid lithium-ion transportation and high lithium storage capacity [15]. The crystalline size (D) of samples was calculated using the Scherrer equation $D = K\lambda/\beta\cos\theta$, where K is a constant (0.943), λ is wavelength of $\text{CuK}\alpha$ radiation, β is the half-peak width of the XRD diffraction peak, θ is the position of the peak. It is found that the average crystalline size of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ powders obtained by means of solid state, molten salt, and sol-gel are 24.7 nm, 23.5 nm, and 50.3 nm, respectively.

The morphology of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ powders prepared via solid-state reaction, molten salt route and sol-gel method was also examined by scanning electron microscopy (SEM), as illustrated in Fig. 2. The SEM images in Fig. 2 (a, b) show the particle morphologies of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ powders synthesized by solid-state reaction. It can be seen that the solid state prepared pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$ powders show obviously agglomeration after high temperature calcination. The images of pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$ powders prepared via molten salt route and sol-gel method are presented in Fig. 2 (c, d) and Fig. 2 (e, f), respectively. With the change of synthesis way, the degree of agglomeration is alleviated and the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ powders obtained by means of sol-gel method have the best dispersion in all three samples. This phenomenon indicates that different synthesis ways have great effect on the agglomeration degree of $\text{Li}_2\text{ZnTi}_3\text{O}_8$

powders, thus affecting the electrochemical performance directly. The obtained results indicating that distributed uniform particles are beneficial to increase the contact area between active material particles and electrolyte and shorten transmission distance of Li^+ , achieving better electrochemical properties.

Fig. 3 (a) illustrates the initial charge-discharge curves obtained at a constant current density of 0.1 A g^{-1} . It can be clearly seen that the charge and discharge curves are similar in shape to all specimens, indicating that the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrodes via three methods have the same electrochemical reaction process. In addition, we see from this that the initial discharge specific capacities of sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is 290.9 mAh g^{-1} , whereas that of the solid state and molten salt formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ are lower and reduced to 200.4 mAh g^{-1} and 268.2 mAh g^{-1} . Moreover, the charge voltage platforms are 1.40, 1.38, 1.37 V and the discharge voltage platforms are 0.92, 0.85, 0.76 V for solid state formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$, molten salt formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$, sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$, respectively. The results indicate that sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ has the smallest voltage difference between charge and discharge voltage platforms, means lowest electrode polarization. The larger capacity and small polarization can be ascribed to nano particle size which can reduce the resistance between particles, improve the speed of electron transfer and increase the amount of active materials for electrochemical reaction. This will improve the cycle capacity and stability.

Fig. 3 (b-c) depicts the cycling performance of the three samples at rate of 1.0 A g^{-1} and 2.0 A g^{-1} from 0.05 V to 3.0 V (vs. Li/Li^+). It can be clearly observed that the reversible capacity of the sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode expresses the highest

discharge capacities at 1.0 A g^{-1} and 2.0 A g^{-1} compared with the other two electrode. At the charge/discharge rate of 1.0 A g^{-1} , the discharge capacity and cycle performance of sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode are superior to solid state and molten salt formed samples. The initial and the 100th discharge capacities are 207.4 mAh g^{-1} and 197.7 mAh g^{-1} can be obtained for sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode, which higher the solid state formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode (147.3 mAh g^{-1} and 82.3 mAh g^{-1}) and molten salt formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode (169.5 mAh g^{-1} and 158.9 mAh g^{-1}), respectively. As the charge-discharge rates increase to 2.0 A g^{-1} , 161.1 mAh g^{-1} can be obtained after 1000 cycles for sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode, which higher than that of others. Moreover, the sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$ exhibits good cycling stability in all samples. Based on the obtained results, $\text{Li}_2\text{ZnTi}_3\text{O}_8$ was prepared via sol-gel route can significantly improve the electrochemical performance at high rates and long-term cycle, because the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ particles come from sol-gel after high temperature calcination have some favorable advantages: i) less agglomeration of secondary particles can effectively increase the utilization of active particles; ii) nanometer scale and uniform particles could enlarge the contact area between active particles and organic electrolyte, which speed up the lithium ion transport and improve kinetics performance; iii) stack holes between secondary particles are conducive to penetration of organic electrolyte which make full use of internal particle surface, and more reusable sites for lithium ions reversible intercalation/de-intercalation.

