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Short Communication

Superior high-rate capability of hierarchically structured flower-like magnetite–carbon–graphene composite for Li-ion anode



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ABSTRACT

A nano/micro hierarchical composite structure is prepared by solvothermal synthesis from iron alkoxide in an inert atmosphere. It consists of graphene sheet and flower-like Fe_3O_4 particle covered by carbon coating (designated as $\text{Fe}_3\text{O}_4@\text{C}$). The synthesized composite is an excellent anode for Li-ion batteries. This is attributed to its double structure of current collector. High reversible lithium storage capacity (1439 mA h/g at 0.2 C after 47 cycles) and superior high-rate capability (619 mA h/g at 5 C) are examples of this property. The carbon coating of the $\text{Fe}_3\text{O}_4@\text{C}$ is in direct contact with the Fe_3O_4 particles to form local conductive connections, $\text{Fe}_3\text{O}_4@\text{C}$ tightly covering graphene sheets can be employed as the current collector as well as bridge connection of the $\text{Fe}_3\text{O}_4@\text{C}$ particles. Therefore, the double structure of current collector can form superior-conductivity networks, providing an efficient electron transport between active materials and Cu current collectors. This double structure prevents the break down of electric connection between the active material and the current collector during protracted cycles of charge and discharge.

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Introduction

Rechargeable lithium-ion batteries (LIBs) have long been considered as the most effective and practical technology for

electrochemical energy storage. The development of electrode materials with high rate performance and sustained life cycles are crucial for the practical application of such battery systems. Creating carbon-based composites containing the active material of Fe_3O_4 have been designed with reversible lithium

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storage capacity [1–5]. However, their low capacity of 200–400 mA h/g at high rate of 2 C–5 C were not satisfied with the practical application. Therefore, in recent years, many researcher began to attempt the truly durable high-rate capability along with high capacity Fe_3O_4 as anode materials for LIBs [6,7]. These synthetic compounds are both based on an optimized composite structure of graphite matrix/metal oxide nanoparticles. Although improvement can be detected in electrode performance, the high-rate capability needs further development in considerations of the durable high-rate capabilities.

Graphene indicates some unique advantages in energy storage applications [8,9]. Compared to the graphite, the high surface-to-volume ratio and open porous systems of graphene show great advantages in fast ion transport enabling the high rate capability, which is a bottleneck for graphite with microsize bulk lithium diffusion. To fully use all the potential advantages of graphene in LIBs, fabrication of graphene/metal oxide composites is expected to be an effective and practical method. From the viewpoint of structure, on one hand, metal oxides anchored or dispersed on graphene not only suppress the agglomeration and restacking of graphene but also increase the available surface area of the graphene alone, leading to high electrochemical activity. On the other hand, graphene as a support of metal oxides can induce the nucleation, growth and formation of fine metal oxide nano-/microstructures with uniform dispersion and controlled morphology on the surface of graphene with high chemical functionality. The final metal oxide-anchored graphene and the graphene-supported metal oxide can form a perfect integrated structure with a developed electron conductive network and shortened ion transport paths.

Based on the aforementioned principles, we report a new kind of nano/micro double structure of current collectors containing graphene sheets and flower-like Fe_3O_4 covered by a carbon coating (designated as $\text{Fe}_3\text{O}_4@\text{C}$). This design reveals the full potential of the composite. Therefore, when employed as anodes for LIBs, the as-obtained nanocomposite may exhibit high reversible lithium storage capacity and superior high-rate capability.

Experimental

In a typical procedure, two different contents of 50 and 100 mg graphene (prepared by chemical exfoliation [10]), 1.2 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 2.7 g urea, and 7.2 g tetrabutylammonium bromide were added to 180 ml ethylene glycol (EG). Two mixture solutions were stirred with a magnetic stirrer bar and heated to reflux (195 °C) for 0.5 h. After the reactions were cooled to room temperature, two mixtures of iron alkoxide precursor/graphene were collected by centrifugation, washed with ethanol four times, and dried at 60 °C in an oven overnight. Afterwards the products were heated to 450 °C and maintained at this temperature for 3 h under nitrogen to obtain black powders. The samples were prepared with 50 and 100 mg graphene were designated as G50 and G100, respectively. Moreover, the same synthesis without graphene was also carried out and designated as $\text{Fe}_3\text{O}_4@\text{C}$.

