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Host Effect on the Properties of AM-GICs

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Host Effect on the Properties of AM-GICs

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Carbon materials (A-1, A-2 and A-3 derived from pitch cokes) with different graphitization degree, were allowed to react with potassium. The hydrogen-sorption behavior at 77 K, electrical resistivity, ESR and Raman spectra of the resulting compounds with the composition of KC_{60} were determined. The sorbed amount at saturation, $(n_{H2}/n_K)_{sat}$, was 0.55 and 1.43 for KC_{60}s prepared from A2 (d_{002}= 0.3377 nm) and A3 (d_{002}= 0.3361 nm), respectively. No H_2 sorption was observed for KC_{60} from A-1 (d_{002}=0.342 nm). Temperature dependence of the resistivity of KC_{60}s from A-2 and A-3 showed metallic behavior, contrary to semiconductive one for the host materials. However, KC_{60} (A-1) showed semiconductive temperature dependence, similarily to the host material. Raman spectra of KC_{60}s from A-2 and A-3 showed doublet structure, similarly to that of K-GICs from HOPG, characteristic for graphite intercalation compounds with stage n > 2. On the contrary, KC_{60} (A-1) gave single peak at around 1597 cm^{-1}. Those facts suggest that potassium exists in the interlayer spaces for KC_{60}s (A-2, A-3), but not for KC_{60} (A-1). It was also shown that g-factor of ESR spectra of KC_{60} can be useful to predicting the H_2-sorption behavior.

Keywords: intercalation; potassium; ESR; Raman; resistivity; H_2 sorption

INTRODUCTION

Intercalation of alkali metals in graphite creates nanospaces in the interlayer spaces. It was discovered by Watanabe et al.[1] that KC_{24} sorbs H_2 at 77K and 1.9 mol of H_2 is sorbed by 1 mol of KC_{24} at saturation. The structure of the nanospace is considered to be determined by several factors, e.g. species of alkali metals, its concentration, and structure and texture of the host carbon material, etc. The host effect on the sorption of ethylene molecules by CsC_{24} has been reported[2], in which the sorbed amount of ethylene molecule increased with the increase of the heat-treatment temperature (HTT) of the host

carbon material of CsC_{24}. This observation means that the net volume of nanospace of CsC_{24} increases with increasing HTT of the host carbon material. The net volume is considered to be equal to the apparent volume increase due to intercalation subtracted the volume occupied by Cs ions. The size of intercalated Cs ions seems to be correlated with the degree of charge transfer. Therefore, it is interesting to investigate the electrical properties of AM-GICs (AM=K,Rb,Cs) prepared from various carbon materials. In the present paper, electrical resistivity, magnetoresistance, Raman and ESR spectra of KC_{60} prepared from carbon materials with different graphitization degree are described.

2. EXPERIMENTAL

2.1 Materials

Artificial graphite blocks (A-1, A-2 and A-3), originated from pitch cokes and heat-treated at different temperatures (1500°C (A-1), 2000°C (A-2) and 2660°C (A-3)), were provided by Nippon Carbon Co. Ltd. Each specimen for the electrical resistivity measurement was typically 1.5 cm long, 0.3 cm wide and 0.15 cm thick. Three arms were on the side faces and are for the use of voltage measurement in longitudinal and transverse directions and the voltage terminal arms were spaced 1.0 cm apart. For the hydrogen-sorption , ESR and Raman experiments, powders from the same blocks were used. Potassium metal with purity of 99 % were used after distillation.

2.2 Preparation of KC_{60}

KC_{60} was prepared by reacting potassium-metal vapor on the carbon materials at 500 K. The molar ratio of potassium metal to carbon materials was adjusted to be 1/60. The specimen was then annealed at 573 K for a few days to ensure the homogeneity of the specimen. KC_x with $x < 60$ from block specimen was difficult to prepare because of crack formation during reaction with potassium.

2.3 Hydrogen-sorption isotherm

The hydrogen-sorption isotherms of KC_{60}s at 77 K were determined by the constant volume method.

2.4 Resistivity, magnetoresistance, Raman and ESR measurements

The resistivity (ρ) and magnetoresistance ($\Delta\rho/\rho$) of the host carbon materials and KC_{60} specimens were determined by 4-point technique. Temperature dependence of the resistivity between 280 and 330K were also determined. Magnetic fields up to 0.67 T were applied perpendicularly to the planar specimen for the determination of the magnetoresistance. Raman spectra of the host materials and the KC_{60}s were determined with excitation wavelength of 514.5 nm at room temperature using JOVAN YVON RAMANOR-T-64000. ESR spectra were taken at temperatures between 100 and 300 K using JEOL JES-TE-100.

3. RESULTS AND DISCUSSION

The H_2-sorption isotherm of KC_{60}s (A-1, A-2 and A-3) at 77 K are shown in Fig. 1. The sorbed amount at saturation, $(n_{H2}/n_K)_{sat}$, was 0.55 and 1.43 for KC_{60}(A-2) and KC_{60}(A-3), respectively. There was no sorption for KC_{60}(A-1).

