

Effect of sorbed molecules on the resistivity of alkali metal–graphite intercalation compounds

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Abstract

Alkali metal–graphite intercalation compounds with the composition of MC_{24} ($M = K, Rb, Cs$) were prepared by heating a mixture of MC_8 (saturated compound) and graphite sheet (Grafoil) at 350–450 °C. The resistivity perpendicular to the layer planes (ρ_c) of the resulting compounds was determined by the two-terminal method. The anisotropy factor of the resistivity, (ρ_c/ρ_a), of KC_{24} prepared from Grafoil was ~ 130 , being about 1/6–1/10 in magnitude compared with that of KC_{24} prepared from highly oriented pyrolytic graphite. The resistivity change during sorption of hydrogen (at 90 K), ethylene (at 194 K) and acetylene (at 194 K) was determined. The resistivity of MC_{24} increased with increase of the sorbed amount of H_2 . The magnitude of the increase was in the order $KC_{24} > RbC_{24} > CsC_{24}$. This resistivity increase was considered to be due to the expansion along c -direction which reduces the charge-transfer interaction between the carbon layers and potassium ions, resulting in the decrease of the density of the conduction electron. The resistivity of MC_{24} increased extensively during sorption of C_2H_4 and C_2H_2 . It was discussed in connection with the in-plane structural transition and chemical interaction between alkali metal ions and sorbed molecules.

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1. Introduction

Alkali metals (K, Rb, Cs) can intercalate graphite, expanding the carbon–carbon interlayer distance. This expansion creates new cavities, “nanospace,” in the interlayer spaces of the resulting alkali metal–graphite intercalation compounds (AM–GICs). Accordingly, AM–GICs are able to accommodate molecules such as H_2 , N_2 , CH_4 , etc. at relatively low temperatures, e.g. 77 K [1]. The sorption–desorption cycle is reversible for H_2 , N_2 , CH_4 , Ar, C_2H_6 , etc., whereas it is irreversible for tetrahydrofuran (THF), C_2H_2 , etc. [2,3]. Such difference may be originated from different ways of interaction between molecules and AM–GICs.

In our previous reports [4,5], change of the in-plane electrical conductivity of AM–GICs prepared from ex-

foliated graphite sheet (Grafoil) during sorption of several molecules was investigated. The conductivity of CsC_{24} decreased during sorption of H_2 , N_2 , C_2H_6 , C_2H_4 and C_3H_6 , and the magnitude of the decrease was less than 20%. For the sorption of NH_3 and C_2H_2 , however, considerable conductivity decrease was observed. It was also found that the conductivity decrease was largely dependent of the species of the alkali metal [5]. For example, the conductivity of KC_{24} decreased largely compared with that of CsC_{24} during ammonia sorption.

On the basis of these experiences, it seemed interesting to measure the resistivity perpendicular to the layer planes of AM–GICs during sorption of molecules, because of the remarkable anisotropic feature of AM–GICs. This paper deals with the resistivity perpendicular to the layer planes of AM–GICs and its change during sorption of H_2 , C_2H_2 and C_2H_4 . Exfoliated graphite sheet (Grafoil) was used as the host material of AM–GICs, because HOPG (highly oriented pyrolytic graphite) was not appropriate for the

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present experiment. It was pointed out that KC_{24} prepared from HOPG showed severe exfoliation during sorption–desorption process [6].

2. Experimental

2.1. Materials

Graphite used was exfoliated graphite sheet, Grafoil (GraffTech International Ltd. Company). The graphite specimen for resistivity measurement ($10 \times 10 \times 0.4 \text{ mm}^3$), two sheets of cushions ($10 \times 10 \times 0.4 \text{ mm}^3$) and small pieces, taken from the same Grafoil sheet, were heat-treated at $\sim 1000^\circ\text{C}$ under vacuum before use. The highly oriented pyrolytic graphite (HOPG), ZYA grade of UCAR Corporation, was used as the standard sample for the resistivity measurement. A schematic drawing of the sample for the resistivity measurement is shown in Fig. 1. The specimen was sandwiched by two Grafoil sheets (cushions) and glass plates. The two glass plates were fixed by screws. Platinum wires were inserted between the specimen and the cushions for the electrical contact. They were taken out of glass tube through glass–platinum seals. The contact between platinum wires and the graphite specimen was realized physically with no pad such as silver paste. Commercially available alkali metals (99.95%) were used without further purification. The purity of molecules was as follows: H_2 , >99%; C_2H_2 , 99.8%; C_2H_4 , 99.9%.

2.2. Preparation of AM–GICs

All the samples of AM–GICs were prepared from Grafoil. A two-step preparation technique was used. At first MC_8 sample ($M = \text{K, Rb, Cs}$) was prepared from small pieces of Grafoil allowing them being exposed to alkali metal vapor at around 230°C . Then, the resulting MC_8 sample and additional small pieces of Grafoil were contacted with graphite specimen for the resistivity measurement and they were heated at different temperatures between 350 and 450°C , depending on the alkali metal species and the composition of the target compounds. The composition of the final compound was

calculated from the supplied amount of alkali metals (in MC_8) and all the graphite (the specimen for the resistivity measurement, the cushions (2 Grafoil sheets), additional small pieces of Grafoil and that in MC_8). The heat-treatment was continued until the resistivity of the specimen became unchanged.

