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Lithium storage properties of graphene sheets derived from graphite oxides with different oxidation degree

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Abstract

Electrochemical properties of graphene sheets (GSs) for lithium ion batteries were investigated. GSs were prepared from graphite through oxidation followed by rapid thermal exfoliation. To synthesize graphite oxides (GOs) with different oxidation degree, the number of times of oxidation of graphite was controlled from 1 to 3 times. GSs electrodes derived from 1, 2 and 3 times oxidized GOs exhibited a high charge capacity of 1252, 1793 and 2311 mAh g^{-1}, respectively, at the 20th cycle at a current density of 100 mA g^{-1}. As the oxidation degree of GO increased, the reversible capacity of GSs was enhanced. The enhanced capacity is assumed to be due to increased surface area and additional lithium storage sites such as defects and edges.

Keywords: E. Batteries; Electrodes; Graphene

1. Introduction

There has been an enormous increase in the demand for energy sources for application in portable electronics, transportation and renewable energy storage. Lithium ion battery (LIB) is considered to be one of the most promising batteries due to its high operating voltage and high energy capacity. For many years, graphite has been the most used anode material for LIBs because of its good life-cycle performance and high coulombic efficiency [1,2]. However, graphite has a limited theoretical capacity of 372 mAh g^{-1}, corresponding to the formation of LiC_6. To improve the energy capacities of LIBs, the use of anode materials with larger capacities is required.

Graphene sheets (GSs), single-atom-thick carbon sheets, have attracted considerable attention for an anode material for lithium ion batteries [3–5]. Compared with graphite, GSs have large specific surface area and more edges, defects and disorder in the structure [4,6]. Research in recent years has suggested that these factors are related to the enhancement of lithium storage capacity [4,7,8]. However, further detailed investigations are still required to clarify the lithium storage mechanism of GSs.

In this study, GSs were prepared by thermal exfoliation of graphite oxides (GOs) with different oxidation degree and their lithium storage properties were investigated.

2. Experimental section

2.1. Synthesis of GO and GSs

GO was synthesized from natural flake graphite by a Brodie method [9]. Graphite powder (1 g) was mixed with fuming nitric acid (20 mL). Then, $KClO_3$ (8 g) was added into the solution. After 4 h of reaction, the acid solution was diluted with distilled water (500 mL). The mixture was immediately filtered and washed with distilled water and methanol. To control the oxidation degree of GO, GO was oxidized using exactly the same oxidation process. Then, the oxidation process was repeated once more to obtain the most oxidized graphite.

GSs were prepared by rapid thermal exfoliation of GO at 1050 °C for 15 s in a muffle furnace.

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2.2. Characterization of GO and GSs

X-ray diffraction (XRD) analysis was conducted using X-ray diffractometer D8 ADVANCE (BRUKER). The morphologies of GO and GSs were observed by scanning electron microscopy (SEM) on a S-4500 (Hitachi) and atomic force microscopy (AFM) using a SPI3800N (Seiko Instruments). The Brunauer–Emmett–Teller (BET) surface areas of GSs were measured by Micromeritics Tristar3000.

2.3. Electrochemical performances of GSs

Electrochemical measurement was performed using a three-electrode cell with lithium strips as the counter electrode and reference electrode. The working electrode was fabricated by pressing a mixture of 90 wt% GSs and 10 wt% polytetrafluoroethylene onto a Ni mesh at a pressure of ~300 MPa. The electrolyte was 1 M $LiClO_4$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v%). Galvanostatic charge/discharge tests were carried out in the voltage range of 0.01–3.6 V (vs. Li/Li^+) on a 1470E Cell Test System (Solartron Analytical).

3. Results and discussion

Fig. 1 shows XRD patterns of graphite, GO and GSs. As shown in Fig. 1a and b, the interlayer spacing (d_{002}) of GO increased from 0.337 nm to 0.643 nm of graphite, which is ascribed to the oxygen containing functional groups and inserted H_2O molecules [4]. After rapid thermal exfoliation, the diffraction peak of GO disappears (Fig. 1c), indicating that functional groups are removed by thermal exfoliation through the release of CO_2 gas [6].

