Publication information

Title	Effects of stage, intercalant species and expansion technique on exfoliation of graphite intercalation compound into graphene sheets
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Source	Journal of nanoscience and nanotechnology , v. 11, (2), February 2011, p. 1084-1091
Version	Published version
DOI	https://doi.org/10.1166/jnn.2011.3063
Publisher	American Scientific Publishers

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Effects of Stage, Intercalant Species and Expansion Technique on Exfoliation of Graphite Intercalation Compound into Graphene Sheets

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Graphite is composed of a series of stacked parallel graphene layers bonded by weak van der Waals forces. Although the weak interactions that hold the graphene sheets together allow them to slide readily over each other, the numerous weak bonds make it difficult to separate the sheets. A graphene sheet is a two-dimensional platelet consisting of a few graphene layers with an overall thickness in nanometer scale. Graphene sheets can be obtained from intercalation and subsequent exfoliation of graphite. To realize the expansion and exfoliation behaviors of graphite, graphite intercalation compound (GIC) is produced using an electrochemical method and three important factors, namely stage structure of GIC, intercalant species and expansion techniques, are taken into account. Graphene sheets produced from a lower stage FeCl_3 -GIC display the best exfoliation behavior in terms of specific surface area, total pore volume and expansion volume. Microwave irradiation gives rise to a more explosive expansion than heating in a furnace.

Keywords: Graphite Intercalated Compound, Exfoliation, Stage Structure, Intercalant Species, Graphene Sheet.

1. INTRODUCTION

The mineral graphite is one of the allotropes of carbon. Graphite is a layered compound: in each layer, carbon atoms are covalently bonded into a hexagonal lattice on the basal plane; and these parallel graphene layers are stacked and bonded by weak van der Waals forces along the *c*-axis perpendicular to the basal plane. Due to the unique layered structure, different species of atoms, ions or molecules, the so-called intercalants, can be inserted into the graphitic galleries, forming a graphite intercalation compound (GIC). A GIC can be classified into a donor or an acceptor type depending on whether the intercalants give up electrons or accept electrons from the host graphite, respectively.¹ The donor species includes alkali metals, alkaline earth metals and rare earth metals, while the acceptor species includes chlorides, fluorides, acids, and halogens. One of the most important and characteristic ordering properties of a GIC is the staging phenomenon that occurs when the intercalate layers are arranged periodically.^{1,2} The intercalants occupy the graphitic galleries periodically along the *c*-axis direction, giving a regular stacking sequence and the number of

graphene layers between two adjacent intercalate layers defines the stage index *n*.

Several methods have been developed to synthesize GICs, such as vapor transport method or thermal method,^{3,4} chemical oxidation^{5–7} and electrochemical technique.^{8,9} The thermal method is usually carried out in a sealed glass ampoule, in which the graphite and intercalant species are placed separately. A vapor pressure is necessary to provide sufficient activation energy for intercalation at an elevated temperature. Although the thermal method can produce well-defined stages for GICs containing alkali metal or metal chloride as the intercalants, it is not suited for practical application in industry because of the severe chemical condition, long duration and difficulty in preparing homogeneous products in a large quantity. The chemical oxidation methods involve oxidation either by an intercalated species in a solution or with a specific oxidizing agent as an auxiliary agent. Sulfur has been widely used as an intercalate species to produce GICs for commercial applications, but these GICs often consist of non-uniform stages due to the low efficiency in intercalation and uncontrolled stoichiometry.² The electrochemical technique is known to be most appropriate amongst the techniques developed to synthesize GICs from both the scale and quality perspectives. Notable advantages of this

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approach include uniform stage structure and the speed and degree of reactions that can be easily controlled by adjusting the electrochemical parameters. For an acceptor-type GIC, the electrochemical process can be divided into three steps, namely anodic oxidation of graphite, insertion of intercalants between graphene layers, and stage formation and transformation. Many different intercalant materials have been studied, including sulfuric and nitric acids,^{5,8} metal chlorides,¹⁰ and alkali metals.¹¹