2.3. Resistivity measurements

The resistivity of AM–GICs was determined by the two-terminal method. Its temperature dependence was determined between 90 K and room temperature. The change of the resistivity during sorption of H_2 , C_2H_2 and C_2H_4 was then determined. A fixed amount of respective molecules was contacted with AM–GICs. Both the resistivity and the pressure of the molecule were followed with time until these values became unchanged. This procedure was repeated until equilibrium pressure became up to around 0.8 atm. The sorbed amount of the molecule was determined by the constant volume method. In this measurement, small pieces of AM–GICs were also placed together with the AM–GICs specimen for the resistivity measurement to enhance the total amount of sorption. It was confirmed that the coexistence of the small pieces of specimens did not interfere with the resistivity measurement. Because the sorption–desorption process was reversible for H_2 and C_2H_4 except C_2H_2 , the same specimen of AM–GICs was used for all the experiments and the C_2H_2 -sorption was carried out finally. In the case of the determination of the a -axis resistivity of Grafoil and derived AM–GICs, the 4-terminal method was used. Details of the experimental procedure were reported in our previous paper [7].

3. Results and discussion

3.1. Resistivities of host graphite samples and derived AM–GICs

The observed c -axis resistivity of HOPG was $1.4 \times 10^{-3} \Omega\text{m}$ at room temperature, being in good agreement with the reported value ($1.2 \times 10^{-3} \Omega\text{m}$) [8]. Therefore, the present experimental procedure is considered to be reliable. The resistivity along the layer planes (hereafter abbreviated as ρ_a), the resistivity perpendicular to the sheet planes (hereafter abbreviated as ρ_c) and anisotropy factor (ρ_c/ρ_a) are summarized in Table 1 for

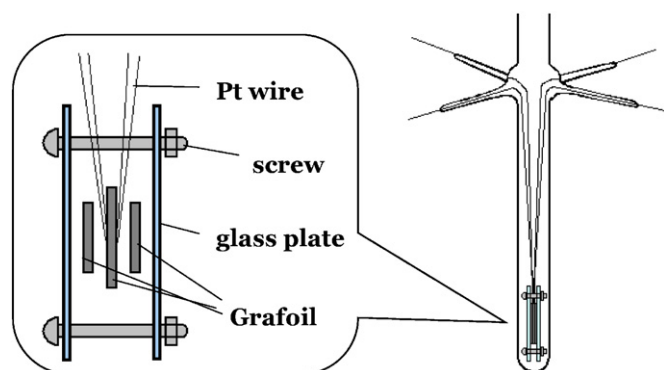


Fig. 1. A schematic representation of the equipment for resistivity measurement.

Table 1

Values of resistivity along the layer planes (ρ_a), resistivity perpendicular to the layer planes (ρ_c) and the anisotropy factor (ρ_c/ρ_a) for HOPG and Grafoil

| | HOPG | Grafoil (present work) |
|-------------------------|--------------------------|------------------------|
| $\rho_a/\Omega\text{m}$ | 4.0×10^{-7} [9] | 80×10^{-7} |
| $\rho_c/\Omega\text{m}$ | 1.2×10^{-3} [8] | 10×10^{-3} |
| ρ_c/ρ_a | 3000 | 1300 |

The values are determined at room temperature.

Grafoil and HOPG. The values of ρ_a and ρ_c for Grafoil are greater about an order of magnitude than the corresponding respective values for HOPG. However, the anisotropy factor of Grafoil is comparable to that of HOPG. Therefore, we can consider that the crystallites of Grafoil are fairly well oriented.

The observed values of ρ_c and ρ_a of KC_{24} derived from Grafoil (hereafter abbreviated as KC_{24} (Grafoil)) and the anisotropy factor are given in Table 2, where literature values for KC_{24} derived from HOPG [9,10] are also shown. The anisotropy factor (ρ_c/ρ_a) of KC_{24} (Grafoil) decreased about an order of magnitude along with the intercalation of potassium. It means that ρ_c decreased significantly upon intercalation in comparison with ρ_a . This observation is in agreement with general behavior of donor GICs [9]. The anisotropy factor of KC_{24} (Grafoil) was about 1/6–1/10 in magnitude compared with that of KC_{24} (HOPG). This can be attributable to the fact that the degree of the orientation of Grafoil is less than that of HOPG.

Temperature dependence of ρ_c of Grafoil and derived Cs-graphite intercalation compounds (Cs-GICs) are comparatively shown in Fig. 2. A continuous variation is clearly seen from semi-conductive behavior of Grafoil,

Table 2

Values of resistivity along the layer planes (ρ_a), resistivity perpendicular to the layer planes (ρ_c) and the anisotropy factor (ρ_c/ρ_a) for KC_{24} samples prepared from HOPG and Grafoil

| | KC_{24} (HOPG) | KC_{24} (Grafoil) [This work] |
|-------------------------|---|--|
| $\rho_a/\Omega\text{m}$ | 6×10^{-8} [9] | 3.5×10^{-7} |
| $\rho_c/\Omega\text{m}$ | 5×10^{-5} [9] 8×10^{-5} [10] | 5×10^{-5} |
| ρ_c/ρ_a | 830~1330 | 130 |

The values were determined at room temperature.