Fig. 2a shows SEM image of GSs. Wrinkled paper-like structured graphene sheets were agglomerated and stacked. Fig. 2b shows AFM image of GSs. GSs were 1–2 nm in average thickness and several hundreds of nanometers in width. This means that GSs were composed of a few layers of graphene. The specific surface area of GSs measured using the BET method was 849 $m^2 g^{-1}$. This result, that a few layers of graphene are agglomerated and stacked, is reasonable because the theoretical surface area of graphene is 2630 $m^2 g^{-1}$ [10].

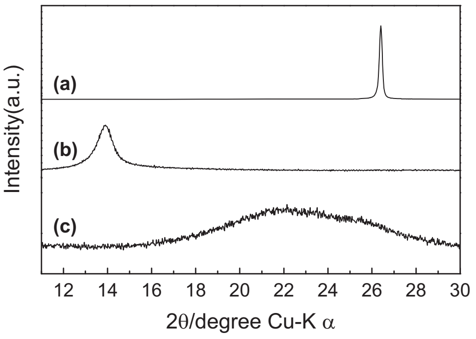

Fig. 1. XRD patterns of (a) graphite, (b) GO and (c) GSs.

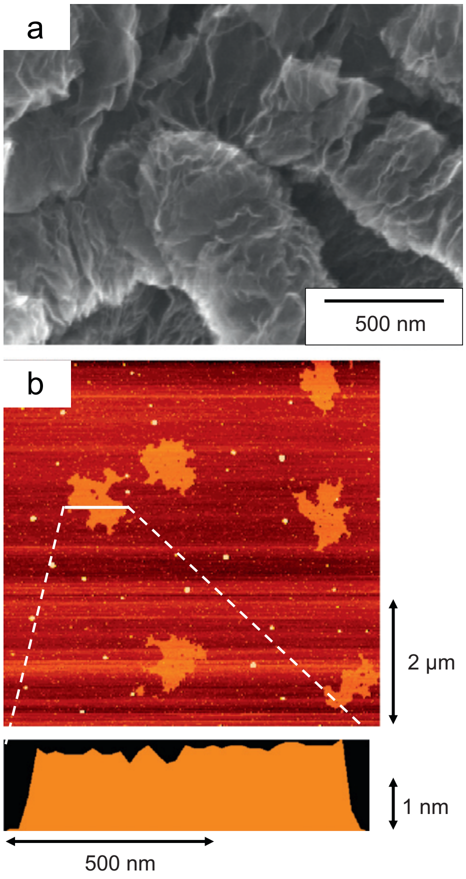

Fig. 2. (a) SEM image and (b) AFM image of GSs.

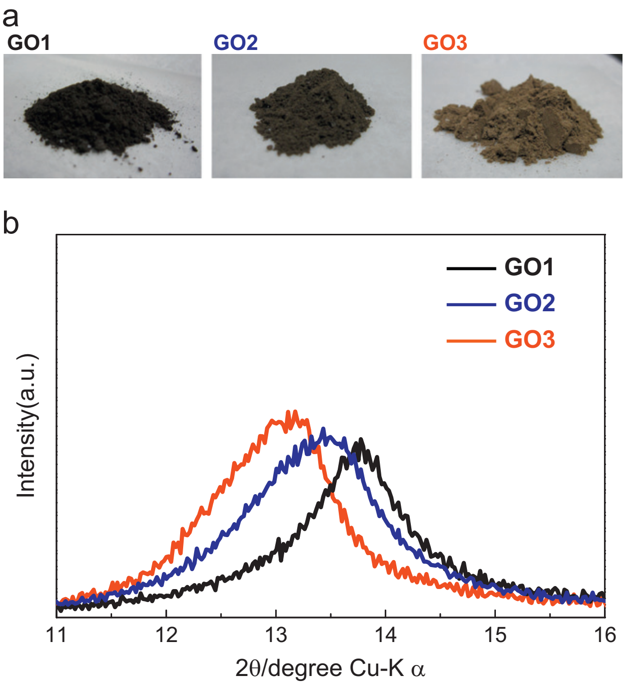

Fig. 3. (a) Photos and (b) XRD patterns of different GOs.

Table 1
Specific surface areas of GSs1, GSs2 and GSs3.

