



Short communication

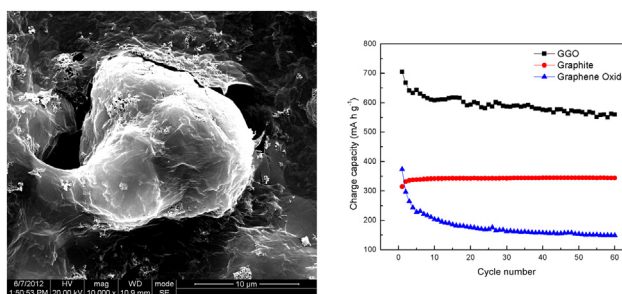
Graphite/graphene oxide composite as high capacity and binder-free anode material for lithium ion batteries

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HIGHLIGHTS

- Graphite/graphene oxide composite is prepared for high capacity and binder-free anode.
- The reversible capacity of this composite exceeds 690 mA h g^{-1} at 0.5 C .
- The composite exhibits excellent cycle performance and rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

A composite of graphite and graphene oxide is synthesized and used as a high capacity and binder-free anode material directly in lithium-ion batteries for the first time. The scanning and transmission electron microscope analyses of the composite show the graphite particles and conductive additive are homogeneously distributed on the graphene oxide surface. The X-ray photoelectron spectroscopy result indicates that the oxygen containing groups of graphene oxide have been partially reduced during the first discharge process. Electrochemical tests reveal that this composite has more than 690 mA h g^{-1} reversible capacity at the rate of 0.5 C ($1 \text{ C} = 372 \text{ mA g}^{-1}$), simultaneously with excellent cycle performance and rate capability.

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1. Introduction

Since the lithium-ion batteries (LIBs) were commercialized by the Sony Company in the early 1990s, carbon-based materials have

been extensively used as anode materials in LIBs owing to their unique physical and electrochemical properties, although they revealed a low theoretical Li-ion storage capacity (372 mA h g^{-1}) [1]. Ongoing research efforts have focused on utilizing various new carbonaceous materials to improve the Li-ion storage capacity as well as cycle life and rate capability.

Graphene, a monolayer of carbon atoms, is often manufactured by reducing graphene oxide [2], has attracted significant attention

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recently [3]. Due to its unusual properties such as high surface area to volume ratio, extraordinary electronic transport property and chemical stability [4], graphene holds many promising applications. One of the exciting possibilities is the application of graphene used as LIBs electrode materials. The studies of graphene-containing electrode materials, such as graphene modified LiFePO_4 cathode materials [5], graphene composites with nanosize alloys or transition metal oxides [6–8], and silicon nanoparticles–graphene paper composites [9], were explored by many researchers. And the Li-ion storage configuration of graphene proposed as anode material was not to be the conventional LiC_6 , but the new LiC_3 [7], Li_2C_6 [10] or LiC_2 [11], which indicated a Li-ion storage capacity of 744, ~ 780 and $\sim 1116 \text{ mA h g}^{-1}$ respectively. Therefore, graphene is suggested to be an ideal candidate to replace graphitic carbon as the commercial anode material.

As the precursor of graphene, graphene oxide also has a higher lithium storage capacity than graphite [12,13] and performs excellent chemical stability and dispersity in water [14]. Besides, the preparation of graphene oxide is simple and feasible, and its cost is lower than graphene itself because it does not need a reduction treatment. However, graphene oxide is still on the periphery of attention, and the reports about its direct use as anode material in LIBs are hardly viewed.

Recently, many graphene-based nanocomposites have been applied as anode materials in LIBs [15–18]. However, these nanocomposites are synthesized costly in the view of commerce applications. In order to find a cheap and simple method to synthesize novel graphene-based materials used as electrode in LIBs, we apply a composite of commercial graphite, carbon black and graphene oxide (termed as GCG). In this composite, graphite can play a great role in holding out aggregation of graphene oxide sheets, stabilizing electrochemical property and providing Li-ion storage capability. Furthermore, this composite could be directly used as electrode without adding any other binders, because graphene oxide is effortless to form self-assembly membrane after drying. As such, the specific weight capacity of the GCG electrode could be improved in comparison with conventional electrodes which are assembled from a mixture of polymer binder, conductive additive and active materials. Electrochemical tests indicate that this GCG electrode exhibits a relatively high capacity, excellent rate capability, and cycling stability, as anode material of LIBs. To the best of our knowledge, for the first time, this could provide a new indication of applying graphene oxide directly in LIBs.

