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Galvanomagnetic properties of air-stable and highly conductive potassium-intercalated graphite sheet

Yumemi Gotoh [a], Koji Tamada [a], Noboru Akuzawa [a,*], Rika Matsumoto [b], Masatsugu Fujishige [c], Kenji Takeuchi [c], Morinobu Endo [c], Yasushi Soneda [d], Tsutomu Takeichi [e]

[a] Tokyo National College of Technology, 1220-2 Kunugida, Hachioji, Tokyo 193-0997, Japan
[b] Tokyo Polytechnic University, 1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan
[c] Shinshu University, 4-17-1 Wakasato, Nagano-shi, Nagano 380-8553, Japan
[d] National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
[e] Toyohashi University of Technology, 1-1 Hibarigaoka, Tenpaku-cho, Toyohashi-shi, Aichi 441-8580, Japan

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ABSTRACT

Magnetoresistance and Hall coefficient of air-stable potassium-intercalated graphite sheets (hereafter abbreviated as K-PGS) were determined at room temperature. The magnitude of the magnetoresistance and the absolute value of Hall coefficient of K-PGS decreased with increasing potassium content of K-PGS, n_K/n_C. Two-carrier model was used for calculating carrier density and mobility. The electron density increased with increasing n_K/n_C: 3.07×10^{20} cm^{-3} (n_K/n_C=0.005), 5.67×10^{20} cm^{-3} (n_K/n_C=0.008) and 6.40×10^{20} cm^{-3} (n_K/n_C=0.011). The value of the electron density of K-PGS with n_K/n_C=0.011 (nominal composition KC_{91}) was about 80% of the reported value, 7.8×10^{20} cm^{-3}, for KC_{48} (n_K/n_C=0.021) prepared from HOPG (highly oriented pyrolytic graphite). The mobility decreased with increasing n_K/n_C: 2.11×10^3 cm^2 V^{-1} s^{-1} (n_K/n_C=0.005), 1.42×10^3 cm^2 V^{-1} s^{-1} (n_K/n_C=0.008) and 1.34×10^3 cm^2 V^{-1} s^{-1} (n_K/n_C=0.011). The value of the mobility of K-PGS with n_K/n_C=0.011 was about 60% of the reported value (2300 cm^2 V^{-1} s^{-1}) for KC_{48} prepared from HOPG.

1. Introduction

A variety of graphite intercalation compounds (hereafter abbreviated as GICs) have been synthesized. They are classified into two groups: p-type such as GICs with metal chlorides and n-type such as GICs with alkali metals. It has been confirmed that GICs with metal chlorides are fairly stable in various circumstances [1]. For example, $NiCl_2$–GICs are highly stable in air and also in a number of organic solvents [2] and $NiCl_2$–$FeCl_3$–GICs showed no decomposition after boiling in water for 1 h [3]. On the other hand, alkali metal–graphite intercalation compounds (hereafter abbreviated as AM–GICs) are usually very unstable in open air. Recent investigations, however, revealed that some of them can be stabilized by suitable selection of host graphite material and chemical modifications of bare AM–GICs. A ternary compound $CsC_{24}(C_2H_4)_{1.4}$ prepared from PGS graphite sheet has been found to be remarkably stable in air [4]. It exhibited a blue colored surface after 10 years of exposure to air. In our previous investigation, preparation and properties of air-stable potassium-intercalated PGS (hereafter abbreviated as K-PGS) was carried out [5]. It showed high electrical conductivity of $\sim1.4\times10^5$ S cm^{-1}, about 10 times larger than that of host PGS and remained constant at least for five months in open air.

