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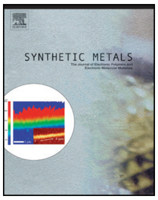

Investigation of the high, stable electrical conductivity in graphite intercalation compounds prepared from flexible graphite sheets

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ABSTRACT

Potassium–graphite intercalation compounds (K–GICs) prepared from flexible graphite sheets are unusually stable in air and their high electrical conductivity can be maintained for long periods. To investigate the reasons for this air-stability, we evaluated the changes in the electrical conductivity as a function of electrical carrier densities and mobilities, upon exposure of the GICs to air. These electrical carrier parameters were estimated using the measured electrical conductivity, magnetoresistance, and Hall coefficient. The decomposition processes varied depending on the characteristics of both the host graphite and the intercalated materials. In the case of K–GICs prepared from flexible graphite sheets, the electron density was decreased by the de-intercalation of K atoms. However, the electrical conductivity hardly changed, because the electron mobility was increased sufficiently to compensate for the decrease in the density. The recovery of the electron mobility was thought to be caused by the flexibility of the graphite layers. Therefore, it was found that the air-stability of GICs could be determined by considering the degree of de-intercalation as well as the flexibility of the graphite layers. Furthermore, the perfect graphite crystal is not suitable to prepare air-stable and high conductive GICs.

1. Introduction

Chemical species such as alkali metal atoms, metal halides, and halogen molecules can intercalate into the interlayers of lamellar graphite and form graphite intercalation compounds (GICs). A result of this intercalation is the occurrence of carrier transfer between the intercalated materials and adjacent graphite planes (graphene), causing the electrical conductivities of GICs to become approximately 10 times higher than those of the host graphite materials. However, GICs are known to be generally unstable in air. Most GICs are immediately decomposed by oxidation or the de-intercalation of intercalated materials when exposed to the atmosphere [1]. Historically, GICs have attracted much attention as light-weight conductive materials. The highest conductivities ever reported for GICs exceeded those of copper and silver [1]. However, the air-instability of GICs has obstructed their practical use.

Improving the air-stability of GICs is considered to be profitable. For example, nanocarbons, i.e., carbon-based nanosized materials such as graphene and carbon nanotubes, have been studied for practical use in electrodes [2,3], large-scale integrated circuits [4], and other applications. However, in order for nanocarbons to be used more effectively, the enhancement of their electrical conductivities is necessary. One technique that can increase the electrical conductivity of nanocarbons is intercalation [5]. However, the decomposition rates of GICs prepared from smaller graphite particles are faster, and they decompose easily in air [6]. Therefore, when carrying out the intercalation of nanocarbons, the lower air-stability of the intercalated products is a problem. In another example, we have studied the thermoelectric properties of GICs, and found that they have possible applications as thermoelectric materials [7–9]. Although, both *n*- and *p*-type GICs are necessary in thermoelectric applications, there are very few air-stable GICs, especially *n*-type GICs, reported in the literature.

In our investigations of GICs stability, we have succeeded in forming air-stable GICs that exhibit high electrical conductivity. In previous papers [10,11], we reported that potassium–graphite intercalation compounds (K–GICs) prepared from commercially available flexible graphite sheets (manufactured by the pyrolysis of polyimide films), exhibited high stability and high electrical conductivity for an extended period of time in air. However, we were unable to thoroughly explain the stabilization mechanism in the previous paper. We also found that Li–GICs could not be stabilized even when using the same flexible graphite sheet. Our ultimate goal is to establish an intercalation technique for carbon/graphite materials, which produces intercalation compounds with

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high electrical conductivity and air-stability. Therefore, it is important to first understand the stabilization mechanism in the previously studied K–GICs.

The air-stabilities of GICs are usually investigated by examining changes in their structure using X-ray diffraction (XRD), or by observing changes in their electrical conductivity. However, since we wish to use the intercalation technique for practical applications, we consider the long-term maintenance of high electrical conductivity in air as a particularly important parameter. Therefore, in this study, “stability” refers to the retention of high electrical conductivity. In our experience, the change in electrical conductivity is a more sensitive indicator of GICs decomposition than changes in the XRD patterns [12].

In this study, the causes for the stabilization of K–GICs prepared from flexible graphite sheets were investigated by monitoring the changes in electrical carrier densities and mobilities. Electrical conductivity is proportional to the product of the electrical carrier density and mobility. The electrical carrier density provides information about the amount of carrier transfer between the graphene and intercalated materials. In other words, it is thought that the electrical carrier density provides an indication of the amount of intercalated materials in the interlayers. Conversely, the electrical carrier mobility provides information about the number of scattering factors of the phonon. It is thought that the mobility also indicates the degree of perfection of the graphite structure. Therefore, an investigation of the carrier density and mobility can lead to an understanding of the amount of intercalated materials and the degree of perfection of the graphite crystalline structure.