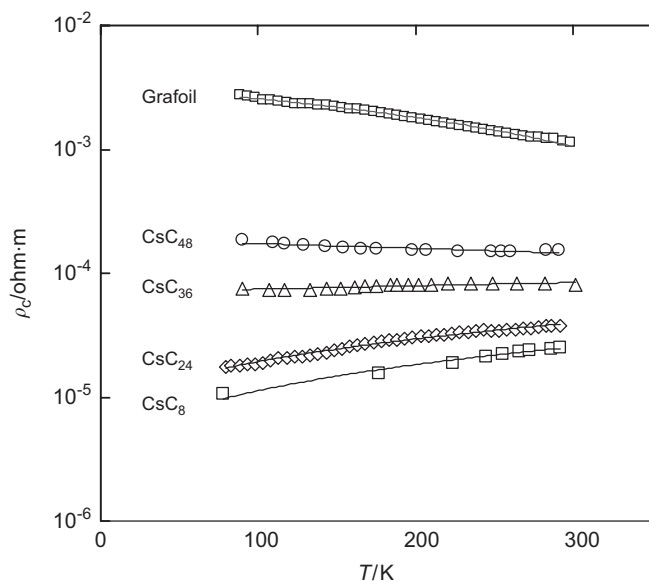


Fig. 2. Temperature dependence of ρ_c of Grafoil and Cs-GICs.

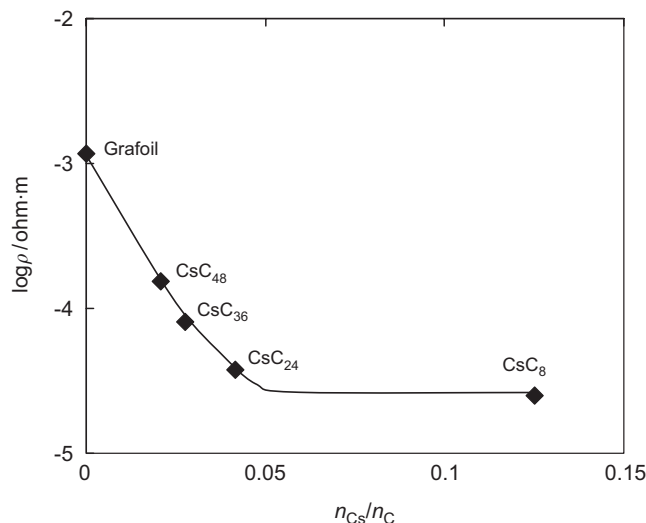


Fig. 3. Logarithmic value of ρ_c determined at 292 K plotted as a function of $n_{\text{Cs}}/n_{\text{C}}$.

through intermediate (CsC_{48} and CsC_{36}), to metallic (CsC_{24} and CsC_8). The absolute values of ρ_c , determined at room temperature, are plotted as a function of Cs concentration ($n_{\text{Cs}}/n_{\text{C}}$) in Fig. 3. It can be seen that ρ_c decreased monotonically with the increase of $n_{\text{Cs}}/n_{\text{C}}$ up to ~ 0.04 (corresponding to CsC_{24}). Only a slight difference of ρ_c was observed for CsC_{24} and CsC_8 . This observation can be reasonably understood by taking into account that there are solely bounding layers in both CsC_{24} and CsC_8 , i.e. all the carbon layers are contacting with Cs ions. On the contrary, the dilute compounds such as CsC_{36} , CsC_{48} , etc. have not only bounding layers but also interior layers which do not contact with Cs ions. The carrier density in the interior layer is less than that in the bounding layer. Therefore, we can consider that with decreasing the number of the interior layer from 2 (stage 4) to 0 (stage 2), ρ_c decreases significantly, whereas it almost unchanged from stage 2 to 1 because both of them have no interior layer.

Temperature dependence of ρ_c of MC_{24} ($M = \text{K}, \text{Rb}, \text{Cs}$) is shown in Fig. 4. There is no big difference among them both in the absolute value and the temperature coefficient. Anomaly at around 110 K was clearly seen only for KC_{24} and it is reproduced in Fig. 5 as a plot of ρ_c vs. temperature. A hysteresis loop was observed between 103 and 112 K. The open circle denotes datum point taken on heating and the closed one on cooling. It should be noted that similar anomaly was also observed in the ρ_a -temperature plot for KC_{24} (Grafoil) in our separate experiment [7], where similar hysteresis loop was observed between 95 and 115 K. This kind of anomaly has already been reported for MC_{24} ($M = \text{K}, \text{Rb}, \text{Cs}$) prepared from HOPG [11]. Double stepwise changes of ρ_a were observed at 95 and 124 K. This anomaly was explained by the structural phase transitions [12]. The anomaly observed for KC_{24} (Grafoil) in the present work can be attributed to the structural phase transitions found in KC_{24} (HOPG),

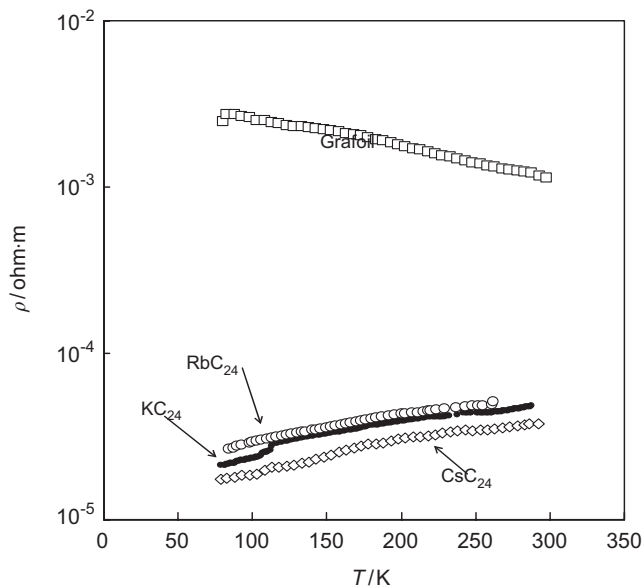


Fig. 4. Temperature dependence of ρ_c for MC_{24} ($M = K, Rb, Cs$).