2. Experimental

2.1. Preparation of graphene oxide and GCG composite

Graphene oxide was synthesized from high-purity natural flake graphite (about 200 meshes, Changsha Shenghua Research Institute, 99.999%) by the Hummers method [19]. And the colloidal dispersion of graphene oxide in deionized water at the concentration of 1 mg ml^{-1} was prepared with the aid of ultrasound (20 kHz ultrasound probe) treatment about 15 min to give a stable brown dispersion. Conductive additive used in the composite was Super-P carbon black (40 nm, $62 \text{ m}^2 \text{ g}^{-1}$, TIMCAL Graphite & Carbon). The anode slurries of graphene oxide, GCG and graphite were prepared by mixing adequate deionized water with (a) graphene oxide and carbon black (in a graphene oxide/carbon black weight ratio of 83:17), (b) graphite, graphene oxide and carbon black (in a graphite/graphene oxide/carbon black weight ratio of 66:17:17, nominated as GCG-17%), (c) graphite, CMC (carboxymethyl cellulose, Aldrich, and M.W. 90,000) and carbon black (in a graphite:CMC:carbon black weight ratio of

66:17:17) through vigorously stirring for 3 h, respectively. Electrodes were fabricated by coating all above three slurries on Cu foil and dried overnight at 110°C . The above processes were repeated with variation of graphite/carbon black/graphene oxide weight ratio to 75:17:8 (GCG-8%), 71:17:12 (GCG-12%), 62:17:21 (GCG-21%) and 58:17:25 (GCG-25%).

2.2. Characterization

Scanning electron microscope (SEM) studies were performed using an INCA PentaFETx3 microscope equipped with energy dispersive X-ray spectroscopy detector (EDS, to determine the chemical composition). The thickness of graphene oxide film was determined by atomic force microscope (AFM, SPI4000). The morphology of the GCG was characterized by transmission electron microscope (TEM, JEM-100CX JEOL). The elemental compositions and the assignments of the carbon peaks were characterized using the X-ray photoelectron spectroscopy (XPS, PHI5600 Physical Electronics). X-ray diffraction (XRD) patterns were obtained from X'Pert MPD DY1219 using $\text{Cu/K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The specific surface areas and porosities were calculated by using the Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–Halenda (BJH) method based on the adsorption branches of isotherms. The results of nitrogen adsorption–desorption isotherms measurements are presented in [Supplementary data](#).

2.3. Electrochemical measurements

Electrochemical measurements were performed at room temperature (25°C) using two-electrode CR2032 coin cells assembled in an argon-filled glove box. A Celgard 2400 was employed as separator. Lithium foil was used as counter electrode. The electrolyte obtained from Capchem. Technology (Shenzhen) Co., Ltd. consisted of a solution of 1 M LiPF_6 in ethylene carbonate, dimethyl carbonate, diethyl carbonate (EC/DMC/DEC, 1:1:1, in volume). Galvanostatic charge and discharge experiments were conducted at various rates on a BS-9300R battery test system, over the potential range 0.01–3.0 V versus Li^+/Li . The cyclic voltammograms (CV) tests were performed on a LK9805 workstation.

3. Results and discussion

According to the TEM, SEM and AFM results of graphene oxide revealed in [Fig. 1a–c](#), it is clear that the single layer graphene oxide (0.55 nm thickness) with typical wrinkled paper-like structure has been prepared successfully by Hummers methods. [Fig. 1d](#) shows the C1s XPS spectrum of graphene oxide. The four dominant peaks emerged at 284.6, 285.7, 286.7 and 288.2 eV correspond to C–C/C=C, C–N, C–O and C=O species, respectively [20,21]. The weak peak at 285.7 eV ascribes to a C–N species, which is resulted from the oxidation process. The peaks at 286.7 and 288.2 eV confirm the presence of hydroxyl, epoxy and carbonyl groups on the surfaces and edges of the graphene oxide sheets.

Microscopic observation results of the graphene oxide, GCG-17% and graphite electrodes are given in [Fig. 2](#). [Fig. 2a](#) shows the micro-appearance of graphene oxide electrode, which has a typical two dimensional (2D) wrinkled paper-like structure. The sole carbon black particles are packaged by graphene oxide sheets and dispersed uniformly. And in [Fig. 2b](#), there are only agglomerate carbon black and graphite particles conglomerated by CMC in graphite electrode. In comparison, as observed in [Fig. 2c](#), the graphene oxide sheets wrapping graphite and carbon black particles can be vividly viewed in GCG-17% electrode. In this composite, the carbon black particles are homo-dispersed between the graphene oxide sheets and graphite particles, which are beneficial for

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