H_2-Sorption by Potassium-Graphite Intercalation Compounds

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Abstract

Potassium-graphite intercalation compounds with 7 different compositions ranging from KC_{300} to KC_{24} were prepared from exfoliated graphite sheet (Grafoil). The resistivity and H_2-sorption capacity of these compounds were determined. KC_{300} and KC_{250} showed semi-conductive temperature dependence of the resistivity as well as host Grafoil, while KC_{168} and more rich compounds showed metallic behavior. Dependence of the resistivity on the potassium concentration was explicitly divided into two regions with a critical concentration at about $KC_{60\sim70}$. The room temperature resistivity value decreased remarkably with increasing potassium concentration below the critical concentration, while it was almost constant above the critical value. The critical concentration was also observed at about KC_{50} in H_2-sorption capacity vs. potassium concentration plot.

Introduction

Potassium intercalates graphite and modifies its structure from dense crystalline solid to a kind of porous material with characteristic nanospace. Accordingly, hydrogen can be accommodated in the nanospace of potassium graphite intercalation compounds (K-GICs) at low temperatures such as 77K. We observed conduction electron spin resonance (CESR) of K-GICs as a function of potassium concentration at room temperature. We found that the *g* value of KC_{200} was the same as that of host graphite (2.006), in contrast to the value of 2.0023 ± 0.0005 observed for KC_{100} and the other K-GICs with higher potassium concentration. This observation suggests that there is a drastic change of the electronic properties between KC_{200} and KC_{100}. This kind of drastic change could be expected to be observed in the other properties such as transport properties, magnetic properties, chemical properties, etc. The present paper investigated the electrical resistivity and H_2-sorption capacity of K-GICs with different potassium concentrations between KC_{300} and KC_{24}.

Experimental

Materials

Graphite specimen used was exfoliated graphite sheet, Grafoil (GrafTech International Ltd. Company). The graphite specimen for resistivity measurement (with typical sizes of 4 x 40 x 0.4 mm^3) and small pieces, taken from the same Grafoil sheet, were heat-treated at ~1000 ºC 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%.

Preparation of K-GICs

A two-step preparation technique was used. At first KC_8 sample was prepared from small pieces of Grafoil allowing them being contacted with potassium metal vapor at around 230 ºC. Then, the resulting KC_8 sample and additional small pieces of Grafoil were contacted with graphite specimen for resistivity measurement and they were heat-treated at 250 ~ 450 ºC, depending on the composition of target compounds. The composition of the final compound was calculated from the supplied amount of alkali metals (in KC_8) and all the graphite (specimen for resistivity measurement, additional small pieces of Grafoil and that in KC_8). The heat-treatment was continued until the resistivity value of the specimen became unchanged.

Resistivity measurement of K-GICs

The in-plane resistivity of K-GICs was determined by the four-terminal method. Its temperature dependence was determined between 77 K and room temperature.

Determination of 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.

Results and Discussion

Temperature dependence of the electrical resistivity of K-GICs is comparatively shown in Fig. 1, where the data of host graphite is also shown. Semi-conductive behavior was observed for KC_{300} and KC_{250} in a similar manner as for Grafoil. It turns to metallic for KC_{168} and more rich compounds. The absolute value decreased monotonically with increasing potassium concentration, and almost saturated in higher concentration region such as KC_{36} and KC_{24}.

