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Facile, mild and green synthesis of Zn_2GeO_4/graphene oxide nanocomposite with superior electrochemical performance

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Introduction

With the global warming problem becomes more severe, urgent demand of green energy pushes the scientists to search new energy production routes to replace the traditional fossil fuel. Rechargeable lithium batteries have been essential for the storage of renewable energy. To meet the increasing demand of high energy density materials, transition metal oxides such as SnO_2, GeO_2, Zn_2SnO_4 and Zn_2GeO_4 have been developed to replace the traditional graphite anode. However, poor cycle performance and low initial coloumbic efficiency become an obstacle for practical application because of huge volume expansion and irreversible of Li_2O. Herein, we develop a facile method to prepare a Zn_2GeO_4/graphene oxide composite with more satisfied electrochemical performances.

Experimental section:

Graphene oxide (GO) was prepared by our previous method and Zn_2GeO_4/GO composites were synthesized by an ion-exchange method. $Zn(Ac)_2$ and Na_2GeO_3 were mixed in a GO solution and stirred for a certain time. Then, the product was filtered and washed with deionized water and ethanol. The electrodes were prepared by mixing the active material, super P, and polyvinyldifluoride (PVDF) with a mass ratio of 70: 20: 10 in N-methylpyrrolidone to form slurry. The slurry was pasted onto a copper foil and dried in vacuum at 80 ºC for 24 h. Then it was cut into pieces with a diameter of 8 mm. The 2032 coin cells were assembled in a glovebox filled with argon. A lithium foil was used as the counter electrode. The mixed solvent (1:1 in volume) of ethylene carbonate and diethyl carbonate (EC/DEC) which contains 1 M $LiPF_6$ was used as the electrolyte. The galvanostatic charge-discharge tests were carried out using the Land battery measurement system (Wuhan, China) with a cut-off potential of 0.001–3 V vs. Li/Li^+.

Results and discussion

Fig.1a presents the XRD pattern of the Zn_2GeO_4/GO composite. All the diffraction peaks are perfectly indexed to the rhombohedral phase of Zn_2GeO_4 (JCPDS no. 11–0687; $a = b = 1.423$ nm, $c = 0.953$ nm). No obvious peaks corresponding to carbon are found in the XRD pattern, indicating that the carbon in the Zn_2GeO_4/GO product is not well crystallized. The size and morphologies were characterized by field-emission scan microscopy (FESEM). As shown in Fig. 1b, the nanorods with an average diameter of 40 nm and length of 500 nm were homogeneously dispersed in the graphene oxide layers. In a typical high-resolution TEM (HRTEM) image (Fig.1d), clear lattice fringes with a space of 0.228 nm are assigned to the {223} planes of rhombohedral Zn_2GeO_4, indicating the highly crystalline nature.

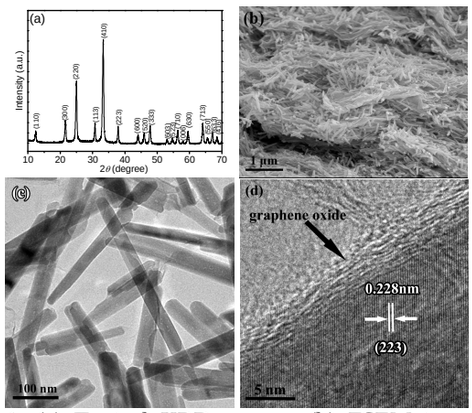

Fig. 1. (a) Typical XRD pattern, (b) FSEM image, (c) TEM image and (d) HRTEM image of as prepared Zn_2GeO_4/GO composite.

Fig. 2a shows the CV curves of the Zn_2GeO_4/GO composite. The anodic peak at about 1.3 V indicates the decomposition of Li_2O. As depicted in Fig. 2b, at the current density of 200 mA g^{-1}, its discharge and charge capacities are 1418 and 841 mAh g^{-1}, respectively. After 100 cycles, it can still maintain a reversible capacity of 1155 mAh g^{-1} with no obvious capacity fading (Fig. 2c). Moreover, it presents outstanding rate capability (Fig. 2d). These excellent electrochemical properties can be ascribed to the well protection of Zn_2GeO_4 nanorods by GO layers. They not only accommodate the volume expansion of Zn_2GeO_4 but also make the Li_2O reversible during the cycles.

In summary, a facile and green route has been developed to prepare Zn_2GeO_4/GO composites. GO layers can effectively prevent the strain arising from volume expansion of Zn_2GeO_4 nanorods and facilitate the decomposition of Li_2O during the cycle processes, leading to superior cyclability and rate capability.

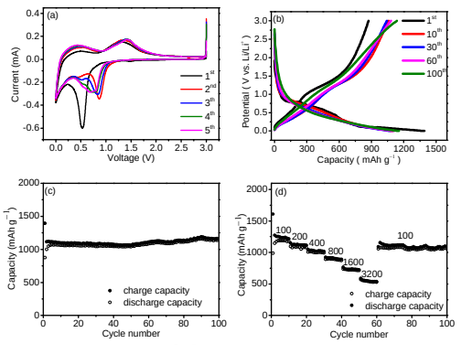

Fig. 2. (a) CV curves of the Zn_2GeO_4/GO composites at a scan rate of 0.2 mV/s between 0.001–3 V. (b) Discharge and charge curves and (c) Cycling performance of the electrode at a current density of 200 mA g^{-1} between 0.001–3 V. (d) Rate performance of the electrode at different current densities of 100, 200, 400, 800, 1600 and 3200 mA g^{-1}

References

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