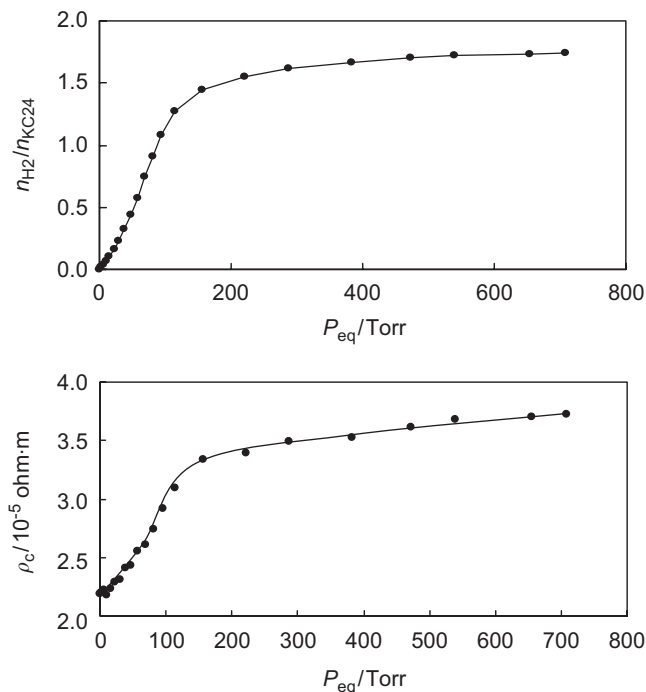


Fig. 6. (a) Isotherm for the system $KC_{24}\text{-H}_2$ at 90 K; (b) ρ_c vs. p_{eq} plot at 90 K; (c) ρ_c vs. $n_{H_2}/n_{MC_{24}}$ plot at 90 K.

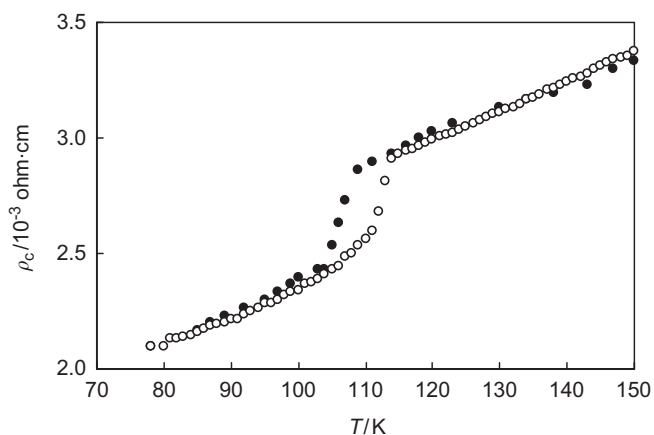
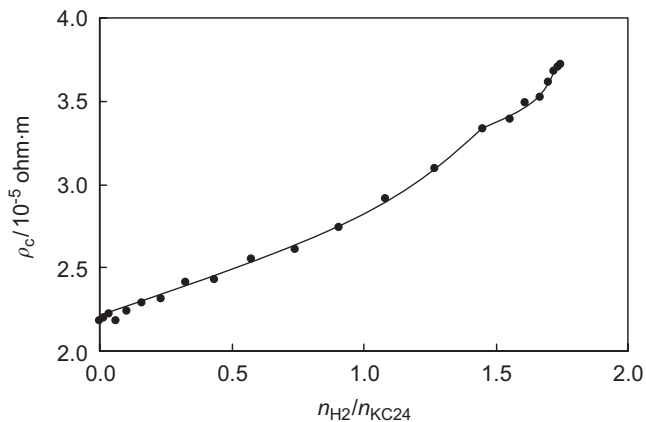


Fig. 5. Temperature dependence of ρ_c for KC_{24} .



although there are small differences both in the transition temperature and in the behavior (a hysteresis loop for KC_{24} (Grafoil) in contrast to double steps for KC_{24} (HOPG)).

3.2. Resistivity change of MC_{24} ($M = K, Rb, Cs$) during sorption of hydrogen at 90 K

The sorbed amount of H_2 by KC_{24} , $n_{H_2}/n_{KC_{24}}$, and corresponding ρ_c values are determined at different equilibrium H_2 pressure, p_{eq} , and they are plotted in Figs. 6(a) and (b), respectively. From these data, the relationship between ρ_c and $n_{H_2}/n_{KC_{24}}$ was obtained as shown in Fig. 6(c). The dependence of ρ_c on $n_{H_2}/n_{KC_{24}}$ can be divided into two regions, i.e. region 1 below the bump at $n_{H_2}/n_{KC_{24}} = \sim 1.5$ and region 2 above the bump. Also from the kinetic point of view different aspects were observed. The sorption equilibrium was attained fairly rapidly in

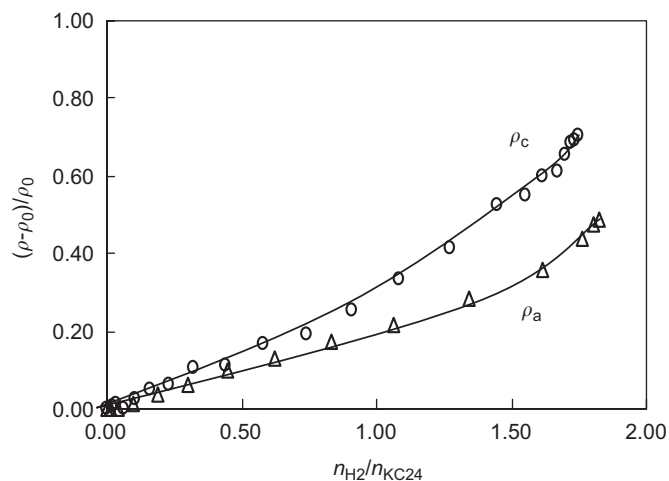


Fig. 7. ρ_c and ρ_a of KC_{24} plotted as a function of $n_{H_2}/n_{KC_{24}}$ at 90 K.