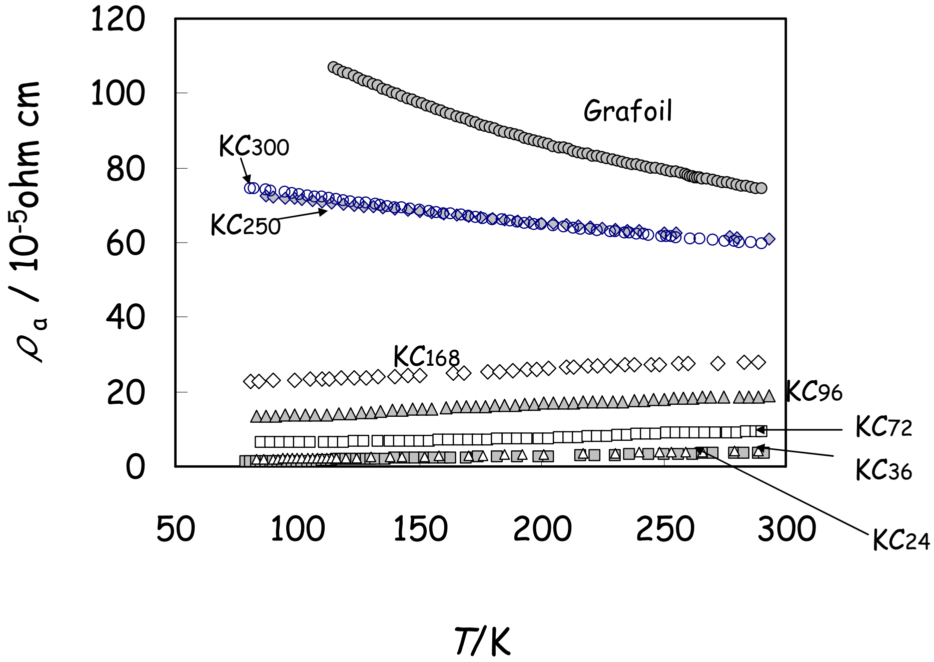

Fig. 1 Temperature dependence of electrical resistivity of K-GICs.

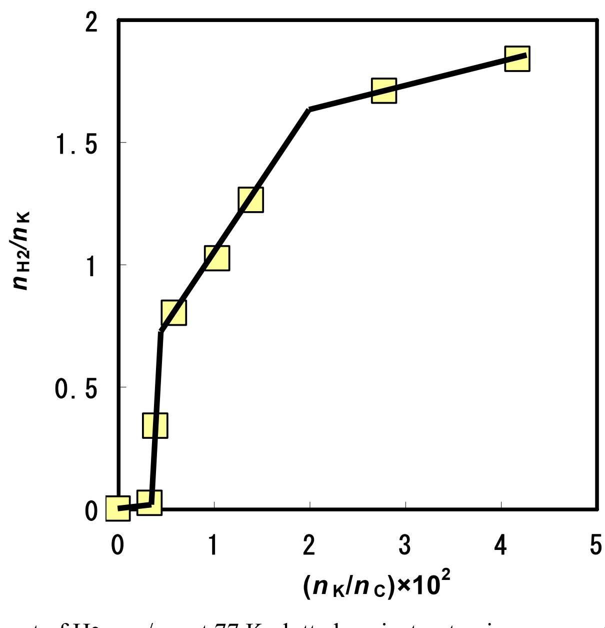

Fig. 2 Saturated sorbed amount of H_2, n_{H2}/n_K, at 77 K plotted against potassium concentration of K-GICs, n_K/n_C.

The saturated sorbed amount of H_2 by K-GICs at 77 K is plotted vs. potassium concentration in Fig. 2. In the region up to KC_{300}, the sorbed amount is substantially zero. A sudden increase of sorbed amount occurred at around KC_{300} ~ KC_{250}. In the region between KC_{200} and KC_{50}, sorbed amount increases considerably with increasing potassium concentration. In the region above KC_{50}, it increased very slightly with increasing potassium concentration.

As noted above, semi-conductive temperature dependence of KC_{300} and KC_{250} is replaced by the metallic one of KC_{168}. In addition, sudden change of *g* value occurs between KC_{200} and KC_{100}. It means that nanospace formation is realized before transition from semiconductor to metal occurs. It can be considered that for very dilute compounds such as KC_{300}, potassium ions distribute randomly in the matrix and are not organized. With increasing potassium concentration up to KC_{60}, ordering of the structure of K-GICs is improved. Therefore, both H_2-sorption capacity and electrical conductivity increase remarkably with increasing potassium concentration in this region. Above KC_{60}, the structural ordering is fairly completed and it is improved very slightly with increasing potassium concentration. The present observation shows that there is a strong correlation between hydrogen-sorption capacity and transport properties of K-GICs.

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