Graphite intercalated by different species presents various physical properties that are useful in different applications,⁷ such as high conductive materials, electrode materials for batteries, catalyzers for organic synthesis, and precursor materials to produce nanofillers for conducting polymer composites.^{6,12–14} The GICs containing intercalants can be expanded along the thickness direction¹⁵ upon rapid heating^{6,12,16} or microwave irradiation,^{11,17,18} through the expulsion of intercalants and thermal shock. The resulting spongy, porous, and accordion-like expanded graphite (EG) can be further exfoliated into graphite nanoplatelets (GNPs) or graphene sheets by ultrasonication.⁶ A high aspect ratio is a predominant criterion for graphene sheets to form conductive networks within polymer matrix for conducting composite applications.^{12,19,20} The aspect ratio of graphene sheets strongly depends on the expansion and exfoliation performance of GICs, which in turn are affected by several factors such as the stage of GIC, the intercalant species as well as the expansion techniques. The effects of these factors on the expansion and exfoliation behaviors of GICs are the subject of this study.

This paper is part of a larger project on the development of highly conducting graphene films and nanocomposites and continuation of our previous work^{12–14,21} on the surface-treated graphene sheets and their composites. Two acceptor-type GICs are synthesized in this study, namely H_2SO_4 -GIC and FeCl_3 -GIC. The electrochemical method is employed here, which can easily control the stage structure by varying the electrochemical parameters, such as electrolyte concentration, current density, potential value and reaction duration. Two different intercalant species, FeCl_3 and H_2SO_4 , are chosen here as they are known to produce stable, low-stage structures. Different expansion techniques, including heating in a furnace and microwave irradiation, are also taken into account.

2. EXPERIMENTAL DETAILS

2.1. Electrochemical Synthesis of GICs

2.1.1. Synthesis of H_2SO_4 -Intercalated GICs

The working electrode (WE) consisted of 0.2 g of natural graphite flakes (of 500 μm in diameter and 99.59% in purity, supplied by Asbury Carbons, USA) that were compressed into a fixture made of Teflon to form a thin plate

of a 1 mm thick 25 mm $\times$ 25 mm square. A platinum plate of 25 mm $\times$ 25 mm square and thickness of 0.5 mm served as the counter electrode (CE). A $\text{Hg}/\text{Hg}_2\text{SO}_4$ (0.615 V versus standard hydrogen electrode) was used as the reference electrode (RE). The experimental setup is shown in Figure 1. The electrochemical reaction was carried out using a computerized potentiostat (VoltaLab PGP 201) and the chronopotentiometry method was adopted for intercalation at room temperature. A 50 mL electrolyte solution was prepared using sulfuric acid with two different concentrations, namely 14 M and 18 M. The applied anodic current density was 0.7 mA/cm² and the reaction lasted for 50 ks. The resulting products were washed with acetone and dried in an oven at 60 °C overnight.

2.1.2. Synthesis of FeCl_3 -Intercalated GICs

The WE and CE were the same as those used in the synthesis of H_2SO_4 -GICs, whereas a Ag/AgCl (0.222 V versus standard hydrogen electrode) was used as RE. The electrolyte was a 50 mL FeCl_3 aqueous solution with concentration of 8 M. HCl was mixed with a FeCl_3 aqueous solution to increase the potential window and promote the intercalation process.⁹ The reaction temperature was

Fig. 1. Experimental setup for electrochemical synthesis of GIC.

kept constant at 75 °C. The chronopotentiometry at a current density of 5 mA/cm² was applied in the synthesis, which lasted for 50 ks. The resulting products were washed with acetone and dried in an oven at 60 °C overnight.