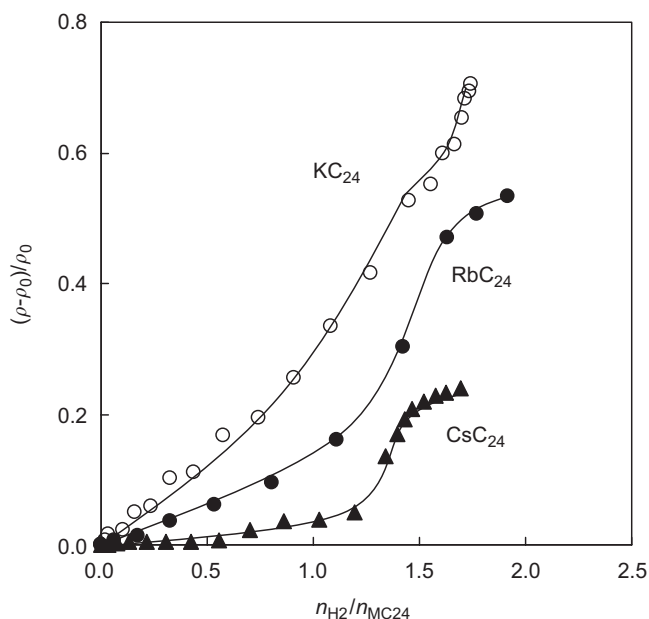


Fig. 8. $(\rho_c - \rho_0)/\rho_0$ vs. $n_{H_2}/n_{MC_{24}}$ plot at 90 K.

region 1, whereas considerably long period, e.g. several hours, was needed in region 2.

A simple picture to explain above behavior is as follows. In the region 1, there are many empty sorption sites and H_2 molecules are easily able to penetrate expanding the carbon–carbon interlayer distance. The expansion along c -direction reduces the charge-transfer interaction between carbon layers and potassium ions, which results in the decrease of the density of the conduction electron. The expansion weakens attractive force between conduction electrons and alkali metal ions. Accordingly, the density of the conduction electron must decrease to reduce the repulsive force between the conduction electrons, in order to keep a balance between the attractive and repulsive forces. In addition, the H_2 molecules might act as scattering center so as to reduce the mobility of the conduction electron. Therefore, ρ_c increased with increase of $n_{H_2}/n_{KC_{24}}$. In region 2, since almost all the sorption sites have been already occupied, H_2 molecules stand up to accommodate additional H_2 as pointed out in the earlier investigations [1,13]. This means further expansion of the carbon–carbon interlayer distance along c -direction and again ρ_c increases with increasing $n_{H_2}/n_{KC_{24}}$.

The change of ρ_c and ρ_a of KC_{24} during H_2 -sorption is comparatively shown in Fig. 7, where the data of ρ_a is cited from our paper [7]. In the figure, normalized resistivity change, $(\rho - \rho_0)/\rho_0$, is plotted against $n_{H_2}/n_{KC_{24}}$, where ρ_0 is the resistivity of binary KC_{24} and ρ is that of the H_2 -sorbed KC_{24} . It was found that ρ_c increased more sensitively during H_2 -sorption rather than ρ_a . This is reasonable because the change of ρ_c upon intercalation of potassium is larger than that of ρ_a as noted above. It could be said that the mobility of conduction electron along c -axis is much more sensitive to the

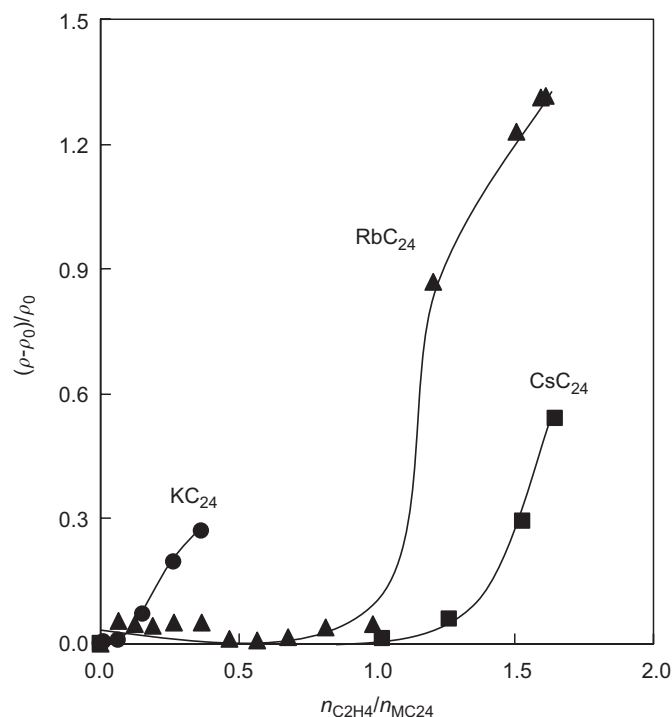


Fig. 9. $(\rho_c - \rho_0)/\rho_0$ vs. $n_{C_2H_4}/n_{MC_{24}}$ plot at 194 K.

variation of the density of the conduction electron compared to that along a -axis.

