

Research Article

Facile Synthesis of Carbon-Coated Zn_2SnO_4 Nanomaterials as Anode Materials for Lithium-Ion Batteries

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Carbon-coated Zn_2SnO_4 nanomaterials have been synthesized by a facile hydrothermal method in which as-prepared Zn_2SnO_4 was used as the precursor and glucose as the carbon source. The structural, morphological, and electrochemical properties were investigated by means of X-ray (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrochemical measurement. The first discharge/charge capacity of carbon-coated Zn_2SnO_4 was about 1248.8 mAh/g and 873.2 mAh/g at a current density of 200 mA/g in the voltage range of 0.05 V–3.0 V, respectively, corresponding to Coulombic efficiency of 69.92%. After 40 cycles, the capacity retained 400 mAh/g, which is much better than bare Zn_2SnO_4 .

1. Introduction

Tin-based oxide materials have been considered as promising anode materials in lithium-ion batteries (LIBs) due to their large lithium-ion capacities (over 600 mAh/g [1]) at low potentials and high densities [2–5], which is greater than that of commercialized graphite anodes (372 mAh/g) [6]. However, the practical usage of these anodes is hindered by their poor capacity retention during cycling as well as the large irreversible capacity during the first discharge/charge cycle [7–10]. This is mainly caused by a large volume change during the lithium insertion and extraction, which is leading to the pulverization of electrodes and rapid capacity fading [11–14]. To overcome the large volume change, numerous efforts have been made to develop anode materials with high energy density and excellent cycling performance, one of which is to synthesize nanosized materials with different shapes and structures. It was also found that nanosized tin-based oxides exhibit especially good electrochemical performance on account of the large specific area and high Li-ion conductivity [15–18]. Another is to prepare carbonaceous materials because carbon materials have high electronic conductivity and favorable electrochemical performance, which not only provides greatly improved electric conductivity, but also helps buffer the severe volume change [19–21].

As an important semiconductor material, Zn_2SnO_4 ($E_g = 3.6$ eV) has attracted much more attention owing to its applications in gas sensors [22, 23], photocatalysts [24, 25], and solar cells [26, 27]. Recently, nanosized Zn_2SnO_4 has been successfully synthesized by various methods and applied in lithium-ion batteries with good electrochemical properties. For instance, Zhu et al. [28] synthesized inverse-spinel by hydrothermal method. After 20 cycles, the reversible capacity decayed to 664.7 mAh/g at a current density of 50 mA/g, with an average capacity fade rate of 3.3% per cycle. Feng et al. [29] synthesized single crystal Zn_2SnO_4 cubes with reversible capacity of 775 mAh/g after 20 cycles at a current density of 50 mA/g. Rong et al. [30] synthesized cube-shaped particles with the reversible capacity of 580 mAh/g and a slowly fading capacity after 50 cycles at a current density of 50 mA/g. To the best of our knowledge, little attention has been paid to carbon-coated Zn_2SnO_4 as anode materials for lithium-ion batteries at a bigger current density. In this study, carbon-coated Zn_2SnO_4 materials were made by a facile hydrothermal method using the Zn_2SnO_4 octahedron as the precursor and glucose as the carbon source. The electrochemical properties were investigated, and the electrochemical tests showed that the carbon-coated Zn_2SnO_4 exhibits high rate capability and long cycle life compared with bare Zn_2SnO_4 , indicating its promising application as anode for lithium-ion batteries.

