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Nanosheets Self-Assembled 3D LiFeO4/Graphene as Cathode Material for Lithium-Ion Batteries

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In order to understand the feasibility of using graphene as cathode materials for lithium-ion batteries, this paper uses graphene as an additive to prepare graphene-coated three-dimensional flower-shaped FeO4 nanostructures by one-step hydrothermal method. The obtained composite nano-material is composed of FeO4 nano flower-balls assembled by graphene and dozens of nanosheets. The crystal structure and morphology of the material were characterized by XRD and SEM, and their electrochemical properties were also studied. After cycling 50 times at a current density of 1000 m Ah/g, the reversible capacity of the FeO4/graphene composite still reaches 503.1 m Ah/g and the capacity retention rate is as high as 82%.

1. Introduction

Battery is very common in modern life, it is a kind of convenient power supply. This premise indicates batteries have high application value, and modern society has a huge demand for electric energy. Traditional batteries can hardly meet the demands in many aspects, so it is necessary to study the batteries so as to improve their performance. Combining with previous studies, this paper learns a battery manufacturing method based on nanosheets self-assembled 3D LiFeO4/graphene. In theory, this kind of battery has a higher performance level, for this reason, this paper will verify it by analysis.

2. Literature review

$LiFeO_4$ is a polyanionic $LiMPO_4$ (M=Fe, Co, Ni, Mn, V) lithium ion battery cathode material with an olivine crystal structure. Generally, in the process of synthesizing $LiFePO_4$ or after the synthesis of $LiFePO_4$, different preparation methods, carbon sources, carbon addition amount, carbon distribution uniformity and other factors can have certain influence on the electrochemical performance of $LiFePO_4$. Graphene is commonly used as a direct carbon source (Tu et al., 2017). When graphene is oxidized, its insulating properties also limit its use in some electronic and energy storage devices. In order to further broaden the application of graphene oxide, its inherent properties are maintained and its conductivity is improved. Novel leaf-shaped graphene oxides with carbon nanotube (CNT) midribs were developed using vapor-grown carbon fibers (VGCF) by the conventional Hummers method. The CNT midrib provides a natural electron diffusion path for the leaf-shaped graphene oxide. Therefore, the leaf-shaped graphene oxide having a CNT midrib exhibits excellent performance when applied to an energy storage device (Guo et al., 2013).

$LiFePO_4$/0.5% graphene composites were synthesized by hydrothermal method using LiOH, H_3PO_4, $FeSO_4$ and reduced graphene as raw materials. Studies have shown that the addition of graphene can further reduce the size of the synthesized $LiFePO_4$ particles. The charge transfer resistance of the composite material is reduced, and the specific discharge capacity at 2.5C rate can reach 130.5 mAh/g (Wang et al., 2015). $FePO_4$/3DG was prepared by hydrothermal method using spherical $FePO_4$ and three-dimensional porous graphene as precursors, and then $LiFePO_4$/3DG/C composites were obtained by carbothermal reduction. The specific capacity of discharge at 1C rate was 144.7 mAh/g, and the capacity retention rate of 100 cycles was 99.6% (Yang et al., 2016). The layer-controlled graphene was prepared by using rapid thermal expansion and hydrogen reduction method as the anode material of the cesium ion battery. Electrochemical test results show that the smaller the number of graphene layers, the higher the first reversible specific capacity. The first

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specific capacity of single-layer graphene is 1175 mAh/g, while the first specific capacity of 5-layer graphene is only 842 mAh/g (Tong et al., 2011). By studying the difference between the small layer of graphene and the bulk graphite with respect to deintercalation, it was found that the single layer of graphene could not be embedded. The mechanism of deintercalation of a few layers of graphene and massive graphite is basically the same. Based on the excellent electrochemical properties of graphene, graphene is also used to modify various anode materials to obtain graphene-containing composite anode materials (Hui et al., 2016). In the hydrothermal reduction process, high concentrations of graphene sheets are easily re-stacked into a three-dimensional structure. At the same time, FeO4 helps stabilize this new graphene network. The obtained FeO4/G-As showed an interconnected graphene network with a large surface area and a large number of macropores.