Fig. 3 (d-f) shows the cyclic voltammograms (CV) of the half cells with the pure

Li₂ZnTi₃O₈ of three different methods as the working electrodes. It can be observed that there is a pair of cathodic/anodic peaks for all samples in the voltage range of 1.0-2.0 V (vs. Li/Li⁺), implying that the as-prepared samples have the same electrochemical reaction process. The values of cathodic peak, anodic peak and difference between cathodic and anodic peaks for pure Li₂ZnTi₃O₈ prepared by solid-state reaction, molten salt route and sol-gel method have been summarized in Table 2. The cathodic/anodic peaks appear at 1.09/1.59 V, 1.19/1.59 V and 1.26/1.57 V for Li₂ZnTi₃O₈ prepared by solid-state reaction, molten salt route and sol-gel method, respectively, which are related to the phase transition between spinel and rock salt [11]. In addition, the potential differences between cathodic and anodic peaks for naked Li₂ZnTi₃O₈ (sol-gel method) is the lowest compared with others, suggesting that it possesses a lower electrode polarization and a higher Li⁺ diffusivity in the bulk. For three samples, there is another small reduction peak at about 0.5 V, which might be attributed to multiple restoration of Ti⁴⁺. The obtained result is in good agreement with the previous literatures by Borghols et al. and Ge et al. [18-19]. In addition, a larger curve area and higher redox peak current can be observed for pristine Li₂ZnTi₃O₈ via sol-gel method compared with others, suggesting that the electrode material has higher capacity and faster kinetics for Li⁺ reversible intercalation and de-intercalation into/out active material particles.

The EIS measurements were carried out for as-prepared Li₂ZnTi₃O₈ electrodes in the two electrode system to further understand the electrochemical performance characteristics before the initial discharge process (Fig. 4a). The measurements were

carried out with an open circuit voltage in the frequency range of 100 kHz to 10 mHz. Shown in Fig. 4a are the EIS in Nyquist plots for $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared by different methods. The EIS plots of all samples are similar which consisted of 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 [21]. Here, a simplified equivalent circuit model (Fig. 4a) is constructed to analyze the impedance spectra. In the equivalent circuit, R_s is solution and contact resistance, R_c is charge transfer resistance, CPE is constant phase element which represent the double layer capacitance and passivation film capacitance, and W means Warburg diffusion impedance. As reckoned from the impedance spectra data, the size of high frequency region semicircle of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared by sol-gel method is the smallest compared with other two samples, indicating it has the lowest charge transfer resistance. Such phenomenon may be ascribed to two facts: (1) less agglomeration lead to uniformly dispersed and larger specific surface area, resulting in shorter diffusion length for Li^+ and sufficient contact between the active materials and electrolyte, which is beneficial for the charge transfer process; (2) stack holes arise from active particles are propitious to more electrolyte penetrate into interior of the particles, and make more transmission channel available for Li^+ transport.

The variable current rate tests of the coin cells containing $\text{Li}_2\text{ZnTi}_3\text{O}_8$ derived from three kinds of methods are shown in Fig.4 (b) (10 cycles per current rate, up to a

maximum of 1500 mA g⁻¹). In contrast to the solid state formed sample, the others resisted capacity fading with the current rates increasing. At the highest applied current rates, sol-gel formed sample expresses the highest capacities amongst the samples. The reasons for the high capacity of Li₂ZnTi₃O₈ derived from sol-gel method at 1500 mA g⁻¹ may be that the smaller particle size, more active sites and faster Li⁺ intercalation and de-intercalation process. Moreover, the results manifest good capacity restoration characteristic of sol-gel formed Li₂ZnTi₃O₈ in all samples. As a 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. 4 (c-d) presents cyclic performance of all as-prepared samples in the voltage range of 0.05-3.0 V at 25 °C. As shown in Fig. 4 (c), the initial specific discharge capacities are 129.0, 184.3, 202.3 mAh g⁻¹ for Li₂ZnTi₃O₈ prepared via solid-state reaction, molten salt route and sol-gel method at 0.5 A g⁻¹ charge and 2.0 A g⁻¹ discharge, and 130.5, 179.7, 189.4 mAh g⁻¹ can be obtained after 50 cycles, respectively. In addition, at 2.0 A g⁻¹ charge and 0.5 A g⁻¹ discharge, the initial specific discharge capacities are 124.6, 160.2, 173.4 mAh g⁻¹ for Li₂ZnTi₃O₈ prepared via solid-state reaction, molten salt route and sol-gel method (Fig. 4 (d)), respectively. After 50 cycles, 124.6, 192.9, 172.8 mAh g⁻¹ are retained, respectively. The naked Li₂ZnTi₃O₈ prepared by sol-gel method exhibits the best rate capacities at various charge-discharge rates compared with other two samples. Moreover, all specimens exhibit good cyclic stability at irregular charge discharge tests. The good high rate charge or high rate discharge electrochemical performance is

very beneficial to its application in portable electronic device and large storage equipment which need to be charged or discharged quickly with large current densities.