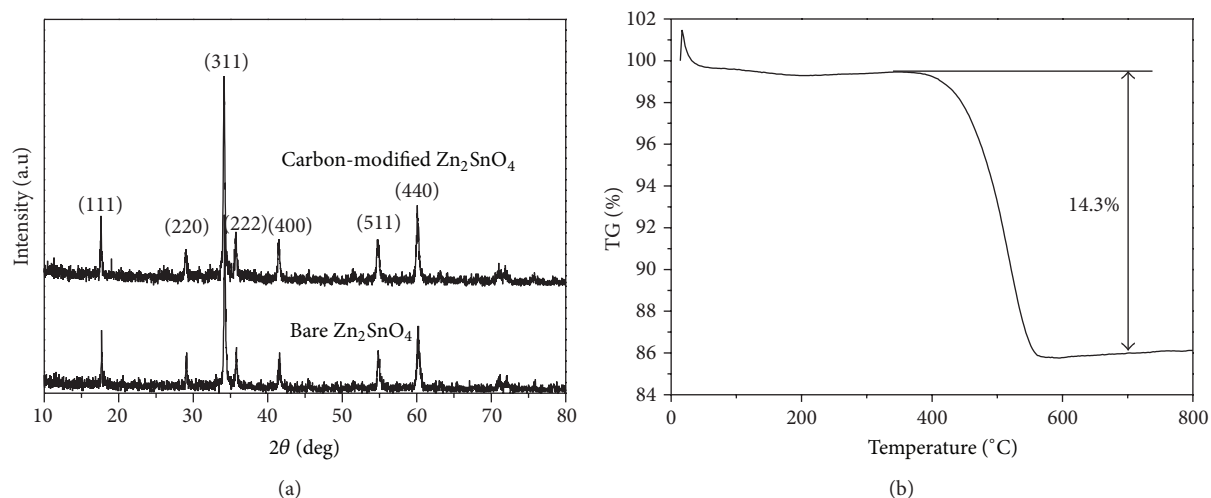


FIGURE 1: (a) XRD result of bare and carbon-coated Zn₂SnO₄ and (b) TGA of the as-obtained carbon-coated Zn₂SnO₄.

2. Experimental

2.1. Preparation of Bare and Carbon-Coated Zn₂SnO₄. In a typical synthesis, 0.025 M SnCl₄ · 5H₂O and 0.05 M ZnSO₄ · 7H₂O were dissolved in 60 mL distilled water, and then 1 M NaOH was added dropwise to the mixture under magnetic stirring. After 20 min, the slurry was transferred to a 100 mL Teflon autoclave, heated at 200°C in an electric oven for 24 h, and then cooled down to room temperature naturally. After the reaction, the precipitate was centrifuged and washed with distilled water and ethanol and then dried at 60°C for 3 h. The bare Zn₂SnO₄ was obtained by carbonizing precursor at 450°C for 3 h under air.

Then, 0.2 g obtained-bare Zn₂SnO₄ was dispersed in mixed solution of distilled and ethanol by ultrasonication, and then 1 g glucose was dissolved in the mixed solution by magnetic stirring for 30 min. The mixed solution was placed in a Teflon autoclave, and then it was placed in an electric oven at 180°C for 16 h. After cooling down in air, the carbon precursor-coated Zn₂SnO₄ was obtained by washing with distilled water and ethanol and dried in a vacuum oven at 60°C for 3 h. Hereafter, the as-prepared product was carbonized at 450°C for 3 h under nitrogen flow to obtain carbon-coated Zn₂SnO₄.

2.2. Sample Characterizations. The morphology of the as-prepared product was characterized by field-emission scanning electron microscopy (FESEM, JEOL, and JSM-6700F). The crystalline structure of the product was analyzed by an X-ray diffractometer (XRD, Y-2000) with Cu Kα radiation (λ = 1.5418 Å) at a scan rate of 0.04° s⁻¹. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations were carried out on a JEOL JEM-2010 instrument in bright field.

2.3. Electrochemical Test. Electrochemical performance evaluations were performed with coin cells using Li foil as

counter electrode. The working electrodes were prepared by mixing the bare Zn₂SnO₄ or carbon-coated Zn₂SnO₄, carbon black and polyvinylidene fluoride (PVDF) at a weight ratio of 70 : 15 : 15. The mixture was dissolved in 1-methyl-2-pyrrolidinone (NMP) forming a slurry and was uniformly cast on a thick copper foil. The electrolyte consists of 1 M solution of LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). Electrochemical cells were assembled in an argon-filled glovebox. The charge-discharge cycling was performed by using a multichannel battery tester (model SCN, Bitrode, USA). Discharge/charge measurements were performed in the voltage range 0.05 V–3.00 V at a current density of 200 mA/g.

3. Results and Discussion

As reported in the literatures, glucose-derived carbon precursor (PS) can be readily integrated onto nanostructure in solution and furthermore carbonized at a temperature as low as 400°C [31]. In this work, throughout a complex polymerization of glucose at 180°C in the autoclave, the color of sample turned from white to puce, indicating that organic carbonaceous layers exist. After heat treatment at 450°C for 3 h under nitrogen atmosphere, the sample became black, indicating existing carbon layer.

All the diffraction peaks of the two samples were consistent with the data of pure reverse spinel Zn₂SnO₄ (JPCDS No. 74-2184), indicating that the glucose did not affect the configuration of sample in the process of hydrothermal synthesis. From the XRD patterns, no other peaks are detected, accounting for the low carbon content or forming amorphous carbon. Figure 1(b) shows the TGA curve of carbon-coated Zn₂SnO₄ in air between 30°C and 800°C. The weight loss before 100°C is due to the loss of water. The continuous weight loss between 400°C and 600°C signifies the removal of the combustion of the carbon layers into carbon oxides. The carbon content in carbon-coated Zn₂SnO₄ is estimated to be 14.3% based on the TGA analysis.