To see the effect of alkali metal species on the resistivity change during H_2 -sorption, $(\rho_c - \rho_0)/\rho_0$ of MC_{24} ($M = K, Rb, Cs$) is plotted against $n_{H_2}/n_{MC_{24}}$ in Fig. 8. The resistivity increased in the order $KC_{24} > RbC_{24} > CsC_{24}$. This is the order of the size of the alkali metal ions. The reported values of the sandwich thickness are 0.539 nm (KC_{24}), 0.570 nm (RbC_{24}) and 0.601 nm (CsC_{24}), respectively [9]. The values of intercalate layer thickness (d_i) for KC_{24} , RbC_{24} and CsC_{24} are 0.204, 0.235 and 0.266 nm, respectively. Because the thickness of H_2 molecule is 0.24 nm [1], the expansion along c -axis is about 17% for KC_{24} and no expansion for CsC_{24} . It can be said that the degree of the expansion is intimately related to the resistivity increase for H_2 -sorption.

The resistivity change of CsC_{48} (stage 4) during H_2 -sorption was also examined. Almost no change was observed up to saturated sorption. This is probable because of the existence of the interior carbon layers in addition to the bounding layers. Because the interior carbon layers are considered to be the principal source of the resistance along c -direction, ρ_c is reasonably insensitive to the H_2 -sorption taking place between the bounding carbon layers.

3.3. Resistivity change of MC_{24} ($M = K, Rb, Cs$) during sorption of ethylene at 194 K

For the system $MC_{24}-C_2H_4$, $(\rho_c - \rho_0)/\rho_0$ is plotted against $n_{C_2H_4}/n_{MC_{24}}$ in Fig. 9. A remarkable resistivity increase was observed for KC_{24} in low concentration region. The

magnitude of the increase was estimated about twice compared with that of H₂-sorption for the same sorbed amount of these molecules ($n_{C_2H_4}/n_{KC_{24}} = n_{H_2}/n_{KC_{24}} = 0.2$). It is simply considered to be due to the difference of the degree of the expansion during H₂- and C₂H₄-sorption. In our previous experiment the identity period (I_c) of the 2nd stage ternary system, CsC₂₄-C₂H₄, was determined to be ~ 1.01 nm by the X-ray diffraction measurement [14]. The thickness of the sorbed C₂H₄ molecule was estimated to be 0.34 nm. It can be considered that the same value is applied to the C₂H₄ molecule sorbed in KC₂₄. Accordingly, the sandwich thickness (d_s) of KC₂₄ changes from 0.539 nm (binary) to 0.675 nm by the sorption of C₂H₄. The ratio of the expansion is estimated to be 25%. This is very large compared with the corresponding value of 7% for the H₂-sorption.

It should be mentioned that the sample fixing glass plate was sometimes broken for further sorption and therefore the resistivity was not observable. It suggests that a relatively high pressure was applied on the sample. The effect of pressure on the resistivity of K-GICs (HOPG) has already been reported [15–17]. For KC₂₄, the in-plane resistivity increased with pressure below phase transition at about 0.32 GPa at 293 K [15]. The relative resistance (R/R_0), however, was very close to 1.0 (~ 1.01) under pressure less than 0.1 GPa. On the other hand, the c -axis resistivity decreased monotonically with pressure up to 0.35 GPa [17]. The change of the relative resistance (R/R_0) was very small in the pressure region below 0.1 GPa. Unfortunately, the pressure applied to the specimen was not measured in the present investigation, but it is improbable such a high pressure as 0.1 GPa is required for breaking the glass plate. Therefore, the observed

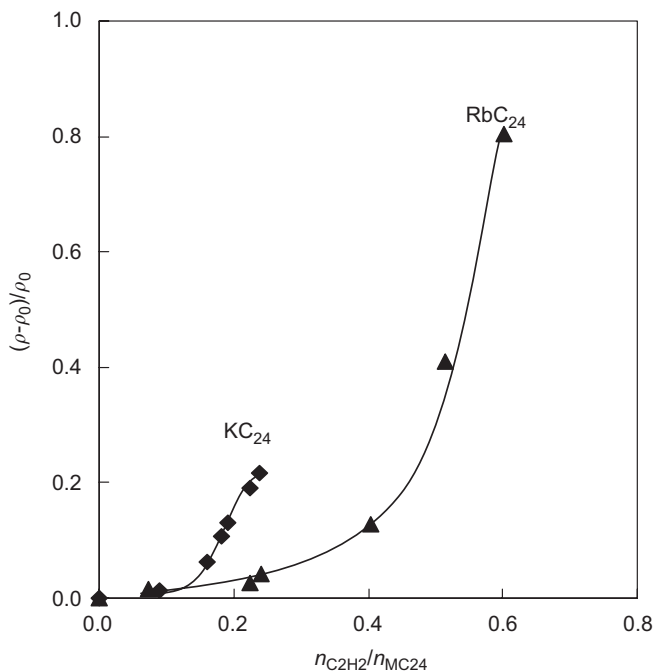


Fig. 10. $(\rho_c - \rho_0)/\rho_0$ vs. $n_{C_2H_2}/n_{MC_{24}}$ plot at 194 K.