According to the above results, the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared via sol-gel method excellent good electrochemical performance in all samples. In order to further understand its nature crystal structure, the HR-TEM was carried out to analytical and the results are shown in Fig. 5. From the Fig. 5 (a), the particle size of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared via sol-gel method is located between 50-100 nm with irregular shapes. In addition, the lattice strips of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ can be clearly seen and no other impurities exist (Fig. 5 (b)), indicating that obtained $\text{Li}_2\text{ZnTi}_3\text{O}_8$ specimen by sol-gel method is pure phase. To better understand the electrochemical performance, the long-term cycling performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared via sol-gel method was tested at current rates of 1000, 2000, and 3000 mA g^{-1} , respectively, as shown in Fig. 5 (c). The initial discharge capacities are 170.7, 183.9, and 209.8 mAh g^{-1} at 3000, 2000, and 1000 mA g^{-1} , respectively. After 1000 charge-discharge cycles, the cells display excellent discharge capacities of 71.2, 90.9, and 150.0 mAh g^{-1} at, respectively, 3000, 2000, and 1000 mA g^{-1} . Moreover, the cells still reach high capacity retention and capacity fadings of only 0.058%, 0.051%, and 0.028% per cycle, at 3000, 2000, and 1000 mA g^{-1} , respectively. The good long-term cycling performance and capacity stability of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ electrode by sol-gel method are attributed to the unique features of the nano particles which i) larger surface area which increase more available active sites, ii) small secondary particles and uniform particle size, iii) packing holes between

$\text{Li}_2\text{ZnTi}_3\text{O}_8$ grains in favor of electrolyte permeate which can accelerate the lithium ion transmission. Overall, the electrochemical performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ via sol-gel method exceeds that of solid state and molten salt methods and excellent long-term cycling performance at large current densities.

4. Conclusion

In summary, pristine $\text{Li}_2\text{ZnTi}_3\text{O}_8$ anode materials were prepared by solid-state reaction, molten salt route and sol-gel method. All prepared samples have pure phase and good crystallinity. Compared with the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ formed by solid-state and molten salt reaction, sol-gel prepared $\text{Li}_2\text{ZnTi}_3\text{O}_8$ shows uniform particle size and more stack holes, which has larger contact surface area between active particles and electrolyte, and good for improving electrochemical performance. Moreover, $\text{Li}_2\text{ZnTi}_3\text{O}_8$ synthesized by sol-gel method expresses the best cycling stability and rate performance among all the as-prepared samples, which benefit by small particle size and more active sites for Li^+ reversible intercalation and de-intercalation. In addition, the excellent long-term cycling performance has obtained for sol-gel formed $\text{Li}_2\text{ZnTi}_3\text{O}_8$.

Acknowledgments

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Table 1

Cell parameters of pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared by three different methods: solid-state reaction, molten salt route and sol-gel method.

Sample	Lattice constant	Volume of unit	Space group
	a (nm)	V (nm ³)	
solid-state reaction	0.8373	0.5870	P4 ₃ 32
molten salt route	0.8374	0.5872	P4 ₃ 32
sol-gel method	0.8394	0.5914	P4 ₃ 32

Table 2 The value of cathodic peak and anodic peak for pure $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared by three different methods: solid-state reaction, molten salt route and sol-gel method, respectively.

	solid-state reaction			molten salt route			sol-gel method		
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
φ_{pa} (V)	1.59	1.67	1.67	1.59	1.59	1.61	1.57	1.61	1.63
φ_{pc} (V)	1.09	1.36	1.37	1.19	1.22	1.26	1.26	1.40	1.41
φ_{p} (V) = $\varphi_{\text{pa}} - \varphi_{\text{pc}}$	0.50	0.31	0.30	0.40	0.37	0.35	0.31	0.21	0.22

List of Figures:

Fig. 1 XRD patterns of pristine $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared by solid-state reaction, molten salt route and sol-gel method.

Fig. 2 SEM images of pristine $\text{Li}_2\text{ZnTi}_3\text{O}_8$ synthesized by different preparation methods. (a, b) solid-state reaction, (c, d) molten salt route and (e, f) sol-gel method.

Fig. 3 Charge-discharge curves of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared by different methods at 100 mA g^{-1} (a). Cycling performance at different charge-discharge rates: (b) 1.0 A g^{-1} , (c) 2.0 A g^{-1} . Cyclic voltammograms of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared by solid-state reaction (d), molten salt route (e) and sol-gel method (f) at a scan rate: 0.5 mV s^{-1} between 0.05 and 3.0 V.

Fig. 4 EIS patterns of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ synthesized by different preparation methods (a). Cycling performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared by solid-state reaction, molten salt route and sol-gel method at various charge-discharge rates (b). Cycling performances of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ at various charge-discharge rates (c-d).

Fig. 5 TEM images of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared via sol-gel method (a-b). Long-term cycling performance of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared via sol-gel method at 1.0 A g^{-1} , 2.0 A g^{-1} , and 3.0 A g^{-1} (c).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5