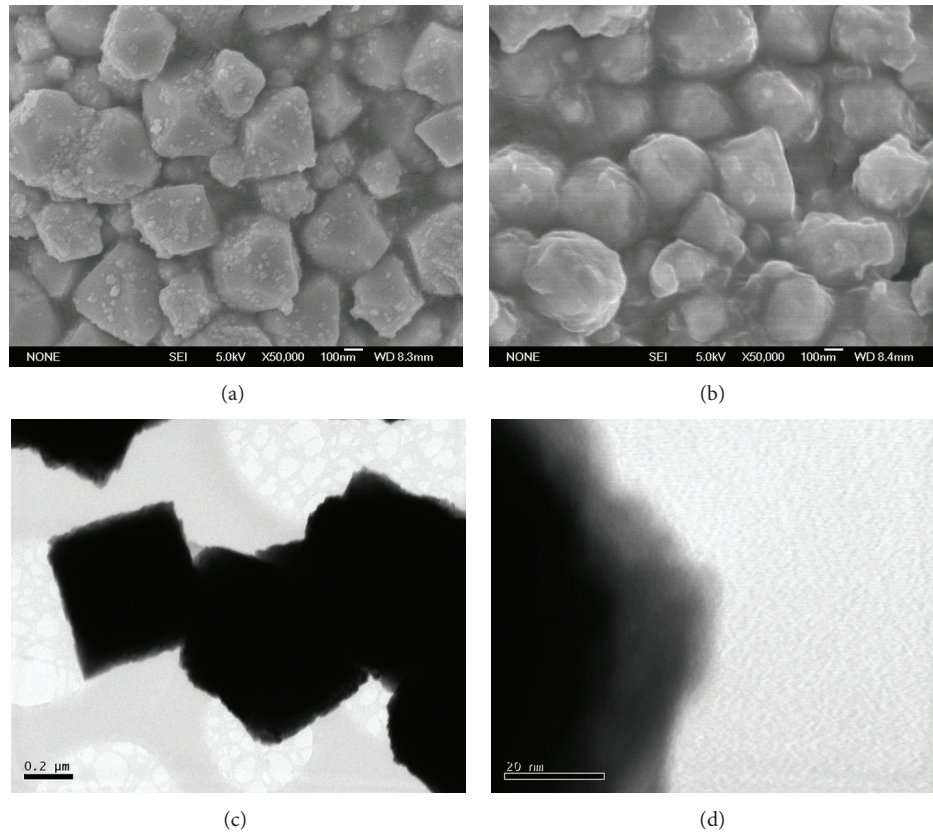
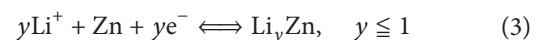
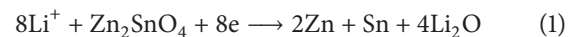


FIGURE 2: SEM images of (a) bare and (b) carbon-coated Zn_2SnO_4 . (c) Low-magnification and (d) high-magnification TEM image of the as-obtained carbon-coated Zn_2SnO_4 .

Representative SEM images of as-obtained products are observed in Figure 2. Figures 2(a) and 2(b) show a typical image of the bare Zn_2SnO_4 and carbon-coated Zn_2SnO_4 , respectively. As can be seen, the sample of bare Zn_2SnO_4 is dispersive quasi-octahedron shape with an average diameter of about 300 nm and nanoparticles on its surface. From Figure 2(b), it can be seen that the nanoparticles on the surface disappear and the morphology of carbon-coated Zn_2SnO_4 shows quasisphere. All of the quasi-octahedron Zn_2SnO_4 is uniformly coated by amorphous carbon layer and the sample is well dispersive as before after coating. The decoration of carbon on the surface of Zn_2SnO_4 is further investigated by TEM in Figures 2(c) and 2(d), from which carbon layer coated on the surface of quasi-octahedron samples is markedly observed. It is noteworthy that introducing the amorphous carbon layer does not affect the other features of Zn_2SnO_4 . From HRTEM image in Figure 2(d), it can be confirmed that the average thickness of carbon layer is about 35 nm and the carbon layer closely sticks to the Zn_2SnO_4 surface without vacant space between the carbon “shell” and Zn_2SnO_4 “core.” It is expected to provide good electric conductivity and help buffer the volume change of anode materials.

