



# A comparative study of electrochemical performance of graphene sheets, expanded graphite and natural graphite as anode materials for lithium-ion batteries



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## ABSTRACT

Three kinds of carbon materials, i.e., graphene sheets (GSs), expanded graphite (EG) and natural graphite (NG) were comparatively investigated as anode materials for lithium-ion batteries via scanning electron microscope, high-resolution transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy and a variety of electrochemical testing techniques. The test results showed that the reversible capacities of GS electrode were 1130 and 636 mA h g<sup>-1</sup> at the current densities of 0.2 and 1 mA cm<sup>-2</sup>, respectively, which were almost twice those of EG electrode and three times those of NG electrode. The first-cycle coulombic efficiency and capacity retention of NG were much bigger than those of GSs and EG. The notable capacity fading observed in GSs and EG may be ascribed to the disorder-induced structure instability. The larger voltage hysteresis in GS and EG electrodes was not only related to the surface functional groups, but also to the active defects in GSs and EG, which results in greater hindrance and higher overvoltage during lithium extraction from electrode. The kinetics properties of GSs, EG and NG electrodes were compared by AC impedance measurements. GS and EG electrodes exhibited higher electrochemical activity and more favorable kinetic properties during charge and discharge process.

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## 1. Introduction

Lithium-ion batteries, as power sources for portable electronic devices and electric vehicles, have attracted much attention in the scientific and industrial fields due to their high energy density, high operating voltage and low self-discharge rate. The energy density and performance of lithium-ion batteries largely depend on the physical and chemical properties of cathode and anode materials. To meet the increasing demand for lithium-ion batteries with high reversible capacity and energy density, much effort has been made to develop new electrode materials or design novel structures of electrode materials [1–10]. Graphite is the widely commercial anode material for lithium-ion batteries because of its high coulombic efficiency and better cycle performance [11]. The electrochemical properties of graphitized carbons as anode materials for lithium-ion batteries have been systematically investigated [12–16]. However, the theoretical specific capacity of graphite is only 372 mA h g<sup>-1</sup> (by forming intercalation compounds (LiC<sub>6</sub>))

[15]. In order to enhance the reversible capacity of electrode, various attempts to introduce the defects, channels and functional groups on the graphite surface have been investigated [17–20].

Graphene is a two-dimensional one-atom-thick planar sheet of sp<sup>2</sup> bonded carbon atoms, which is considered as the fundamental foundation for all fullerene allotropic dimensionalities. It is regarded as the “thinnest material in the universe” with tremendous application potential [21,22]. Since the paper on the freestanding graphene was published by Novoselov et al. [23], the preparation, structure and property of graphene have attracted great attention owing to its particular quantum Hall effect, sensitivity, mechanical hardness, electrical conductivity and so on [24–28]. Recently, graphene nanosheets as anode materials were investigated and exhibited large reversible capacity [11,29–32], it has been demonstrated that the graphene sheets (GSs) of ca. 0.7 nm thickness could provide the highest storage density (with a Li<sub>4</sub>C<sub>6</sub> stoichiometry) by density of states calculations [33]. Yoo et al. [29] investigated the possibility of higher lithium storage capacity by controlling layered structures of graphene nanosheet materials. The flexible graphene papers were fabricated by Wang et al. [30], and it was found that the graphene paper exhibits distinguishable electrochemical properties compared with graphite. Tong et al. [31]

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investigated the controllable synthesis of GSs with different numbers of layers and effect of the number of graphene layers on the specific capacity of anode material in lithium-ion batteries.

In this work, high quality GSs with fewer layers (1–4 layers) were successfully prepared by a rapid heating process and a following ultrasonic treatment using flake natural graphite (NG) powder as the starting material. Expanded graphite (EG) was prepared from NG by intercalation reaction and thermal exfoliation. The electrochemical performances of GSs, EG and NG as anode materials for lithium-ion batteries were comparatively investigated in coin-type cells.

