



Effects of sulfur doping on graphene-based nanosheets for use as anode materials in lithium-ion batteries



Young Soo Yun^{a,c}, Viet-Duc Le^b, Haegyeom Kim^c, Sung-Jin Chang^{d,h}, Seung Jae Baek^e,
Sungjin Park^f, Byung Hoon Kim^g, Yong-Hyun Kim^b, Kisuk Kang^c, Hyoung-Joon Jin^{a,*}

^a Department of Polymer Science and Engineering, Inha University, Incheon 402-751, South Korea

^b Graduate School of Nanoscience and Technology, KAIST, and Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon 305-701, South Korea

^c Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, South Korea

^d Division of Materials Science, Korea Basic Science Institute (KBSI), Daejeon 305-333, South Korea

^e Department of Nano Science and Technology, Seoul National University, Seoul 151-747, South Korea

^f Department of Chemistry and Chemical Engineering, Inha University, Incheon 402-751, South Korea

^g Department of Physics, Incheon National University, Incheon 406-772, South Korea

^h Department of Chemistry, Chung-Ang University, Seoul 156-756, South Korea

HIGHLIGHTS

- Sulfur-doped graphenes are utilized for anode materials in lithium-ion battery.
- Sulfur doping on graphenes contributes to the high specific capacity of the battery.
- A first-principles calculation shows good agreement with the experimental results.
- High rate performance is achieved by the improved electrical conductivity of anodes.
- A stable cycle life over 500 cycles is achieved at a high current density of 1488 mA g⁻¹ (4 C).

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ABSTRACT

Graphene-based nanosheets (GNS) have been studied for use in electrochemical energy storage devices. A deeper understanding about the system is required for achieving enhanced power output and high energy storage. The effects of sulfur doping on the electrochemical properties of GNS are studied for their use as an anode material in lithium-ion batteries. Sulfur doping in GNS contributes to the high specific capacity by providing more lithium storage sites due to Faradaic reactions. In addition, superior rate performance of sulfur-doped GNS (S-GNS) is achieved through the improved electrical conductivity of S-GNS (1743 S m⁻¹), which is two orders of magnitude higher than that of GNS (32 S m⁻¹). In addition, good cyclic stability of S-GNS is maintained even after 500 cycles at a high current density of 1488 mA g⁻¹ (4 C).

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1. Introduction

Lithium-ion batteries (LIBs) have attracted considerable academic and industrial interest as an energy storage device owing to their ever-increasing and urgent demand in widespread applications such as portable electronics and electrical/hybrid vehicles [1].

As such, studies worldwide are focusing on developing LIBs with high reversible capacity, excellent rate capability, and good cycling stability [1–4]. But traditional graphite-based anode materials show low Li-storage capacity (372 mA h g⁻¹) owing to the limited Li ion storage sites (LiC₆) within the sp² carbon hexahedrons, and relatively low rate capability, owing to the intrinsic nature of the intercalation process [5,6].

Graphene, a single layer of sp²-hybridized carbon atoms, has attracted considerable interest for use in various applications because of its outstanding physical properties [7–9]. Single-layer

* Corresponding author. Tel.: +82 32 860 7483; fax: +82 32 865 5178.

E-mail address: hjjin@inha.ac.kr (H.-J. Jin).

graphene with a disordered structure was speculated to form Li_2C_6 because both graphene surfaces can host Li ions [10–14]. In addition, heteroatoms, nanoscale cavities, and active defects such as edges and vacancies in graphene nanosheets have been suggested to accommodate additional Li ions [13,14]. Graphene-based nanosheets (GNS) induced by oxidation and reduction contain numerous oxygen heteroatoms, nanoscale holes, and defects owing to the imperfect restoration of the original sp^2 bonding character as well as the disordered structure [15,16]. Consequently, GNS can exhibit high Li ion storage capability. Furthermore, shortening the diffusion length of Li adatoms and increasing the electronic conductivity by doping in GNS can lead to fast kinetics [11,17,18]. Several studies have already achieved high electrochemical performances using defect-engineered GNS [19–22]. In particular, Wang et al. [19] reported that a GNS anode showed a reversible capacity of 650 mA h g^{-1} during the first charging cycle at a current density of 1 C within the voltage range $0.02\text{--}3.0 \text{ V}$ and a specific capacity of 460 mA h g^{-1} even after 100 cycles. Guo et al. [18] reported a similar result. These properties of a GNS are closely related to oxygen content, which greatly enhances the electrochemical performance of the GNS anode.

Sulfur, a chalcogen, can be incorporated into carbon-based anode materials. Sulfur-doped carbon-based materials have been reported to show increased reversible capacity [23,24]. Moreover, sulfur-doped porous carbon hybridized with graphene has been reported to show high capacity and excellent rate performance [25]. These results suggest that sulfur doping can be used for enhancing the electrochemical performances of carbon-based anodes. But studies have not yet clarified the effects of sulfur doping as well as the effects of sulfur heteroatoms on LIB anodes. In addition, the use of sulfur-doped GNS (S-GNS) as an anode material for LIBs has not yet been attempted.

In this study, the effects of sulfur doping on GNS for potential use as an anode material for LIB were investigated. This study attempts the first fundamental understanding of the effect of sulfur in GNSs with the intention of gaining insights into GNS-based anode materials.

