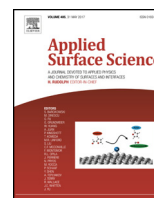




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## Full Length Article

## Facile preparation of a zinc-based alloy composite as a novel anode material for rechargeable lithium-ion batteries

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## ABSTRACT

We report a new Zn-based nanocomposite anode material (Zn-Ti-C) for lithium-ion batteries synthesized by thermal treatment and a high energy mechanical milling process. X-ray diffraction and high-resolution transmission electron microscopy revealed the formation of active Zn nanoparticles finely dispersed in the hybrid titanium carbide (TiC) and carbon matrix. Electrochemical analyses show that the formation of the TiC and carbon buffer matrix significantly contributed to the improved performance of the Zn-based electrode by mitigating the volume changes of the Zn nanoparticles during the charge/discharge processes. Furthermore, we optimized the stoichiometric ratio of Zn and Ti in terms of specific capacity, cycling performance, and rate capability in the presence of carbon. The material with a 2:1 atomic ratio (ZnTi(2:1)-C) exhibited the best cycle life, with a gravimetric capacity of 363.6 mAh g<sup>-1</sup> and a volumetric capacity of 472.7 mAh cm<sup>-3</sup> after 300 charge/discharge cycles (78.1% retention). At this ratio, Zn-Ti-C consistently showed the best rate capability measurements up to 3000 mA g<sup>-1</sup> (85% of its capacity at 100 mA g<sup>-1</sup>). Therefore, our Zn-Ti-C composite is a promising alternative negative electrode material for lithium-ion batteries.

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## 1. Introduction

Lithium-ion batteries (LIBs) are one of the most promising rechargeable batteries for mobile electronic devices, hybrid electric vehicles (HEVs), and stationary storage applications owing to their high gravimetric and volumetric capacity, high power, and excellent rate capability [1–8]. Graphite, which is currently used as a commercial anode material in LIBs, exhibits limited capacity (372 mAh g<sup>-1</sup>) and low tap density (< 1 g cm<sup>-3</sup>), and there are safety concerns associated with its low reaction potential vs. Li/Li<sup>+</sup> [9–11]. Accordingly, recent years have seen an increasing demand for the development of new and improved anode materials that do not have the drawbacks of graphite.

Li alloy materials have attracted a great deal of attention because they have extremely high theoretical capacities, e.g., Li<sub>4.4</sub>Si: 4200 mAh g<sup>-1</sup> [12,13], Li<sub>3</sub>P: 2596 mAh g<sup>-1</sup> [14,15], Li<sub>4.4</sub>Sn: 990 mAh g<sup>-1</sup> [16–18], and Li<sub>3</sub>Sb: 660 mAh g<sup>-1</sup> [19,20], resulting

from the large number of Li atoms accommodated per corresponding metal atom during the alloying/dealloying reaction. Some additional advantages of these materials are the alleviation of risks related to Li plating, and the improvement of their Li<sup>+</sup> diffusion kinetics due to the suppression of solid-electrolyte interphase (SEI) layer formation that can occur at higher reaction potentials [21,22]. However, the primary limitation in adopting these materials is the large volume change upon lithiation/delithiation, which can cause mechanical cracking and crumbling of the electrode [23].

The introduction of titanium carbide (TiC) and carbon to Li-alloying materials has been proposed as an effective approach to overcome this volume change problem [24,25]. The improved cycling behavior of this hybrid buffer is based on the synergetic benefits of TiC and carbon. TiC reinforces the buffer matrix owing to its excellent mechanical properties, thereby mitigating the volume change of the electrode [26,27]. In addition, the high electric conductivity of TiC improves the kinetics of the material and thus battery performance. The presence of carbon increases the conductivity further by providing a continuous pathway for electrons. It also prevents active particles from aggregating during repeated charge/discharge cycles [28].

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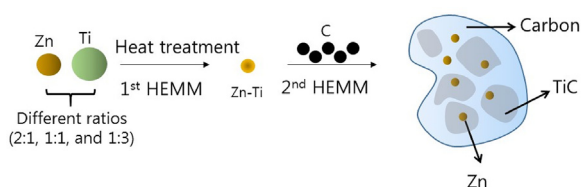


Fig. 1. Brief illustration of synthesis for Zn-Ti-C nanocomposite at different ratios.