The products were characterized by scanning electron microscopy (SEM, PHILIPS, XL-30FEG), X-ray diffraction pattern (XRD, X'Pert PRO with CuK α radiation, $\lambda = 0.1542$ nm, 40 kV, 100 mA), and Raman spectra (Renishaw inVia + Reflex Raman spectrometer, excitation wavelength 514 nm). The content of carbon element in $\text{Fe}_3\text{O}_4@\text{C}$, G50 and G100 was determined with an Element Analyzer (EA, VarioEL III). The electrochemical properties of the G50, G100 and $\text{Fe}_3\text{O}_4@\text{C}$ as anode materials in LIBs were evaluated by a galvanostatic charge–discharge technique. The test electrodes were prepared by mixing 80 wt.% active materials ($\text{Fe}_3\text{O}_4@\text{C}$, G50 or G100) with 10 wt.% acetylene black and 10 wt.% poly(vinylidene fluoride) dissolved in N-methyl-2-pyrrolidone to form a homogeneous slurry, which was then uniformly coated onto the copper foil substrate with a blade. The as-prepared electrode sheets were placed in a vacuum oven at 120 °C to evaporate the solvent. Afterwards, the copper foil was punched into small disks with a diameter of 14 mm. The capacity was based on the mass of the G50, G100 and $\text{Fe}_3\text{O}_4@\text{C}$. Coin cells were assembled in an argon-filled glove box with the samples as the test electrode, metallic lithium as the counter/reference electrode, a mixture of 1 M LiPF_6 in ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate (1:1:1 vol) as the electrolyte and Celgard 2400 polypropylene as the separator. The discharge–charge tests were performed in the voltage range of 0.01–3.0 V (vs. Li/Li^+) at current rates from 0.2 C to 5 C (The theoretical capacity of $\text{Fe}_3\text{O}_4@\text{C}$, G50 and G100 will be calculated in Part 3). EIS measurements were measured on P4000 electrochemical workstation with the frequency range from 0.01 Hz to 100 kHz.

Results and discussion

Fig. 1(a) shows the SEM image of $\text{Fe}_3\text{O}_4@\text{C}$ composed of many uniform, flowerlike architectures samples were approximately 3–5 μm in diameter. The detailed morphology of the flowerlike nanostructures is shown in Fig. 1(b), which reveals that the entire structure is built from several dozen nanopetals with smooth surfaces. These nanopetals are about 60–90 nm thick and 1 μm wide, and connected with each other through the center to form 3D flowerlike arrangement. The morphology of $\text{Fe}_3\text{O}_4@\text{C}$ is very similar to those of the reported samples [11]. The crystallographic structure in the XRD pattern (Fig. 1(c)) of $\text{Fe}_3\text{O}_4@\text{C}$ was identified to be magnetite Fe_3O_4 (JCPDS No. 19-0629). The strong diffraction peaks indicate good crystallinity of the Fe_3O_4 phase, while no diffraction peaks of the graphite were detected in the XRD pattern, indicating the poorly crystallized nature of the carbon layer. Raman spectroscopy was performed to analyze the phase composition of the products after the solvothermal reaction, as shown in Fig. 1(d). For $\text{Fe}_3\text{O}_4@\text{C}$, broad weak bands centered at around 670 cm^{-1} were observed, corresponding to the A1g mode of Fe_3O_4 . The characteristic D and G bands for the carbon were observed at 1355 and 1582 cm^{-1} , respectively. The above results confirm that the sample $\text{Fe}_3\text{O}_4@\text{C}$ is composed of the magnetite Fe_3O_4 phase and carbon.

It can be clearly seen in Fig. 2(a) and (b) that the flowerlike iron alkoxide precursor and the $\text{Fe}_3\text{O}_4@\text{C}$ particles are distributed on graphene sheet surface before and after

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