## 2. Experimental

GSs were prepared in three steps: the oxidation of flake NG via a modified Hummers' method [34], rapid heat treatment and ultrasonication.  $\text{KMnO}_4$  was employed as the oxidant to obtain graphite oxide (GO). Firstly, 1 g of flake NG powder with the mean diameter of 15  $\mu\text{m}$  (provided by Dong Xing Electrical Carbon Co., Ltd., China) was added to 23 ml of cooled ( $0^\circ\text{C}$ ) concentrated  $\text{H}_2\text{SO}_4$ . Then 3 g of  $\text{KMnO}_4$  was added gradually with stirring and cooling, so that the temperature of the mixture was maintained below  $10^\circ\text{C}$ . The mixture was then stirred at  $35^\circ\text{C}$  for 30 min. After this, 46 ml of distilled water was slowly added to cause an increase in temperature to  $98^\circ\text{C}$  and the mixture was maintained at that temperature for 15 min. The reaction was terminated by adding 140 ml of distilled water followed by 10 ml of 30%  $\text{H}_2\text{O}_2$  solution. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution until sulfate could not be detected with  $\text{BaCl}_2$ , and then the resultant GO was dried at  $65^\circ\text{C}$  overnight. GO were quickly sent to a muffle furnace pre-heated to  $1050^\circ\text{C}$  in the air atmosphere to obtain EG. EG was dispersed into ethanol and delaminated into GSs under a 600 W ultrasonic agitation for 15 h. The desired GSs were obtained after vacuum drying.

The morphology and structure of the samples were observed by scanning electron microscope (SEM, Hitachi S-4700) and high-resolution transmission electron microscope (HRTEM, JEOL 3010). X-ray diffraction (XRD) analysis was conducted on a Rigaku D/max-2500B2+/PCX system using  $\text{Cu}/\text{K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The information of functional groups was measured by Fourier transform infrared spectroscopy instrument (FTIR, Nicolet Nexus 670). Raman spectra were recorded on JY HR800 (France) in plus laser Raman spectrometer with a 532 nm laser (0.1 mW). Nitrogen adsorption and desorption isotherms were performed at 77 K on a Quantachrome NOVA4200e (USA) volumetric adsorption system. The specific surface areas were calculated from the adsorption data using the BET (Brunauer–Emmett–Teller) method.

The electrochemical performances of GSs, EG and NG were measured with the coin-type cells. The lithium sheets were used as both reference and counter electrodes, and composite electrodes comprising active mass (GSs, EG or NG, 85 wt.%), carbonaceous additive (acetylene black, 5 wt.%) and poly(vinylidene difluoride) (PVDF, 10 wt.%) binder were used as working electrodes. 1 M  $\text{LiPF}_6$  solution in a 1:1 (volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) from Merck Co. was used as electrolyte. The Celgard 2400 microporous polypropylene film provided by Jimitex Electronic (Shenzhen) Co., Ltd. was used as separator. The coin-type cells were galvanostatically discharged (Li insertion) and charged (Li extraction) in the voltage range from 0.01 to 3.50 V vs.  $\text{Li}/\text{Li}^+$  at the current densities of  $0.2 \text{ mA cm}^{-2}$  and  $1 \text{ mA cm}^{-2}$ , respectively. Electrochemical impedance spectroscopy measurements of the electrodes were carried out on an electrochemical workstation (Princeton VersaSTAT3-200) using the frequency response analysis. The impedance spectra were obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz.

## 3. Results and discussion

### 3.1. Morphology and structure of GSs, EG and NG

The morphology and structure of GSs and EG were characterized by SEM and HRTEM and their images are shown in Fig. 1. Fig. 1a exhibits the SEM image of EG with a porous structure, showing that the graphite has been efficiently exfoliated to ultrathin sheets with wavy structures. Fig. 1b exhibits the SEM image of GS agglomerate, consisting of almost transparent carbon nanosheets with thin wrinkled structure. GSs are entangled with each other and resemble crumpled papers as shown in Fig. 1c. Moreover, the thin wrinkled structure represents a curled and corrugated structure that the graphene owns intrinsically [35]. Fig. 1d is a HRTEM image with larger magnification of GSs with fewer layers (1–4 layers).