A lot of investigations on the magnetoresistance and Hall coefficient of GICs have been carried out for estimating carrier mobility and density [6–29]. For example, Lang et al. [14] reported that carrier density increased upon intercalation of arsenic pentafluoride up to 1.6×10^{21} cm^{-3} for stage 1 (C_8AsF_5) and 2 ($C_{16}AsF_5$) compounds, being two orders of magnitude greater than in host HOPG (highly oriented pyrolytic graphite) and two orders lower than in conventional metals. For K-GICs prepared from HOPG, Hall coefficient and magnetoresistance were also determined by Onn et al. [9] and Suematsu et al. [11]. It was shown that the electron density at 300 K increased with increasing concentration of potassium, from 7.8×10^{20} cm^{-3} (KC_{48}) through 2.5×10^{21} cm^{-3} (KC_{36}) and 7.1×10^{21} cm^{-3} (KC_{24}) to $\sim4\times10^{22}$ cm^{-3} (KC_8) [9]. On the other hand, the mobility decreased with increasing concentration of potassium: 2300 cm^2 V^{-1} s^{-1} (KC_{48}), 466 cm^2 V^{-1} s^{-1} (KC_{36}), 251 cm^2 V^{-1} s^{-1} (KC_{24}) and 130 cm^2 V^{-1} s^{-1} (KC_8). The present investigation describes galvanomagnetic properties of the air-stable K-PGS.

* Corresponding author. Tel.: +81 426685072.
E-mail address: noboru@tokyo-ct.ac.jp (N. Akuzawa).

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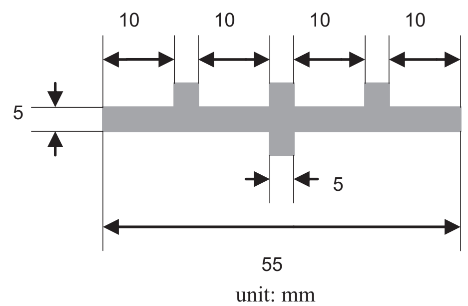

Fig. 1. Schematic representation of PGS sample used for galvanomagnetic measurements.

2. Experimental

The PGS (EYGS with thickness of 25 μm, Panasonic Co.), cut into a shape shown in Fig. 1, was buried in excessive amounts of K-GICs prepared from natural graphite in a Pyrex glass tube under vacuum and annealed for several days. Three different potassium-intercalated PGS samples with chemical compositions of KC_{36}, KC_{48} and KC_{84} were prepared. These samples were then put into 6 M-HCl aqueous solution for 1 h and washed with pure water and dried in open air. Details of the preparation and characterization of the air-stable K-PGS were described in our previous paper [5]. The electrical conductivity of air-stable K-PGS was determined by the four-terminal method at room temperature. For measurements of magnetoresistance and Hall coefficient, magnetic field was applied perpendicular to the *a*-axis (sheet plane) of K-PGS, up to 0.64 T.

3. Results and discussion

In our previous work [5] the following results were obtained: (1) About 40% of potassium in the starting potassium–graphite intercalation compounds remained in the matrix after treated with 6 M-HCl aqueous solution for KC_{84}, KC_{48} and KC_{36}. (2) The absolute values of the conductivity of the air-stable K-PGS samples, containing potassium of 0.005, 0.008 and 0.011 in molar ratio of potassium to carbon, were 1.0×10^5 S cm^{-1}, 1.3×10^5 S cm^{-1} and 1.4×10^5 S cm^{-1}, respectively. (3) These values were comparable to that of iron (1.0×10^5 S cm^{-1}) and about 1/3 of that of aluminum (3.6×10^5 S cm^{-1}). (4) It was considered that potassium is concentrated in inner part of a crystallite and the periphery region is composed of graphite, because about 60% of potassium was removed mainly from the periphery region by the treatment in 6 M-HCl aqueous solution. The surface graphitic layers thus formed should be effective for protecting potassium in the inner part from the oxidation by oxygen and water vapor in air. In fact, the values of the electrical conductivity of the specimens were constant in open air at least for five months.