2. Experimental

2.1. Preparation of S-GNS and GNS

Graphene oxide (G–O) was prepared from natural graphite (Sigma–Aldrich) using the Hummers method. Aqueous G–O suspensions were frozen in liquid nitrogen and then freeze-dried using a lyophilizer (LP3, Jouan, France) at $50 \text{ }^\circ\text{C}$ and 4.5 Pa for 72 h. After lyophilization, low-density and loosely packed G–O powders were obtained [26]. 100 mg of the as-obtained lyophilized G–O powder and 100 mg of elemental sulfur powder (Sigma–Aldrich, 99.98%) were mixed in a mortar. The mixture was thermally treated in a tubular furnace from room temperature to $600 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ and an Ar flow rate of 200 mL min^{-1} . The reaction mixture was held at this temperature ($600 \text{ }^\circ\text{C}$) for 2 h. The resultant product was stored in a vacuum oven at $30 \text{ }^\circ\text{C}$ without any washing process. In addition, GNS without sulfur was prepared by repeating the same procedure without the elemental sulfur powder.

2.2. Characterization

The topographical images of GNS and S-GNS were obtained using an atomic force microscope (NT-MDT, Russia) with a NSG-10 cantilever (NT-MDT, Russia) in semicontact operation mode. Raman measurements were performed using a NTEGRA Spectra

spectrometer (NT-MDT, Russia) equipped with a 473 nm (2.62 eV) laser in backscattering configuration. The spectral resolution was $\sim 2 \text{ cm}^{-1}$ with a 600 grooves/mm grating. A $100\times$ objective (N.A. 0.9) provided a laser spot size of $\sim 330 \text{ nm}$. The laser power was kept well below 0.3 mW for nondestructive Raman measurements. The spectrometer was equipped with a piezoelectric scanner that allowed Raman mapping of an area up to $130 \times 130 \text{ }\mu\text{m}$. Elemental analysis (EA) was performed using an EA1112 (CE instrument, Italy). X-ray photoelectron spectroscopic analysis (XPS, PHI 5700 ESCA) was performed using monochromated Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). The samples for XPS measurement were pressed onto metal substrates in order to correct the charge-up. Infrared spectroscopy (IR) was performed using VERTEX 80v (Bruker Optics, Germany). To measure the electrical transport properties, S-GNS and GNS flakes were deposited on $300\text{-nm-thick SiO}_2/\text{highly p-doped Si}$ wafers. The electrodes were fabricated by conventional electron beam lithography (acceleration voltage: 30 keV). Ti/Au ($5/50 \text{ nm}$) were deposited using an e-gun evaporation system in high vacuum ($< 1 \times 10^{-3} \text{ Pa}$) and lift-off procedures. Temperature-dependent $I\text{--}V$ characteristics were determined by the conventional two-probe method in the Janis cryogenic system with a semiconductor characterization system (4200-SCS, Keithley). The electrical measurements were performed after vacuum degassing for 12 h ($< 5 \times 10^{-4} \text{ Pa}$).

2.3. Electrochemical characterization

The electrochemical performances of GNS and S-GNS were evaluated using a Wonatec automatic battery cycler and CR2016-type coin cells. The working electrodes were prepared by mixing the active material (80 wt.%) with conductive carbon (10 wt.%) and polyvinylidene fluoride (10 wt.%) in *N*-methyl-2-pyrrolidone (NMP). The resultant slurries were uniformly applied to Cu foil. The electrodes were dried at $120 \text{ }^\circ\text{C}$ for 2 h and roll pressed. The coin cells were assembled in a glove box filled with argon and employing a composite electrode with metallic lithium foil and 1 M LiPF_6 (Aldrich, purity: 99.99%) dissolved in a solution of ethylene carbonate/dimethyl carbonate/diethyl carbonate ($1:2:1 \text{ v/v}$) as the electrolyte. The cells were galvanostatically cycled between 0.01 and 3.0 V vs. Li/Li^+ at various current densities.

2.4. First-principles simulation

We employed density functional theory (DFT) with Perdew–Burke–Ernzerhof (PBE) exchange correlation and all-electron-like projector-augmented plane wave (PAW) potential as implemented in the Vienna ab initio simulation package (VASP). All simulations were performed with a 6×6 graphene supercell and a vacuum region of 15 \AA . A plane-wave basis set with a kinetic energy cutoff of 500 eV and a k -point grid ($4 \times 4 \times 1$) were used for total energy calculations. All structural relaxations were carried out until atomic forces became less than $0.015 \text{ eV \AA}^{-1}$.

The thermodynamic stability of S-related defects in graphene was examined by calculating the defect formation energy,

$$E_{\text{formation}} = E_{\text{tot}} - E_{\text{graphene}} - n \times \mu_{\text{S}} + n \times \mu_{\text{C}} \quad (1)$$

where E_{tot} and E_{graphene} are the DFT total energies of the S-doped system and pristine graphene, respectively, n is the number of C atoms replaced by S, and μ_{S} and μ_{C} are the chemical potentials of S and C, respectively, taken from alpha phase bulk sulfur and pristine graphene. The S-binding energy to defect sites was also calculated using

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