The novel three-dimensional structure of FeO4/G-As can provide abundant sites for absorbing lithium ions and promote electrolyte contact and ion diffusion. Combined with the synergistic effect between layered FeO4 and graphene, FeO4/G-As achieve high levels of reversible capacity (Jiang et al., 2013). A novel flower-like nanostructured V_3S_4/graphene aerogel (V_3S_4-GA) hybrid was successfully synthesized as an effective electrocatalyst for oxygen reduction reaction (ORR). The flower-like V_3S_4 is uniformly grown on the surface of the graphene, which provides a large contact surface area with an electrolyte and a rich active site. This unique nanostructure provides excellent ORR catalytic performance for the synthesized V_3S_4/GA hybrid, including a high electron transfer rate of 3.97 per oxygen molecule (Deng et al., 2017). Zheng et al. coupled the FeO4 nanoparticles with three-dimensional reduced graphene oxide (3DRGO) to produce the FeO4@3DRGO complex. It exhibits remarkable cycle performance and high reversible capacity as an anode material for sodium ion batteries. The FeO4@3DRGO composite is equipped with 30nm FeO4 nanoparticles that can be firmly attached to 3DRGO. Compared with FeO4, FeO4@3DRGO has a higher specific capacity of 753.8 mAhg^{-1} at 0.1Ag^{-1} and has an excellent long cycle life. The capacity retention rate after 7 cycles of 2Ag^{-1} was 75.4% (Zheng et al., 2018).

In summary, using graphene as the main raw material, the synthesis of battery electrode materials is carried out by hydrothermal method, rapid thermal expansion and hydrogen reduction method, and coupling. According to the physical properties of graphene and unique active sites, the capacity of the material is increased. Although there are many reports on the synthesis of three-dimensional flower-like FeO4 nanostructures and graphene by hydrothermal synthesis of electrode materials, their capacity is generally low. Therefore, XRD and SEM techniques were used to synthesize a conforming material with better electrochemical performance and higher capacity retention.

3. Method

3.1 Experimental materials and tests

Experimental materials mainly include experimental drugs, FeO4 and FeO4/graphene composite material, button batteries, samples and electrochemical performance test, as described below.

3.1.1 Experimental drugs. All drugs used in the synthesis were AR and not further purified; graphene powder (GP).

3.1.2 FeO4 and FeO4/graphene composite materials. First, prepare a mixed solution of 40 mL water and 30 mL tetrahydrofuran, add 0.904g citric acid, 0.03g GP, stir for a while and uniformly disperse ultrasonically, then continue to add SnCl2·5H2O and Na2S2O3·5H2O with a molar ratio of 1:2, and then move the obtained solution to a 100mL PTFE-lined stainless-steel autoclave, seal and place it into an air blast oven at 200°C for 24 h, and then cooled to room temperature. Wash the sample several times with deionized water and absolute ethanol, collect the precipitate and dry it. At last, place the sample in a tube furnace at 450°C and calcined in a nitrogen atmosphere for 3h to obtain the FeO4/graphene composite (FeO4/GP), collect the obtained sample for subsequent characterization and performance testing. For comparison, prepare pure FeO4 sample without adding GP under the same conditions.

3.1.3 Button cell. The active material, the conductive agent (acetylene black), and the binder (PVDF) were mixed in a mass ratio of 8:1:1 and then ground uniformly. Move the mixture into a beaker, and add an appropriate amount of N-methylpyrrolidone (NMP), and then ultrasonically disperse to obtain a slurry with a certain viscosity. The slurry was evenly painted on a copper foil, dried in a vacuum oven at 80°C for 12h, compressed into sheets, weighed, transferred to an argon-filled glove box and assembled into a CR2032 button cell. The counter electrode was a lithium plate, and the electrolyte was a mixed solution of 1 mol/L Li PF6/ethylene carbonate (EC) + diethyl carbonate (DEC) (volume ratio is 1:1), and the diaphragm was a microporous polypropylene film.

3.1.4 Sample and electrochemical performance test. The structure and composition of the sample were analyzed using a Bruker D2 PHASER X-ray diffractometer, a Cu target source (Kαλ = 0.154 18 nm) was adopted, the tube voltage was 40 kV and the tube current was 30 mA; and a JEOLS-3400N SEM was used to observe the morphology of the product.

Electrochemical performance test: perform charge and discharge test (voltage range 0.01~1.2 V) with BT5-5 V/500 mA at different current densities; then, on the CHI660E electrochemical workstation, perform Cyclic Voltammetry (CV) test (scan speed is 0.1 m V/s, the scan voltage range is 0.01 to 2.0 V) and electrochemical impedance spectroscopy (EIS) test (AC battery potential is 0.5 V, frequency range is 100 kHz to 0.1 Hz). All tests were performed at room temperature.