Zn is a Li alloying material that has been investigated as a potential alternative for graphite. While Zn has a relatively low theoretical capacity ( $410 \text{ mAh g}^{-1}$ ), it has high volumetric capacity ( $1511 \text{ mAh cm}^{-3}$ ) and low reaction voltage (generally  $<0.4 \text{ V}$  vs.  $\text{Li/Li}^+$ ) [29,30]. In addition, Zn is environmentally friendly, abundant, and cheap. Because of its relatively small volume expansion ( $\sim 71\%$  for  $\text{LiZn}$  [31] compared to that of other alloys (e.g.,  $\sim 300\%$  for  $\text{Li}_{15}\text{Si}_4$  and  $\sim 280\%$  for  $\text{Li}_{22}\text{Sn}_5$ ), it can be considered as an appropriate alternative to graphite as an anode material. However, very few previous studies on Zn-based anodes have reported impressive performances in terms of gravimetric (or volumetric) capacity, long-term cycling, and rate capability [32,33].

In this study, we introduce a simple method to synthesize a Zn-Ti-C nanocomposite alloy as a new anode material. Using a series of synthetic steps, i.e., a heat treatment and two high-energy mechanical milling (HEMM) steps, Zn nanoparticles are uniformly incorporated into a hybrid matrix of TiC and carbon. The combination of TiC and carbon not only allows mechanical integrity and high conductivity for the active Zn, but also prevents the agglomeration of Zn nanoparticles, resulting in a dramatic improvement in electrochemical performance. We also optimize the Zn/Ti atomic ratio in order to achieve the best electrochemical performance for the given strategy. In addition, the mechanism for the reaction of our Zn-based materials with Li is investigated in order to better understand the electrochemical reactions.

## 2. Experimental

### 2.1. Material synthesis

The general method for synthesizing the Zn-Ti-C nanocomposite was to use thermal annealing and two HEMM steps (Pulverisette 5, Fritsch). This synthetic route is briefly described in Fig. 1. Mixtures of Zn ( $<10 \mu\text{m}$ ,  $\geq 98\%$ , Aldrich) and Ti (325 mesh, 99.99%, Alfa Aesar) at three different atomic ratios (2:1, 1:1, and 1:3) were physically mixed using a pestle and mortar. The Zn/Ti mixture was then thermally annealed at  $600^\circ\text{C}$  (ramping rate of  $10^\circ\text{C min}^{-1}$ ) in Ar gas for 6 h at a gas flow rate of  $10 \text{ cc min}^{-1}$ , followed by manual grinding. These mixtures were introduced into a zirconium oxide bowl ( $80 \text{ cm}^3$ ) with zirconium oxide balls (diameters  $3/8''$  and  $3/16''$ ) at a ball-to-powder ratio of 20:1, which was then sealed under Ar atmosphere in a glove box. The total amount of powder (Zn and Ti) was 2.0 g. The first HEMM process was applied at room temperature at 300 rpm for 1 h 40 times. Subsequently, 70 wt% of the ball-milled Zn/Ti mixture was mixed with 30 wt% carbon black (Super P, Alfa Aesar, 99.99%) and the second HEMM process was performed for 1 h. For comparison, a mixture of Zn and Ti at a 2:1 atomic ratio was prepared without C by applying the same procedure except for the second HEMM step.

### 2.2. Material characterization

The crystal structures of each sample were characterized by X-ray diffraction XRD, D/MAX-2200 with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , Rigaku, Japan). The microstructure, composition, and elemental distributions of the synthesized nanocomposites were investi-

gated by scanning electron microscopy (SEM, Hitachi S4700, Japan) coupled with energy dispersive X-ray spectroscopy (EDS), and high-resolution transmission electron microscopy (HRTEM, TECNAI G2F30). For *ex situ* SEM observation, a coin-type cell was disassembled using wolf looping pliers after 100 cycles in an Ar-filled glove box. The electrode was removed from the cell, thoroughly rinsed with dimethyl carbonate (DMC, anhydrous), and then dried. After complete drying, SEM was performed.

