Hydrogen-sorption capacity and transport properties of potassium-graphite intercalation compounds

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Potassium-graphite intercalation compounds with 7 different compositions ranging from KC300 to KC24 were prepared from exfoliated graphite sheet (Grafoil). Resistivity, magnetoresistance and hydrogen-sorption capacity of these compounds were determined. KC100 and KC250 showed semi-conductive temperature dependence of the resistivity as well as host Grafoil, while KC168 and more rich compounds showed metallic behavior. Dependence of the resistivity and magnetoresistance on the potassium concentration was divided into two regions with a critical concentration at about KC60~70. Both of these properties decreased considerably with increasing potassium concentration below this critical concentration, and then became almost constant above it. A remarkable correlation between transport properties and hydrogen-sorption capacity was suggested.

KEYWORDS: Intercalation compounds, Transport properties, Adsorption

1. Introduction

Intercalation of potassium into graphite modifies the structure and gives different properties from those of host graphite. A characteristic feature of intercalation compounds is the staging phenomenon. It is mentioned that even for very dilute compounds such as KC<sub>120</sub> the staging phenomenon is confirmed<sup>1)</sup>. We observed the conduction electron spin resonance of potassium-graphite intercalation compounds (hereafter abbreviated as K-GICs) prepared from artificial graphite and found that the g-value suddenly decreased between 1/200 and 1/100 of nK/nC (relative molar ratio of potassium to carbon)<sup>2)</sup>. This observation stimulated us to investigate dilute compounds such as KC<sub>200</sub>. The standard technique such as X-ray diffraction measurement is no longer useful for such dilute compounds. Transport properties such as electrical resistivity are considered to be very sensitive even for the intercalation in mere trace amounts. Therefore, resistivity and magnetoresistance of K-GICs were determined as a function of potassium concentration. We also examined hydrogen-sorption behavior at 77 K to get information about nanoparticle formation in K-GICs.

2. Experimental

2.1 Materials

Graphite specimen used was exfoliated graphite sheet, Grafoil (GrafTech International Ltd. Company). The graphite specimen for resistivity measurement (with typical sizes of 4 × 40 × 0.4 mm<sup>3</sup>) and small pieces, taken from the same Grafoil sheet, were heat-treated at 1000°C under vacuum before use. Platinum wires were fixed to the specimen for resistivity measurement. They were taken out of glass tube through glass-platinum seals. The contact between platinum wires and the graphite specimen was made physically with no pad such as silver paste. Commercially available potassium metal (with purity of 99.95%) was used without further purification. The purity of hydrogen was >99%.

2.2 Preparation of K-GICs

All the samples of K-GICs (with 7 different compositions between KC24 and KC300) were derived from Grafoil. A two-step preparation technique was used. At first KC8 sample was prepared from small pieces of Grafoil allowing them being contacted with potassium metal vapor at around 230°C. Then, the resulting KC8 sample and additional small pieces of Grafoil were contacted with graphite specimen for resistivity measurement and they were heat-treated at 250 ~ 450°C, depending on the composition of target compounds. The composition of the final compound was calculated from the supplied amount of alkali metals (in KC8) and all the graphite (specimen for resistivity measurement, additional small pieces of Grafoil and that in KC8). The heat-treatment was continued until the value of the resistivity of the specimen became unchanged.

2.3 Resistivity and magnetoresistance of K-GICs

The in-plane resistivity of K-GICs was determined by the four-
terminals method. Its temperature dependence was determined between 77 K and room temperature. The magnetoresistance of K-GICs were determined at room temperature under magnetic field strength up to 0.62 T.

2.4 Hydrogen-sorption isotherm

A fixed amount of hydrogen was contacted with K-GICs at 77 K and the sorbed amount of hydrogen was determined by the constant volume method.

3. Results

3.1 Resistivity of K-GICs

Temperature dependence of the resistivity of K-GICs is shown in Fig.1, where the data of host graphite (Grafoil) is also shown for comparison. Semi-conductive behavior was observed for KC24 and KC36 in a similar manner as for Grafoil. It turns to metallic for KC168 and more rich compounds. The absolute value decreased monotonically with increasing potassium concentration. It should be noted that anomaly between 95 and 115 K is clearly observed for KC24. It is magnified and reproduced in Fig.2, where data of KC36 is also shown. We have observed this kind of anomaly between 103 and 112 K in the temperature dependence of resistivity perpendicular to the layer planes of KC36 prepared from Grafoil4). The reported anomaly between 95 and 124 K for KC24 prepared from highly oriented pyrolytic graphite (HOPG) is considered to be due to the order-disorder structural phase transition4). There is quite a slight indication of such anomaly at around 100 K for KC36 as seen in Fig.2. The anomaly between 87 and 112 K is also observed in the case of KC36 prepared from HOPG5). Thus we can consider that the anomaly observed for KC24 and KC36 is due to the structural phase transition as is the case of KC24 and KC36 prepared from HOPG.

To see the effect of composition of K-GICs on the absolute value of resistivity, logarithmic value of room-temperature resistivity is plotted vs. potassium concentration, nK/nC (relative molar ratio of potassium to carbon) in Fig.3. When the concentration is rather low the resistivity decreased remarkably with increasing nK/nC. But the resistivity did not change so much when the composition exceeds about 1/60 of nK/nC.