Recently, different morphology and structures of Zn_2SnO_4 electrodes have been demonstrated to improve the cycling capability, but the electrochemical performance of dispersive carbon-coated Zn_2SnO_4 nanomaterials at higher

current density was rarely investigated. To demonstrate the potential use of the carbon-coated Zn_2SnO_4 as an anode for LIBs, we carried out a comparison of the electrochemical performance of the bare Zn_2SnO_4 and carbon-coated Zn_2SnO_4 . Galvanostatic charge-discharge test was carried out at a current density of 200 mA/g between 0.05 and 3.00 V. The bare Zn_2SnO_4 and carbon-coated Zn_2SnO_4 electrodes show similar voltage profiles which agree well with that previously reported Zn_2SnO_4 materials. As reported, the electrochemical reaction mechanism of Li with Zn_2SnO_4 can be described in (1)–(3). The theoretical maximum capacity of Zn_2SnO_4 is about 547 mAh/g based on (2) and (3) according to the reaction mechanism proposed by Rong et al. [30]:



Figures 3(a) and 3(b) show the first, second, and twentieth charge-discharge curves of the two different samples. As can be seen, there is a wide steady discharging plateau around 0.5–1.0 V (versus Li^+/Li) for the lithium reaction with Zn_2SnO_4 and subsequent metallic Sn or Zn between 0.05–0.5 V. From the second cycle afterward, the potential plateaus shift upward to 1.0 V gradually and display more inclined shape. The initial charge and discharge capacity