2.2. Expansion of GIC and Exfoliation of EG

To investigate the effects of intercalant species and stage on the expansion and exfoliation behaviors, the GIC synthesized by electrochemical reactions described above were put into a pre-heated furnace (Multitherm type S19) at 1050 °C for 30 s. Upon rapid heating, EG was obtained. The effect of expansion technique was studied using commercial GICs (supplied by Asbury Carbons, USA) with sulfur content of 2.8 wt% based on two different ways including thermal shock and microwave irradiation. The GICs were subjected to a thermal shock in a pre-heated furnace at a temperature ranging from 600 to 1100 °C at

an interval of 100 °C for 30 s. The GICs were also subject to microwave irradiation in a microwave oven (Whirlpool P801) at a frequency of 2.45 GHz for 30 s at three levels of power: 450 W, 650 W and 800 W.

The as-produced EG was ultrasonicated in acetone using a probe ultrasonicator (Branson 1510) at a power of 70 W and frequency of 42 KHz to separate the conjoint part of the accordion-like structure into pieces. Multi-layer graphene sheets were obtained after evaporation of acetone and drying in an oven at 80 °C overnight.

2.3. Characterization of GIC, EG and Graphene Sheets

The stage index of synthesized GICs was determined by X-ray diffraction (XRD, Powder X-ray diffractometer, X'pert Pro) analysis with Cu-K α radiation, 40 kV anodic voltage and 50 mA current. Scanning electron microscopy (SEM, JEOL6300) was employed to examine the morphologies of the samples at different steps of synthesis. Particle size was measured using a particle size analyzer (Coulter LS 230) based on the laser diffraction technique, and the thickness of graphene sheets were evaluated using a high resolution transmission electron microscopy (HRTEM, JEOL 2010F).

Fig. 2. XRD patterns of (a) stage-5 and (b) stage-7 H₂SO₄-GICs.

Fig. 3. XRD pattern of FeCl₃-GIC.

Table 1. BET results and expansion volume of EG produced from H₂SO₄-GICs and FeCl₃-GIC.

Intercalant species	Stage	Specific surface area (m ² /g)	Total pore volume (mL/g)	Expansion volume (mL/g)
H ₂ SO ₄	5	38.8	0.134	340
	7	24.3	0.073	210
FeCl ₃	5	49.5	0.164	421

Fig. 4. SEM images of (a, b) natural graphite flakes; (c, d) stage-5 H_2SO_4 -GIC; and (e, f) stage-5 FeCl_3 -GIC.

To measure the surface area and pore volumes of EGs produced using different intercalants, a Brunauer-Emmett-Teller (BET) surface area analyzer (Coulter SA3100) was used based on the nitrogen adsorption technique. The as-produced EGs were pretreated for outgassing at 300 °C for 3 h, followed by nitrogen adsorption at a cryogenic temperature. The volume/density method was used to estimate the expansion volume of EG. The weighed EG particles were poured into a measuring cylinder and tapped gently till the particles were completely settled down, and the approximate volume was then recorded. The expansion volume was determined from the volume to weight ratio (mL/g).

3. RESULTS AND DISCUSSION

3.1. Stage Determination

The stage structure of GIC was determined from the XRD diffractograms.^{22,23} Figure 2 presents the XRD patterns of stage-5 and stage-7 H_2SO_4 -GICs, which were synthesized in 18 M and 14 M H_2SO_4 electrolytes respectively, at the same current density of 0.7 mA/cm². The sandwich thickness d_s were given 7.95 Å and 7.98 Å for stage-5 and stage-7 GICs, respectively, both of which are consistent with the literature value of 8 Å.¹ Seen from Figure 2(b), a small peak marked “G” represents the original peak of graphite, which is due to incomplete intercalation.

The FeCl_3 -GIC presented in Figure 3 was synthesized in the aqueous solution mixed with 8 M FeCl_3 and 3 M HCl using the chronopotentiometry method. A constant current density of 5 mA/cm^2 was applied for 50 ks. In this XRD pattern, two reflections, (006) and (007) of stage-5 FeCl_3 -GIC were detected, although some peaks corresponding to the higher stages were also observed. The d_s calculated from stage-5 reflections was $9.63 \text{ \AA}$, which is close to the reported value of $9.40 \text{ \AA}$.¹⁰