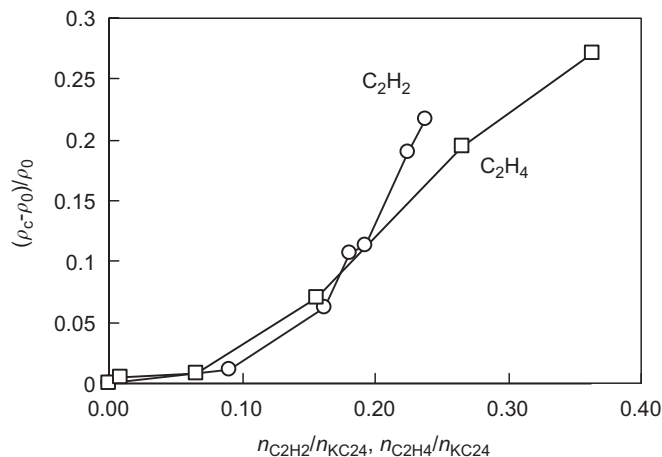


Fig. 11. $(\rho_c - \rho_0)/\rho_0$ vs. $n_{C_2H_2}$ ($n_{C_2H_4}$)/ $n_{KC_{24}}$ plot at 194 K.

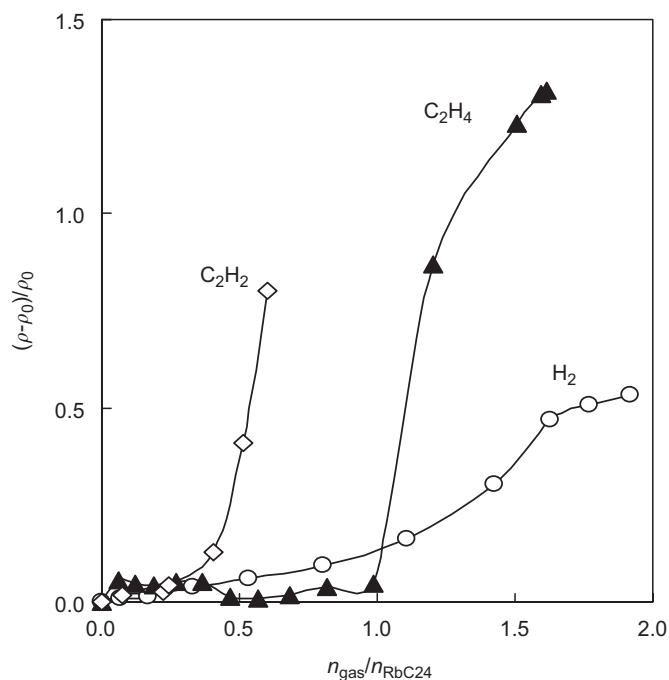


Fig. 12. $(\rho - \rho_0)/\rho_0$ vs. $n_{molecule}/n_{RbC_{24}}$ plot at 90 K (H₂) and at 194 K (C₂H₄ and C₂H₂).

resistivity change cannot be attributable to the pressure increase during C₂H₄-sorption.

For RbC₂₄ and CsC₂₄, $(\rho_c - \rho_0)/\rho_0$ was almost unchanged until ~ 1.0 of $n_{C_2H_4}/n_{MC_{24}}$, and then increased significantly with increase of $n_{C_2H_4}/n_{MC_{24}}$. The sorption equilibrium was attained rapidly up to ~ 1.0 of $n_{C_2H_4}/n_{MC_{24}}$. These observations are different from that for KC₂₄. This is possibly an indication of the molecular sieving effect, as reported in the earlier investigation [1]. Fairly large molecules such as Ar and CH₄ are accommodated in the nanospace of RbC₂₄ and CsC₂₄, but not in that of KC₂₄. The values of the molecular diameter for Ar and CH₄ are 0.38 and 0.40 nm, respectively [1]. Therefore, the thickness of C₂H₄ molecule (0.34 nm) is fairly large for the nanospace

of KC_{24} , whereas it is quite acceptable for the nanospace of RbC_{24} and CsC_{24} .

A steep increase of $(\rho_c - \rho_0)/\rho_0$ is observed above ~ 1.0 of $n_{\text{C}_2\text{H}_4}/n_{\text{MC}_{24}}$. In this region, the datum point came close to the plateau region on the isothermal curve and the rate of the sorption became very slow. The structural change of CsC_{24} during C_2H_4 -sorption has already been clarified by in-situ X-ray diffraction measurements [14]. Up to 0.7 of $n_{\text{C}_2\text{H}_4}/n_{\text{CsC}_{24}}$, mixture of a stage 2 ternary ($I_c = 1.01$ nm) and a stage 1 binary ($I_c = 0.595$ nm) was observed. Above 1.0 of $n_{\text{C}_2\text{H}_4}/n_{\text{CsC}_{24}}$, a pure stage 1 ternary ($I_c = 0.685$ nm) was formed. Therefore, we can consider such structure change is strongly connected with the resistivity increase of RbC_{24} and CsC_{24} during C_2H_4 -sorption.

For the H_2 -sorption, H_2 molecules are simply fixed in the nanospace of MC_{24} . There is no movement of alkali metal ions in the nanospace during H_2 -sorption. In the case of C_2H_4 -sorption, on the contrary, the sorbed molecules are necessarily to enlarge the nanospace by moving the adjacent alkali metal ions. This is the requirement from the fact that C_2H_4 molecule has larger size also in the direction of the layer planes with respect to that of the nanospace. From the fact that steep increase of ρ_c started at the composition corresponding to the structure change, we can consider that the increase of ρ_c is caused by the structure transition for C_2H_4 -sorption.