The structural changes from NG to GSs were investigated by XRD measurement, and the patterns are shown in Fig. 2. The XRD pattern of NG exhibits a characteristic peak (002) of graphite at  $26.52^\circ$ . After oxidation, the (002) peak of graphite disappears and an additional peak at  $11.56^\circ$  is observed, which is corresponding to the (001) diffraction peak of GO. The *d*-spacing of GO increased to 0.765 nm from 0.335 nm of graphite, which is ascribed to the oxide-induced O-containing functional groups and inserted  $\text{H}_2\text{O}$  molecules [30,36] that can be confirmed by FTIR. These results suggest that NG has been completely oxidized. After rapid heat treatment, the diffraction peak of GO disappears, indicating that GO has successfully exfoliated to GSs. Fig. 3 shows FTIR spectra of NG, GO, EG and GSs. NG shows a skeletal vibration of C–C in hexahydric ring at  $1005 \text{ cm}^{-1}$ , corresponding to the planar  $\text{sp}^2$  structure that graphite owns intrinsically [24]. For GO, the peak at  $3405 \text{ cm}^{-1}$  can be attributed to O–H stretching vibrations of adsorbed water molecules and structural OH groups, and the peak at  $1619 \text{ cm}^{-1}$  can be attributed to O–H bending vibrations. The presence of carboxyl and epoxy functional groups can also be detected at around  $1724 \text{ cm}^{-1}$  and  $1224 \text{ cm}^{-1}$ ,  $1053 \text{ cm}^{-1}$ , respectively [30,36]. These evidences indicate that during the oxidation process of NG with  $\text{KMnO}_4$  in the concentrated sulfuric acid, the original extended conjugated  $\pi$ -orbital system of NG were destroyed and oxygen-containing functional groups were inserted into carbon skeleton. However, after a rapid thermal treatment, these functional groups derived from the intensive oxidation were eliminated, which can be proved by the disappearance of the peaks at  $1724 \text{ cm}^{-1}$ ,  $1619 \text{ cm}^{-1}$ ,  $1224 \text{ cm}^{-1}$  and  $1053 \text{ cm}^{-1}$  while an appear of a new peak at  $1570 \text{ cm}^{-1}$  reflecting the skeletal vibration of GSs [11,36]. These evidences indicate that GO have been successfully exfoliated to GSs by thermal exfoliation.

Raman technology was performed to indicate the structures of NG, EG and GSs by the resulting characteristic G and D bands sensitive to defects and disorder, respectively. The G band arises from the zone center  $E_{2g}$  mode, corresponding to ordered  $\text{sp}^2$  bonded carbon, while the D band is ascribed to edges, other defects and disordered carbon [24,30]. Significant structural changes occurring during the chemical processing from NG to EG and to GSs were characterized by Raman spectroscopy, as shown in Fig. 4. The existing exclusive G band at  $1580 \text{ cm}^{-1}$  and extremely weak D band at  $1350 \text{ cm}^{-1}$  in the spectrum of NG indicate the ordered planar  $\text{sp}^2$  structure held by graphite. After oxidation and rapid heat process, the G bands of GSs and EG get broad and weakened, while D bands become increasingly strong. The Raman spectra of GSs and EG also contain both D and G bands (at  $1596 \text{ cm}^{-1}$  and  $1351 \text{ cm}^{-1}$ ,  $1587 \text{ cm}^{-1}$  and  $1368 \text{ cm}^{-1}$ , respectively). However, the D/G intensity ratios of GSs ( $I_D/I_G = 0.721$ ) and EG ( $I_D/I_G = 0.717$ ) are larger than that of graphite ( $I_D/I_G = 0.162$ ). The data indicate that extensive oxidation and rapid thermal exfoliation have induced a substantial decrease of the size of the in-plane  $\text{sp}^2$  domains, as well as an

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