3.2. Effect of Stage on Expansion Behavior of GIC

To understand the effects of stage on the expansion behavior of GIC, the specific surface area and the total pore volume of EG were determined using a BET surface area analyzer, as summarized in Table I. Upon heating GICs underwent dramatic and anisotropic expansion due to the expulsion of intercalants, resulting in the formation of an accordion-like porous structure with a large surface area. The BET results indicate that the EG produced from stage-5 GIC had a much larger specific surface area and total pore volume than that from stage-7 GIC. The stage phenomenon is described by a regular stacking sequence of intercalants in graphitic galleries. In the stage-5 GIC, the intercalants occupy galleries every 5th graphitic layers, which is more frequent than the stage-7 GIC. Therefore,

the lower the stage of GIC, the higher the surface area and pore volume to be produced.

Apart from the total pore volume obtained from the gas adsorption technique, the expansion volume is another parameter that is relevant to the porosity of a material. Based on the volume/density method, the expansion volume of EG was measured and is included in Table I. The stage-5 GIC gave a higher expansion volume of 340 mL/g than the stage-7 GIC of 210 mL/g , which is consistent with the BET results.

3.3. Effect of Intercalant Species on Expansion and Exfoliation Behaviors of GIC

Similar comparisons were made to investigate the effects of intercalant species. Also included in Table I are the BET results of EG obtained from GICs with different intercalants and of the same stage, as well as the corresponding expansion volumes. Assuming the same stage index, EG produced from FeCl_3 -GIC had a larger specific surface area and total pore volume than that produced from H_2SO_4 -GIC counterpart, indicating a much better exfoliation behavior of the former. Different in-plane structures of the intercalants along with different sandwich thicknesses of GICs were mainly responsible for the difference in exfoliation behavior. In H_2SO_4 -GIC, the sulfuric acids

Fig. 5. SEM images of EG obtained from stage-5 FeCl_3 -GIC at (a) low and (b) high magnifications (Scale bar: $100 \mu\text{m}$ and $10 \mu\text{m}$).

Fig. 6. SEM images of graphene sheets obtained from stage-5 (a) H_2SO_4 -GIC; and (b) FeCl_3 -GIC.

are intercalated as a liquid-like layer along with randomly-oriented HSO_4^- ions.¹ The density of intercalant layer was higher than that of liquid sulfuric acid,²⁴ suggesting the presence of a condensed 2D sulfuric acid layer within H_2SO_4 -GIC. In sharp contrast, the structure of FeCl_3 at graphite interlayers was found almost identical to the crystal structure of pristine FeCl_3 ,¹ and the sandwich thickness d_s of FeCl_3 -GIC was ~ 9.4 Å which is larger than that of H_2SO_4 -GIC (8 Å).

The SEM images presented in Figure 4 show typical morphologies of natural graphite flakes and stage-5 GICs with different intercalants. The surface of natural graphite flake was quite smooth and the edge was round. There were no sign of separation between graphene layers along the edge (Figs. 4a-b). After intercalation, however, the GICs exhibited a much rougher basal plane with sharp and delaminated edges (Figs. 4(c-f)). Delamination

is a direct reflection of the insertion and continuous diffusion of intercalants during the electrochemical reaction. A notable difference in morphology between H_2SO_4 -GICs and FeCl_3 -GICs is that the basal plane of the latter was in general rougher than the former GIC as a result of partial exfoliation of FeCl_3 -GICs (Figs. 4(c) vs. (e)).

The morphologies of EG obtained from stage-5 FeCl_3 -GIC are shown in Figure 5. At a low magnification (Fig. 5(a)), a large number of pores were observed on the surface, and each pore exhibited highly exfoliated thin graphitic layers (Fig. 5(b)). The comparison of the morphologies of the graphene sheets as shown in Figure 6 indicates that the graphene sheets obtained from FeCl_3 -GIC were almost transparent (Fig. 6(b)), suggesting they were thinner than those produced from H_2SO_4 -GIC (Fig. 6(a)). This observation further confirmed the better exfoliation behavior of FeCl_3 -GIC.