4. Results

4.1 Analysis of structure and morphology

The XRD spectra of the FeO4 and FeO4/GP composite are shown in Figure 1. It can be seen from Figure 1 that all the diffraction peaks of the pure FeO4 sample matched well with the hexagonal Berndtite-2T type FeO4 (JCPD card number: 23-0677, space group: P-3m1), the diffraction peaks at 2θ of 15, 28.3, 32.1, 41.9, 50.0, 52.5, 54.9, 60.7, and 67.2° correspond to (0 0 1), (1 0 0), (1 0 1), (1 0 2), (1 1 0), (1 1 1), (1 0 3), (2 0 1), (2 0 1) crystal faces of the FeO4, respectively. All diffraction peaks were narrow and sharp, and no other impurity peaks were found, indicating that the product was pure phase FeO4 with good crystallinity. In addition to the diffraction peak corresponding to the pure phase FeO4, the two sets of FeO4/GP composite showed a new diffraction peak at 26.5°, which corresponded to the characteristic diffraction peak of graphene on the (0 0 2) crystal face. The results showed that the composite consisted of FeO4 and graphene.

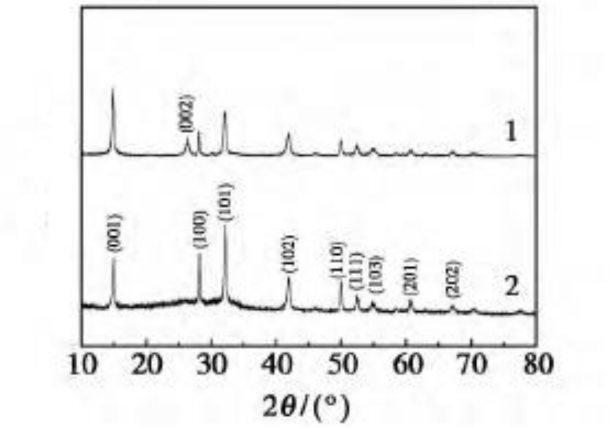

Figure 1: XRD spectra of the samples

The SEM images of the pure FeO4 sample and the FeO4/GP sample are shown in Figures 2, 3, 4. It can be seen from Figure 2 and Figure 3 that dozens of nanosheets were interlaced and self-assembled into a nanoflower-like morphology. The average size of each nanoflower is between 1.5 and 2 μm. The nanosheets that make up the nanoflowers have a thickness of about 80 nm. Some of the FeO4 nanoflowers are uniformly grown on the graphene surface and some are wrapped between the graphene layers. As can be seen from Figure 4, the average size of the FeO4 nanoflowers is between 2 and 2.5 μm, and the thickness of the composed nanosheets is about 20 nm. The thickness of FeO4 in the composite material is significantly thinner because the hydrothermally synthesized FeO4 has a typical sheet structure, the upper and lower surfaces of the nanosheets are (±001) crystal faces, and the addition of graphene provides template for nucleating and growth of FeO4, which inhibits the growth of FeO4 in the C-axis direction to a certain extent and reduces the accumulation of the FeO4 layers, so the thickness of the FeO4 nanosheets becomes thinner. More sheets were interdigitated into a rose-like FeO4, and these rose-like sheets have a morphology with relatively large specific surface area, which can increase the contact area between the material and the electrolyte and shorten the diffusion path of Li+.

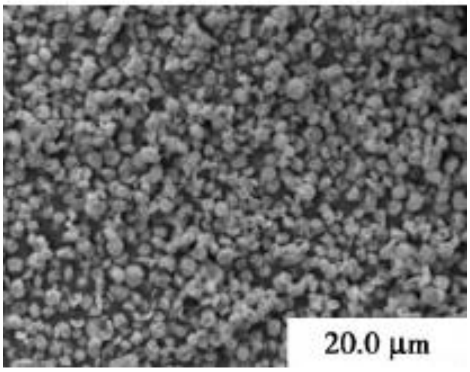

Figure 2: SEM diagram of sample (a)