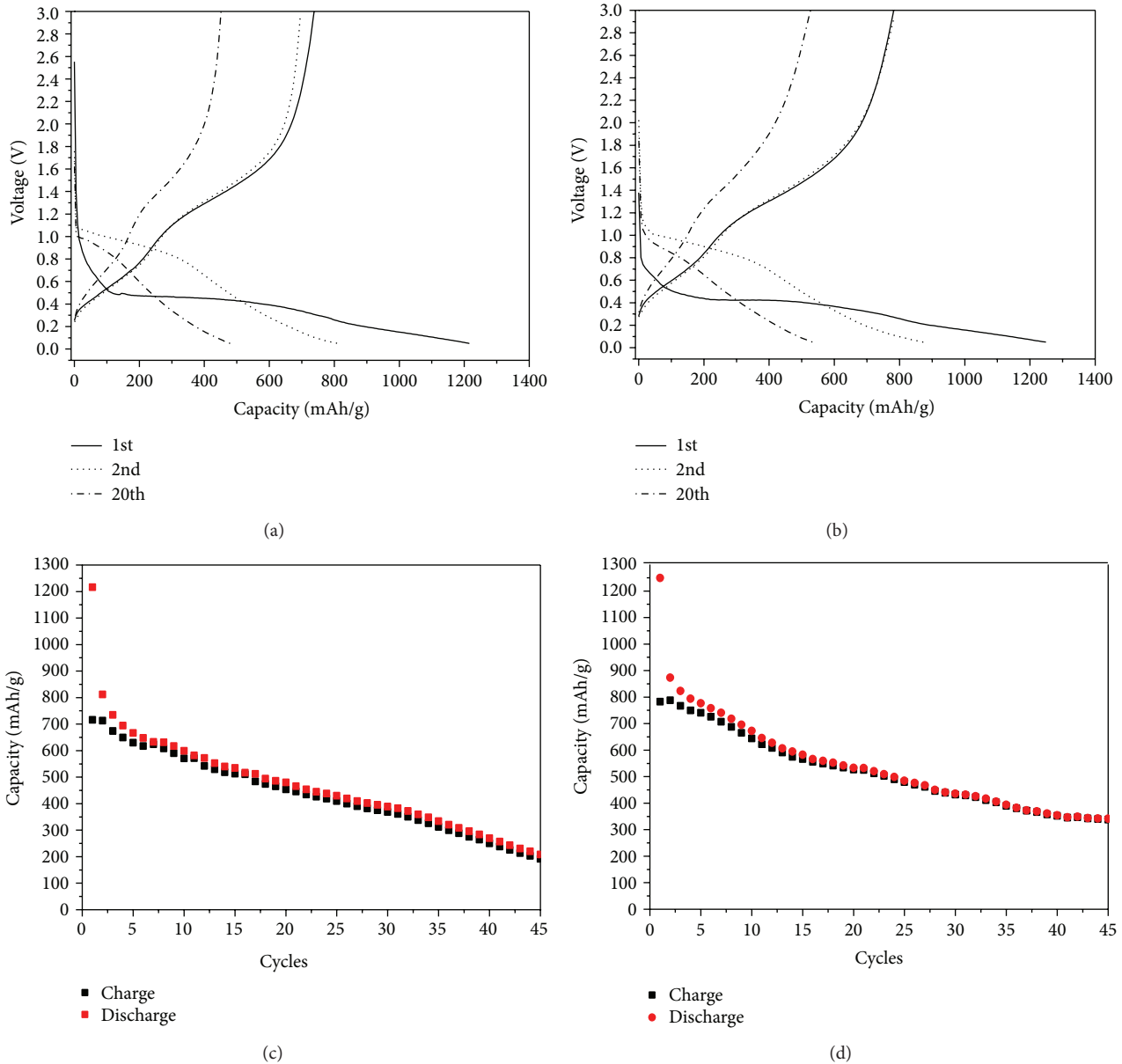


FIGURE 3: The discharge-charge profiles of (a) bare and (b) carbon-coated Zn_2SnO_4 . The cycling performance of (c) bare and (d) carbon-coated Zn_2SnO_4 electrodes in a voltage range of 0.05–3.0 versus Li^+/Li at current density of 200 mA/g.

is 1215.9 mAh/g and 812.1 mAh/g for bare Zn_2SnO_4 and 1248.8 mAh/g and 873.2 mAh/g for carbon-coated Zn_2SnO_4 , respectively. The extra capacity resulted from the formation of solid electrolyte interphase film and possibly interfacial lithium storage during the first discharging process [32]. The initial Coulombic efficiency for the first cycle is 66.79% and 66.92%, which is higher than many corresponding reports. However, for both materials a large first irreversible capacity is observed, due to the decomposition of the electrolyte and the formation of the solid electrolyte interphase (SEI) [30].

The comparison of cycling stability between bare Zn_2SnO_4 and carbon-coated Zn_2SnO_4 is shown in Figures 3(c) and 3(d). It can be seen that the capacity retain rate of carbon-coated Zn_2SnO_4 is obviously better than that of

bare Zn_2SnO_4 . The charge capacity of bare Zn_2SnO_4 and carbon-coated Zn_2SnO_4 retains 479.7 and 533.2 mAh/g after 20 cycles at 200 mA/g, which is higher than the theoretical capacity of graphite. However, the charge capacity of bare Zn_2SnO_4 drops rapidly after 30 cycles. For carbon-coated Zn_2SnO_4 , the charge capacity fades slowly and a charge capacity of 341 mAh/g can still be retained after 45 cycles at 200 mA/g. The better electrochemical properties of carbon-coated Zn_2SnO_4 can be ascribed to the carbon shell. First, carbon has enough mechanical strength to buffer volume expansion [33]. Thus, the presence of carbon shell on the Zn_2SnO_4 surface would effectively alleviate the strains caused by the volume variation of Zn_2SnO_4 and prevent the disintegration. For carbon-coated Zn_2SnO_4 , the

preservation of structure during the Li^+ insertion/extraction processes helps to keep physical contact between the anode materials and the current collector, leading to better cycling stability. Second, carbon itself is an electronic conductor [34], which ensures good electrical contact of Zn_2SnO_4 with the current collector and ensures the charge transfer/ Li^+ transport. Because of uniform and full coating of carbon, electrons can easily reach all the positions where Li^+ ion intercalation takes place [35]. Thirdly, carbon is a very stable electroactive anode material for LIBs. The solid electrolyte interphase (SEI) film on carbon surface was reported to be relatively stable compared with that on bare transition metal oxides [36]. The stable SEI film will also be useful for the maintenance of inner Zn_2SnO_4 structure. Therefore, all of these advantages contribute to the improved battery performance for carbon-coated Zn_2SnO_4 .

4. Conclusions

In summary, dispersive carbon-coated Zn_2SnO_4 was synthesized by a hydrothermal method using bare Zn_2SnO_4 as the precursor and glucose as the carbon source. The as-made electrodes of carbon-coated Zn_2SnO_4 have shown high reversible capacity, good cycle stability, and enhanced rate capability as anode material in LIBs. The carbon introducing can help prevent crack and pulverization, maintain the integrity of electrodes, and provide good electric conductivity, eventually leading to better electrochemical performance than bare Zn_2SnO_4 . The good electrochemical performance of carbon-coated Zn_2SnO_4 makes it a promising anode material for LIBs.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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