Sample	GSs1	GSs2	GSs3
Specific surface area ($m^2\ g^{-1}$)	849	884	991

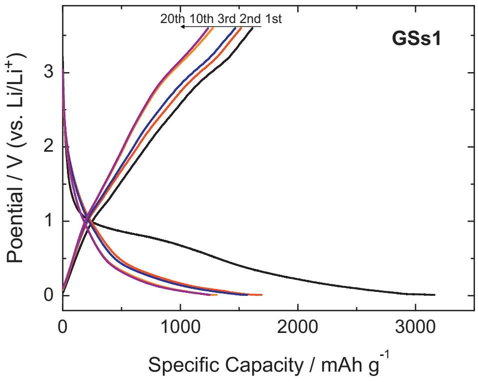

Fig. 4. Charge/discharge profiles of GSs1 at a current density of 100 mA g^{-1}.

The number of times of oxidation of graphite was controlled from 1 to 3 times in order to synthesize GOs with different oxidation degree. The three samples will be denoted henceforth as GO1, GO2 and GO3. The color of GO is related to the oxidation degree [11]. As shown in Fig. 3a, GOs become brighter as the number of times of oxidation is increased, indicating that oxidation degree is increased. Fig. 3b shows XRD patterns of GOs. The diffraction peak was shifted to lower angles (GO1: 13.77°, GO2: 13.47° and GO3: 13.12°), indicating that the interlayer distance of GOs (GO1: 0.643 nm, GO2: 0.657 nm and GO3: 0.674 nm) is increased due to the concentration of functional groups. GSs were synthesized by thermal exfoliation of GOs with different oxidation degree. Graphene sheets derived from GO1, GO2 and GO3 are GSs1, GSs2 and GSs3, respectively. Specific surface areas of the obtained GSs are shown in Table 1. As the oxidation degree of GO increased, specific surface area of GSs became larger. This indicates that GO which is highly oxidized is easier to exfoliate.

Fig. 4 shows charge/discharge profiles for GSs1. GSs1 exhibited large voltage hysteresis and no distinguishable potential plateaus which is similar to the disordered carbons [12]. Charge/discharge profiles of GSs2 and GSs3 are not shown in Fig. 4, but the shape of curve is similar to GSs1. The first charge capacity of GSs1 was 3163 mAh g^{-1}. However, the first discharge capacity was only 1615 mAh g^{-1}. This high irreversible capacity could be explained from the formation of the solid electrolyte interface (SEI) film on the electrode surface and the reaction of lithium ions with functional groups on the GSs [13,14]. After 20 cycles, it was found that the charge capacity was still maintained at 1252 mAh g^{-1}.

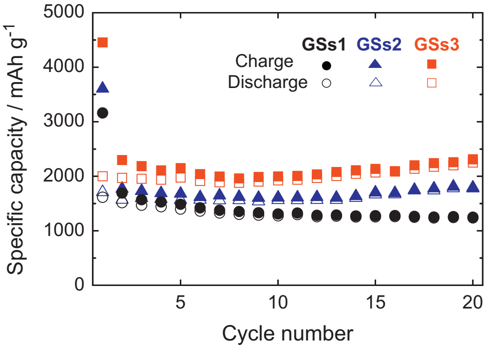

Fig. 5. Cycle performances of GSs1, GSs2 and GSs3 at a current density of 100 mA g^{-1}.

Fig. 5 shows the cycling performances of the obtained GSs at a current density of 100 mA g^{-1} for 20 cycles. The reversible capacity and cycle performance of GSs2 and GSs3 are improved in comparison with GSs1. In the cases of GSs2 and GSs3, the charge capacity was 3606 and 4453 mAh g^{-1} at the first cycle and 1793 and 2311 mAh g^{-1} at the 20th cycle, respectively. These enhanced capacities are assumed to be due to an increase in the surface area of GSs [4]. The difference in capacities of the obtained GSs indicates that large reversible capacity is related to the surface area. In addition, an increase in the reversible lithium storage sites, such as lattice defects and edges in the electrode structure could be another reason for the enhancement [4,15]. Defects are introduced into graphene sheets when GSs are prepared by thermal exfoliation because of the release of CO_2 [6]. Graphene sheets derived from GO with higher oxidation degree can have more lithium storage sites such as defects and edges, indicating that enhancement of capacities is reasonable.

4. Conclusions

GSs were prepared from graphite through oxidation followed by rapid thermal exfoliation. The obtained GSs showed a large specific surface area though a few layers of graphene are agglomerated and stacked. Furthermore, GSs derived from GOs with different oxidation degree were prepared. As the oxidation degree of GO increased, the reversible capacity of GSs became larger. The enhanced capacities are assumed to be due to increased surface area and additional lithium storage sites such as defects and edges.

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