3.2 Magnetoresistance of K-GICs

The observed magnetoresistance of K-GICs and Grafoil at room temperature is plotted vs. magnetic field strength in Fig.4. For KC36 and KC24, data falled on the abscissa and were not shown in Fig.4 Room-temperature resistivity of potassium-graphite intercalation compounds plotted as a function of potassium concentration, nK/nC.
the figure. The magnitude of the magnetoresistance decreased monotonically with increasing potassium concentration. This can be considered to be due to inequality of the densities of conduction electrons and holes caused by the charge-transfer interaction between carbon and potassium layers. The increase of potassium concentration results in the increase of the density of conduction electron in contrast to the decrease of the density of holes. The values of magnetoresistance determined at 0.62 T is plotted as a function of the potassium concentration, \( n_K/n_C \), in Fig. 5. It can be divided into two regions. The magnetoresistance decreased considerably below the critical concentration, about 1/70 of \( n_K/n_C \), and then almost zero above it. This critical concentration is comparable to that (1/60) found in the dependence of the resistivity on the potassium concentration as already described.

3.3 Sorbed amount of hydrogen by K-GICs at 77 K

The saturated sorbed amount of hydrogen by K-GICs at 77 K is shown in Table 1. It increased with increasing potassium concentration. The value 1.84 of KC_{24} is about 10% less than the reported value (2.1) for KC_{24} prepared from natural graphite^6.

### Table 1 Saturated sorbed amount of hydrogen by potassium-graphite intercalation compounds at 77 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( n_{K}/n_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KC_{300}</td>
<td>0.02</td>
</tr>
<tr>
<td>KC_{250}</td>
<td>0.34</td>
</tr>
<tr>
<td>KC_{16}</td>
<td>0.80</td>
</tr>
<tr>
<td>KC_{95}</td>
<td>1.02</td>
</tr>
<tr>
<td>KC_{72}</td>
<td>1.26</td>
</tr>
<tr>
<td>KC_{30}</td>
<td>1.70</td>
</tr>
<tr>
<td>KC_{24}</td>
<td>1.84</td>
</tr>
</tbody>
</table>

4. Discussion

4.1 Transport properties and hydrogen-sorption capacity of K-GICs

The saturated sorbed amount of hydrogen by K-GICs at 77 K is plotted vs. potassium concentration in Fig. 6. It can be divided to 3 regions. In the first region, up to 1/300 of \( n_K/n_C \), the sorbed amount is substantially zero. A sudden increase of sorbed amount occurred at around 1/300 ~ 1/250. The second region locates between ~1/200 and ~1/60 of \( n_K/n_C \), where sorbed amount increases considerably with increasing \( n_K/n_C \). In the third region above ~1/60 of \( n_K/n_C \), it increased very slightly with increasing \( n_K/n_C \). We remember that semi-conductive temperature dependence of KC_{300} and KC_{250} is replaced by the metallic one of KC_{16}. Therefore, the transition
Fig. 7 Resistivity of KC24 and KC36 plotted as a function of sorbed amount of hydrogen, \( n_{H_2}/n_K \), at 77 K.

from region 1 to region 2 corresponds to the change from semi-conductive to metallic. It suggests that some extent of the charge-transfer interaction between intercalated potassium layers and carbon layers is necessarily for nanospace formation. The charge transfer results in the ordering of structure of potassium caused by the electrostatic force. We may suppose that for very dilute compounds such as \(<1/300\) of \( n_K/n_C \), potassium ions distribute randomly in the matrix and are not organized.

In the second region, the structure of K-GICs is considerably organized with increasing \( n_K/n_C \). In the third region, the structural ordering is almost realized and very slightly improved by the increase of \( n_K/n_C \). The critical concentration between 2\(^{nd}\) to 3\(^{rd}\) regions is at \( \approx 60 \) of \( n_K/n_C \). As already mentioned previously, the observed critical concentrations where the manner of the dependence of resistivity and magnetoresistance on the potassium concentration varies were \( \approx 60 \) and \( \approx 70 \) of \( n_K/n_C \), respectively. Thus, we can consider that there is a strong connection between hydrogen-sorption capacity and transport properties.

### 4.2 Resistivity change of K-GICs during sorption of hydrogen at 77 K

In the course of the investigation, it was found that the resistivity of KC24 and KC36 increased during hydrogen sorption at 77 K. Normalized resistivity, \( (\rho/\rho_0)/\rho_0 \), is plotted vs. sorbed amount of hydrogen, \( n_{H_2}/n_K \) in Fig. 7, where \( \rho \) and \( \rho_0 \) denote the resistivities of hydrogen-sorbed KC24 (KC36) and original KC24 (KC36), respectively. The increase of the resistivity along with hydrogen sorption can be explained as follows. The sorbed hydrogen molecules expand carbon-carbon interlayer distance and reduce the charge transfer interaction between potassium and carbon layers. The density of conduction electrons consequently decreases. Such effect is considered to be more sensitive to rich compounds, because the degree of increase is larger for KC24 rather than KC36 as seen in Fig. 7.

### 5. Conclusions

Potassium-graphite intercalation compounds with different composition were prepared from Grafoil. Temperature dependence of the resistivity, magnetoresistance and hydrogen-sorption capacity were determined for these compounds. For very dilute compounds such as KC300 and KC250, temperature dependence of the resistivity was semi-conductive, while metallic for KC168, KC36, KC36, and KC36. The magnetoresistance decreased with increasing potassium concentration down to almost zero for KC36 and KC36. The hydrogen-sorption capacity at 77 K was also determined. It increased with increasing potassium concentration, from almost no sorption for KC300 to 1.84 of molar ratio of saturated sorbed amount of hydrogen to potassium for KC24. Transport properties and hydrogen-sorption capacity showed a remarkable correlation in the dependence on the potassium concentration.

### References

3) N. Akuzawa et al., submitted to Carbon.