Temperature dependence of the resistivity of K-PGS is shown in Fig. 2. All the K-PGS samples show metallic temperature dependence and anomaly at around 230 K. McRae et al. [30] reported similar anomaly at around 230 K in the resistivity-temperature plot for stage 5 K-GICs (KC_{60}) derived from HOPG. The anomaly was explained by the phase transition from organized intraplanar-ordered state of the potassium layers to liquid state. It can be considered that the anomaly observed in the present investigation is attributable to the same phase transition as what McRae et al. reported. This means that even for such dilute compounds with nominal compositions of KC_{91}, KC_{125} and KC_{200} the ordered in-plane structure of potassium layers developed well.

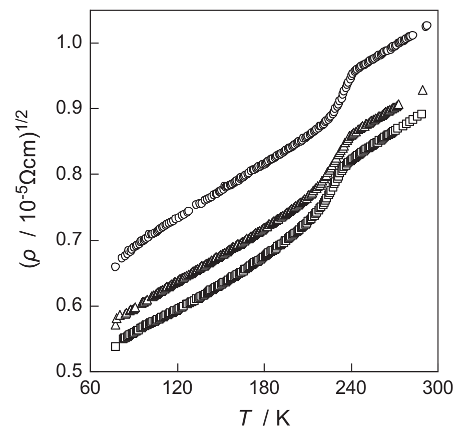

Fig. 2. Temperature dependence of electrical resistivity of K-PGS: ○, K-PGS (n_K/n_C (XRF)=0.005); Δ, K-PGS (n_K/n_C (XRF)=0.008); □, K-PGS (n_K/n_C (XRF)=0.011).

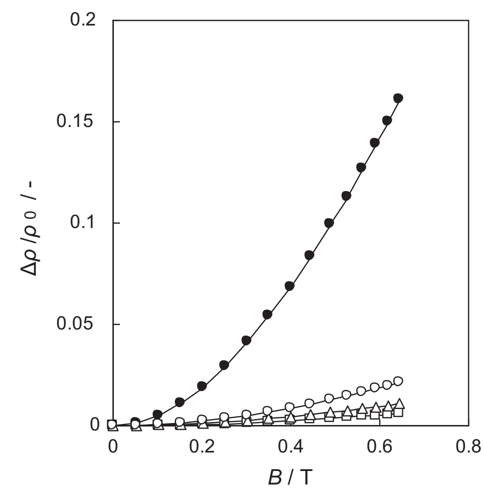

Fig. 3. Magnetoresistance of PGS and K-PGS plotted as a function of magnetic field strength: ●, PGS (host); ○, K-PGS (n_K/n_C (XRF)=0.005); Δ, K-PGS (n_K/n_C (XRF)=0.008); □, K-PGS (n_K/n_C (XRF)=0.011).

The values of magnetoresistance, $\Delta\rho/\rho$, of K-PGS are shown as a function of magnetic field strength (B) in Fig. 3, where the data for host PGS is also shown for comparison. The magnitude of the magnetoresistance decreased with increasing potassium content, n_K/n_C. This is a reflection of the charge transfer interaction between potassium and graphene layers, which leads to increase of the electron density and decrease of the hole density. The values of Hall voltage of K-PGS are plotted as a function of magnetic field strength in Fig. 4, where the data for host PGS is also shown. A linear relationship can be seen. It means that the Hall coefficient, being equal to the slope of the straight line in Fig. 4, is independent of the magnetic field strength. The absolute value of the Hall coefficient decreased with increasing n_K/n_C. The values of electrical conductivity (σ), magnetoresistance ($\Delta\rho/\rho$) at 0.64 T and Hall coefficient (R_H) are summarized in Table 1. It should be noted that the values of electrical conductivity and Hall coefficient of K-PGS with $n_K/n_C=0.011$ (nominal composition KC_{91}) are fairly close to the reported values (2.2×10^5 S cm^{-1} and -8.0×10^{-3} cm^{3}C^{-1}) for KC_{48} ($n_K/n_C=0.021$) prepared from HOPG [9].

The classical two-carrier model was adopted with an assumption that product of the densities of electron and hole is constant [15]. The Eqs. (1)–(4) are used for the calculation, where n_e, n_h, μ_e, μ_h and e denote electron density, hole density, electron mobility,