2. Experimental

2.1. Preparation and measurements

PGS® graphite sheets with a thickness of 0.1 mm (Panasonic Co., EYGS 182310), GRAFOIL® sheets with thicknesses of 0.1 mm and 0.3 mm (GrafTech Co., GTA grade), and highly ordered pyrolytic graphite plates (HOPG) (NT-MDT Co., grades ZYH and ZYA) were used as the host graphite materials. PGS is produced by the thermal decomposition of a polyimide film [13–15]. GRAFOIL is made from H_2SO_4–GICs, which are prepared from pure graphite flakes. After the exfoliation of the GICs, the resulting exfoliated graphite is sheeted. The PGS and GRAFOIL sheets were cut into $3–5 \times 20–25\,\text{mm}^2$ rectangles. HOPG ($10 \times 10 \times 2\,\text{mm}^3$) was cleaved with the edge of a cutter and an adhesive tape, and cut into $10 \times 5 \times 0.3\,\text{mm}^3$ rectangles. GRAFOIL was heat treated under vacuum at 900 °C for 4 h before use to remove S, which is a common impurity.

Potassium, lithium, and anhydrous copper(II) chloride ($CuCl_2$) were used as the intercalate species without further purification. The GICs were prepared by allowing graphite to react with the vapor of the intercalate species at specific temperatures under vacuum. The reaction temperatures and durations for K, Li, and $CuCl_2$ intercalation were 473 K for 3 days, 723 K for 7 days, and 753 K for 45 days, respectively. The structures formed were saturated stage-1 structures, where the intercalated layers existed in all the graphite interlayers. The intercalated layers are inserted in an orderly manner into the graphene layers. In a stage-1 structure, there are intercalated layers between all the graphene layers, whereas in stage-2 and stage-*n* structures, the intercalated layers occur at intervals of two layers and *n* layers, respectively.

Measurements of the in-plane electrical conductivity (σ), magnetoresistance ($\Delta\rho/\rho$), and the Hall coefficient (R_H) were performed by the five-terminal method after the GICs specimens were exposed to air, as shown in Fig. 1, with magnetic fields (B) up to 0.5 T at room temperature. To measure the changes in the values over time, the specimens were kept on a measurement holder in air. The average temperature and humidity during the measurements, and storage were 293–300 K and 50%, respectively.

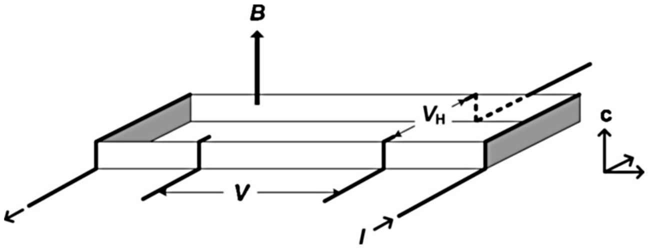

Fig. 1. Measurement set-up for the electrical conductivity (σ), magnetoresistance ($\Delta\rho/\rho$), and Hall coefficient (R_H).

2.2. Estimation of carrier density and mobility

The electrical carrier densities (n_e and n_h) and mobilities (μ_e and μ_h) were estimated from the values of σ, $\Delta\rho/\rho$, and, R_H [16,17]. In cases where $\Delta\rho/\rho$ was not detected, the transport was considered to occur through one-carrier conduction by either electrons or holes. Therefore, the carrier density (n) and mobility (μ) were estimated from Eqs. (1) and (2), where e is the electron charge.

$$\sigma = en\mu \tag{1}$$

$$R_H = -(1/ne) \tag{2}$$

In cases, where $\Delta\rho/\rho$ was detected, the transport was considered to occur via two-carrier conduction by both electrons and holes. The carrier densities and mobilities were then estimated using Eqs. (3)–(5).

$$\sigma = e(n_e\mu_e + n_h\mu_h) \tag{3}$$

$$R_H = -\frac{1}{e} \times \frac{n_e{\mu_e}^2 - n_h{\mu_h}^2}{(n_e\mu_e + n_h\mu_h)^2} \tag{4}$$

$$\Delta\rho/\rho = \frac{n_e n_h \mu_e \mu_h \times (\mu_e + \mu_h)}{(n_e n_h + \mu_e\mu_h)^2} \times \mathrm{B} \tag{5}$$

Furthermore, the approximations shown in Eqs. (6) and (7) were adopted for simplicity. Eq. (6) was used for graphite, whereas Eq. (7) was used for GICs.

$$\mu = \mu_e = \mu_h \tag{6}$$

$$(n_e \times n_h)_{\text{Graphite}} = (n_e \times n_h)_{\text{GIC}} \tag{7}$$

For practical calculations, we adopted Newton’s method for a quick and correct analysis [18]. In cases where the Newton’s method of analysis was not adopted, the trial and error methods were used. The set of parameter values (n_e,n_h, μ_e, and μ_h) to minimize the error was searched by scanning.

3. Results and discussion

3.1. Measured and estimated electrical properties of host graphite and K–GICs

In our previous work [10], the changes in the electrical conductivity of K–GICs specimens (with a composition of KC_8)