A HRTEM was employed to examine the dimensions of graphene sheets. The thickness of graphene sheets was estimated by carefully observing the folding area so as to count the number of graphene layers using the dark or light parallel lines. From the known d-spacing of graphite, 3.35 Å, the thickness of graphene sheet was calculated. Figure 8 shows the high resolution TEM images of typical graphene sheets with different thicknesses. Seen from Figure 7(a), the sharp edge without parallel lines indicates it consisting of a single-layer graphene. However, the majority of graphene sheets were multi-layered, as shown in Figure 7(b).

The particle size distribution of the above graphene sheets measured after ultrasonication for 5 h is given in Figure 8. The distribution was shown in the form of an asymmetric Gaussian function with a mean particle size of ~ 22 μm, which represented the dimension of the basal plane. Their average thickness estimated by HRTEM was ~ 1.6 nm, and the corresponding aspect ratio was approximated to an order of 10^4 , similar to our previous study on GNPs.¹²

Fig. 7. TEM images of (a) single layer; and (b) multilayer graphene sheets.

Fig. 8. Particle size distribution of graphene sheets.

3.4. Effects of Expansion Technique on Expansion Behavior of GIC

Figures 9 and 10 present the changes in the specific surface area and expansion volume of the EG produced at different temperatures in the furnace. It was clearly shown that both the properties increased linearly with increasing temperature. The specific surface area reached a maximum of $\sim 50 \text{ m}^2/\text{g}$ at $\sim 1000^\circ\text{C}$. The maximum expansion volume occurred at 1100°C was 292 mL/g . EG was also produced using the microwave oven at three different power levels, and the corresponding results are given in Table II. It is interesting to note that the intermediate power level of 650 W exhibited the highest efficiencies in terms of both surface area and expansion volume. When comparing the exfoliation behaviors between the EG produced using different techniques, the microwave irradiation in general gave rise to larger specific surface area and expansion volume. The increase in surface area and porosity is a reflection of the expansion of the gaseous cavities and exfoliation of the graphene sheets. In the thermal method, the pressure generated by the intercalants at a gas state is

Fig. 9. Specific surface area of EG produced in a furnace.

Fig. 10. Expansion volume of EG produced in a furnace.

Table II. Specific surface area and expansion volume of EGs produced by microwave irradiation.

Power (W)	Specific surface area (m^2/g)	Expansion volume (mL/g)
450	63.0	305
650	71.6	479
800	66.6	371

the major driving force for the fast and explosive expansion causing a large increase in surface area. There are several factors that are considered important in the expansion by microwave irradiation. H_2SO_4 molecules intercalated in the graphite galleries are a dipolar molecule whose vibration has a frequency similar to that of microwave vibration in an electromagnetic field.^{17, 18} The alternative changes of the electronic field may cause rotation, vibration and rapid oscillation of the dipolar moments, which in turn generates high heats and energies, allowing the activation state of the molecules in a very short time. These combined effects result in explosive expansion of GICs during microwave irradiation. Furthermore, because of the strong impact of expansion, the brittle conjoint part of EG may be separated, thus exposing more surface area with associated reduction in overall particle size.

4. CONCLUSIONS

The stage structure and intercalant species play important roles in determining the exfoliation behavior of GIC. The lower stage GIC exhibited a better expansion behavior, as reflected by higher specific surface area, total pore volume and expansion volume. The intercalated FeCl_3 , which maintains the crystal structure of itself, displayed a better expansion behavior than H_2SO_4 -GIC.

Different expansion technique also attributes to the expansion and exfoliation behaviors of GIC. Due to the integrated effects, microwave irradiation gives rise to a more explosive expansion than heating in a furnace.

Acknowledgment: This project was supported by Henkel International, formerly Imperial Chemical Industries Limited (Project number: ICIPLC001.07/08). Technical assistance from the Materials Characterization and Preparation Facilities (MCPF) and the Advanced Engineering Materials Facility (AEMF) of HKUST is appreciated.

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Received: 31 December 2009. Accepted: 9 February 2010.