### 2.3. Electrochemical measurements

To prepare the electrodes, a well-mixed slurry was prepared by dispersing 70 wt% active Zn-based powder material, 15 wt% Super P, and 15 wt% poly(vinylidene fluoride) (PVDF, average  $M_w$  534,000 by GPC, Aldrich) in *n*-methyl-pyrrolidone (NMP). The slurry was cast onto a Cu foil ( $12 \mu\text{m}$  thickness) and dried in a vacuum oven at  $70^\circ\text{C}$  overnight. After pressing, the film was punched as a disk shape to fabricate a coin-type electrochemical cell (CR2032). The typical mass loading of the electrode material was  $\sim 2\text{--}3 \text{ mg cm}^{-2}$ . The coin cells were assembled in an Ar-filled glove box using a Li foil counter electrode and a polyethylene (PE) separator. The electrolyte solution used was 1 M  $\text{LiPF}_6$  dissolved in ethylene carbonate (EC)/diethylene carbonate (DEC) (1:1 v/v).

The charge/discharge measurements were performed galvanostatically at a current density of  $100 \text{ mA g}^{-1}$  over the voltage range  $0.0\text{--}2.0 \text{ V}$  (vs.  $\text{Li/Li}^+$ ) using a battery cycler (NanoCycler NC-803, Nanobase). The specific capacity was calculated based on the total weight of the active materials. For volumetric capacity measurement, the tap density ( $\text{g cm}^{-3}$ ) of the sample (Zn-Ti-C) was calculated from the measured volume and weight of the powder. The volumetric capacity ( $\text{mAh cm}^{-3}$ ) was acquired using the tap density ( $\text{g cm}^{-3}$ ) and measured specific capacity ( $\text{mAh g}^{-1}$ ). The rate capability of the cell was tested with a WonAtech battery tester (WBCS3000) at current densities of 100, 500, 1000, and 3000  $\text{mA g}^{-1}$ .

## 3. Results and discussion

### 3.1. Crystallography and microstructures of the Zn-Ti-C nanocomposites

Fig. 2 shows the XRD patterns of the Zn-Ti-C nanocomposites prepared using three different Zn/Ti atomic ratios (2:1, 1:1, and 1:3) along with that of  $\text{ZnTi}(2:1)$ . The peaks observed for the Zn-Ti-C nanocomposites are clearly distinct from those of the Zn-Ti counterpart. For the Zn-Ti-C nanocomposites, three main common peaks are observed at  $\sim 36^\circ$ ,  $\sim 39^\circ$ , and  $\sim 43^\circ$ , which are well-matched with Zn reference peaks (PDF#65-3358). This suggests that the majority of Zn atoms are present independently in the nanocomposites after the two HEMM steps. The peaks found at  $\sim 36^\circ$  and  $\sim 72^\circ$  in the Zn-Ti-C nanocomposites correspond to the TiC phase (PDF#65-0971), which is in good agreement with the results reported for similar previous approaches [24]. The peak at  $\sim 72^\circ$ , which is not observed in  $\text{ZnTi}(2:1)$ , clearly confirms the formation of TiC in the Zn-Ti-C mixture.

A comparison of the XRD peaks for Zn-Ti-C prepared using the three different metal ratios reveals the presence of pure Ti (at  $\sim 64^\circ$ , PDF# 88-2321) that did not participate in the formation of TiC during the HEMM processes. As the Ti content increases, the existence of pure Ti becomes more pronounced. Because pure Ti does not contribute to the increase in capacity due to its inertness toward Li ions, high content of pure Ti can reduce the specific capacity of the electrode. Conversely, in the absence of carbon (i.e., in  $\text{ZnTi}(2:1)$ ), several additional peaks at  $\sim 47^\circ$ ,  $49^\circ$ ,  $56.5^\circ$ ,  $64^\circ$ , and  $68^\circ$  that can be indexed to  $\text{Zn}_2\text{Ti}$  (PDF#65-3575) are found along with the Zn peaks.

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