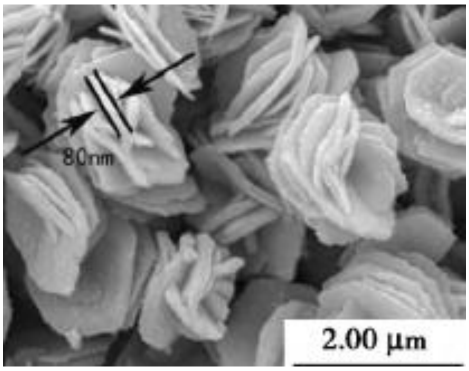

Figure 3: SEM diagram of sample (b)

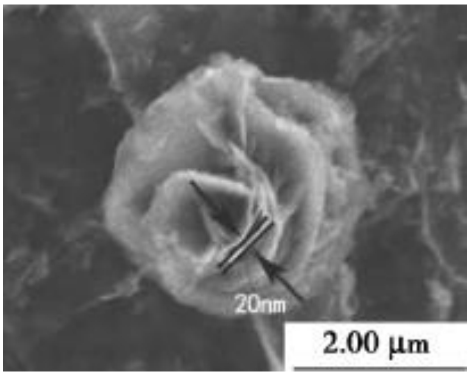

Figure 4: SEM diagram of sample (d)

4.2 Electrochemical performance analysis

The charge and discharge curves of the pure FeO4 and FeO4/GP samples are shown in Figure 5. In the measurement, the current density was 1000 m Ah/g and the electrochemical window was set between 0.01 and 1.2 V. As can be seen from the figure, the first-time discharge capacity and the first-time charge capacity of pure FeO4 are 1171. 5 m Ah/g, 371. 19 m Ah/g, respectively, and the first coulombic efficiency (CE) is only 31%. The first-time discharge capacity and the first-time charge capacity of the FeO4/GP samples are 1525. 34 m Ah/g, 582.7 m Ah/g, respectively, and the first coulombic efficiency (CE) is 38%. The first large irreversible capacity is due to the LixFeO4 embedded in Li was irreversibly decomposed into Sn and amorphous Li2S, and it's also influenced by the decomposition of the electrolyte components and the growth of the solid electrolyte (SEI) film on the electrode surface. After the second cycle, the discharge capacities of the pure FeO4 and FeO4/GP samples are 340.9 m Ah/g, 619.9 m Ah/g, respectively, and the charge capacities are 330. 3 m Ah/g, 579. 4 m Ah/g, respectively. The composite has a higher capacity than pure FeO4.

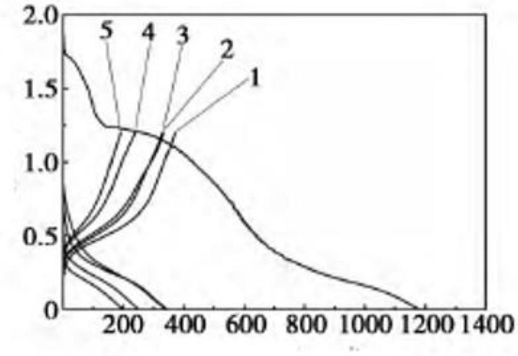

Figure 5: Charge-discharge curve

4.3 Comprehensive analysis

After the addition of graphene, the composite has faster charge transfer rate, and faster lithium ion migration rate, resulting in high reversible capacity and good rate performance. Compared with pure FeO4 material, FeO4/GP composite effectively improves the electrochemical property of the material.

5. Conclusion

In this paper, a simple one-step hydrothermal method was used to synthesize graphene-composite three-dimensional flower-like FeO4 nanostructures. These three-dimensional flower-like FeO4 nanostructures were assembled from dozens of nanosheets and grown between the layered networks of graphene. It can be seen that the FeO4/GP composite has better cycle performance and rate performance. Other research results are as follows.

FeO4 nanoflowers and graphene nanosheets are interconnected to form a 3D network structure, so that graphene can effectively wrap the FeO4 nanoflowers, and the excellent flexibility of graphene can effectively buffer the volume expansion of FeO4 anode material during charging and discharging, so as to improve the cycle performance of the material.

The addition of graphene greatly improves the electronic conductivity of the material, and the electrons can quickly pass through the graphene sheet layers, which can effectively improve the rate performance of the material.

Looking forward, the battery includes cathode and anode electrodes as a whole, but this paper only studies the cathode electrode of lithium-ion battery. In terms of battery manufacturing, the research in this paper is incomplete, and the research on anode electrode should be supplemented in the subsequent studies.

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