3.4. Resistivity change of MC_{24} ($M = \text{K}, \text{Rb}, \text{Cs}$) during sorption of acetylene at 194 K

Fig. 10 shows the plots of $(\rho_c - \rho_0)/\rho_0$ vs. $n_{\text{C}_2\text{H}_4}/n_{\text{MC}_{24}}$ for the systems KC_{24} - and RbC_{24} -acetylene. For KC_{24} , the result is reproduced in Fig. 11 together with that for C_2H_4 -sorption. A similar dependence on the sorbed amount is seen up to ~ 0.20 of $n_{\text{C}_2\text{H}_2}$ or $n_{\text{C}_2\text{H}_4}/n_{\text{KC}_{24}}$. The resistivity increase below ~ 0.20 of $n_{\text{C}_2\text{H}_4}/n_{\text{KC}_{24}}$ can be considered to be caused solely by the expansion. For further sorption above ~ 0.20 of $n_{\text{C}_2\text{H}_4}/n_{\text{KC}_{24}}$, additional increase is recognized for the C_2H_2 -sorption. Because acetylene molecule has linear structure with triple bond, it is able to interact easily with potassium ion in the nanospace. On the other hand, the ethylene molecule has planar structure with double bond. The existence of additional two hydrogen atoms in the ethylene molecule makes it difficult to interact with the potassium ion [18]. It has been reported also that alkali metals dissolved in liquid ammonia are converted to alkali acetylides by flowing C_2H_2 gas at 233 K and the stability of the resulting compounds decreases in the order $\text{K} > \text{Rb} > \text{Cs} > \text{Na} > \text{Li}$ [19]. Therefore, we can consider that there is possibly strong chemical interaction between alkali metal ions and acetylene molecules in the nanospace of MC_{24} , even at 194 K. We are able to summarize the change of the resistivity of KC_{24} during C_2H_2 -sorption as follows. In the dilute region below ~ 0.20 of $n_{\text{C}_2\text{H}_4}/n_{\text{KC}_{24}}$, the resistivity increases by the decrease of the density of the conduction electron which was caused by the expansion of the

sandwich thickness. Above ~ 0.20 of $n_{\text{C}_2\text{H}_2}/n_{\text{KC}_{24}}$, both the expansion and the chemical interaction between potassium ion and C_2H_2 molecule contribute to decrease the density of the conduction electron.

The resistivity change of RbC_{24} during C_2H_2 -sorption is reproduced in Fig. 12 together with the data for H_2 and C_2H_4 . The threshold concentration for steep increase of $(\rho_c - \rho_0)/\rho_0$ is ~ 0.4 for C_2H_2 and ~ 1.0 for C_2H_4 . Among these molecules, C_2H_2 induces remarkable increase of the resistivity of RbC_{24} . The difference from the C_2H_4 -sorption can be attributed to the effect of the chemical interaction between rubidium ions and C_2H_2 molecules. Thus, the chemical interaction between alkali metal ions and C_2H_2 molecules becomes important in such a case as the thickness of the nanospace is large relative to the size of C_2H_2 molecule.

4. Conclusions

Alkali metal-graphite intercalation compounds (AM-GICs) were prepared from exfoliated graphite sheet (Grafoil). The resistivity perpendicular to the layer planes (ρ_c) and the resistivity along the layer planes (ρ_a) were determined for both pristine Grafoil and derived AM-GICs. The values of ρ_a and ρ_c of Grafoil were determined to be 80×10^{-7} and $10 \times 10^{-3} \Omega \text{m}$ at room temperature, respectively. Both of them were larger about an order of magnitude compared with respective values of highly oriented pyrolytic graphite (HOPG). The anisotropy factor (ρ_c/ρ_a) of Grafoil was 1300. This was comparable to 3000 of HOPG. The anisotropy factor of the derived KC_{24} (Grafoil) was ~ 130 , being 1/6–1/10 in magnitude compared with that of KC_{24} (HOPG). In the ρ_c vs. temperature plot for KC_{24} (Grafoil), anomaly due to phase transition was found at around 110 K.

The change of ρ_c of MC_{24} ($M = \text{K}, \text{Rb}, \text{Cs}$) during H_2 -sorption at 90 K was determined. It increased with the increase of the sorbed amount of H_2 . The magnitude of the resistivity increased in the order $\text{KC}_{24} > \text{RbC}_{24} > \text{CsC}_{24}$. It was considered that the expansion along c -direction reduces the charge-transfer interaction between carbon layers and potassium ions, which results in the decrease of the density of the conduction electron.

The change of ρ_c of MC_{24} ($M = \text{K}, \text{Rb}, \text{Cs}$) during sorption of C_2H_4 and C_2H_2 at 194 K was also determined. The resistivity increased extensively during sorption of C_2H_4 and C_2H_2 . The magnitude of the increase was larger than the case of the H_2 -sorption. The resistivity of RbC_{24} increased steeply at ~ 0.4 of $n_{\text{C}_2\text{H}_2}/n_{\text{RbC}_{24}}$ for C_2H_2 -sorption and at ~ 1.0 of $n_{\text{C}_2\text{H}_4}/n_{\text{RbC}_{24}}$ for C_2H_4 -sorption. It was considered that the resistivity increase of RbC_{24} during C_2H_4 -sorption is solely due to the structural transformation, whereas the resistivity increase during C_2H_2 -sorption can be attributable to the chemical interaction between rubidium ions and C_2H_2 molecules.

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