The resistivity of the host carbon materials at room temperature are listed in TABLE 1, where XRD parameters (the interlayer spacing,d_{002} and the crystallite size along the c-axis, L_c values) and R values (defined as relative intensity, (I_{1360} / I_{1580}), of Raman spectrum) are also shown.

The magnetoresistance of the host carbon materials (A-1, A-2, and A-3) and Grafoil (Union Carbide Co. Ltd.) are plotted against magnetic field in Fig. 2. The large value of the magnetoresistance of A-3 shows that this specimen is well graphitized in accord with the XRD parameters shown in TABLE 1.

Temperature dependence of the resistivity of KC_{60} (A-2) is shown in Fig. 3, where data of the host material are also shown. It is clearly seen that KC_{60} (A-2) has metallic character in contrast to the host material. The resistivity ratio of KC_{60} to host material at room temperature, $\rho(KC_{60})/\rho$(host), was about 0.20. KC_{60}(A-3) also showed the metallic temperature dependence and $\rho(KC_{60})/\rho$ (host) was 0.17. Those values are very close to that (0.15) of HOPG[3].

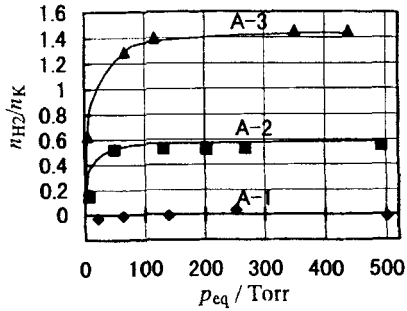

FIGURE 1 H_2-sorption isotherms (77K) of KC_{60} prepared from A-1, A-2 and A-3.

TABLE 1 Resistivity and structure parameters of the host carbon materials

carbon materials	ρ / ohm cm	d_{002} /nm	Lc_{002} / nm	R value (Raman)
A-1 (HTT-1500)	4.30 x 10^{-3}	0.342	11	1.11
A-2 (HTT-2000)	2.28 x 10^{-3}	0.3377	43	0.35
A-3 (HTT-2660)	0.81 x 10^{-3}	0.3361	70	0.25

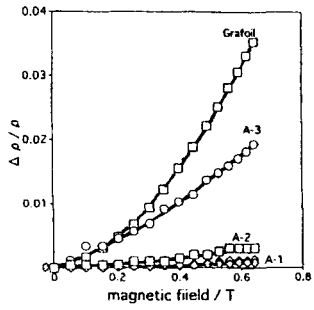

FIGURE 2 Magnetoresistance of host carbon materials and Grafoil plotted against magnetic field.

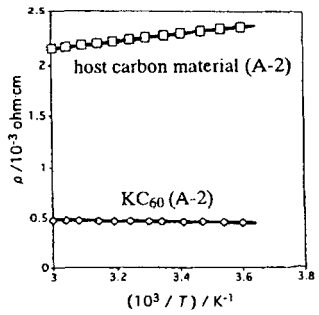

FIGURE 3 Temperature dependence of the resistivity of A-2 and derived KC_{60}.

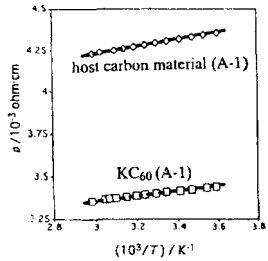

FIGURE 4 Temperature dependence of the resistivity of host material (A-1) and derived KC_{60}.

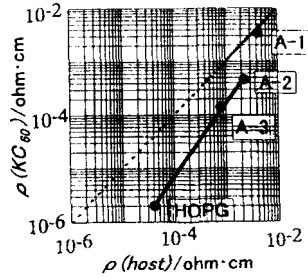

FIGURE 5 Plot of $\rho(KC_{60})$ vs. ρ(host)

The temperature dependence of the resistivity of KC_{60} (A-1) was semiconductive similarly to the host material, as shown in Fig. 4. Only small decrease in the resistivity was observed through the reaction with potassium; the resistivity ratio, $\rho(KC_{60})/\rho$(host), was 0.8.

The resistivity values of KC_{60}s were plotted against those of the host materials in Fig. 5, where the literature value of HOPG[3] is also shown. The data of A-2, A-3 and HOPG fall on a straight line, except A-1. From the above observations (H_2-sorption behavior, temperature dependence of the resistivity and the values of $\rho(KC_{60})/\rho$ (host)), it can be considered that A-1 does not have ability to accomodate potassium in the interlayer spaces, beeing distinct from A-2 and A-3. It is also confirmed by the fact that almost no magnetoresistance was observed for KC_{60}s (A-2 and A-3), which is due to the increase of conduction electron through the charge transfer between potassium and carbon layers.

Raman spectra of KC_{60}s are shown in Fig. 6. For KC_{60} (A-2), doublet structure at frequencies of 1588 and 1612 cm^{-1} was observed, which is characteristic for graphite intercalation compounds with stage number > 2[4]. Similarly, KC_{60} (A-3) has doublet

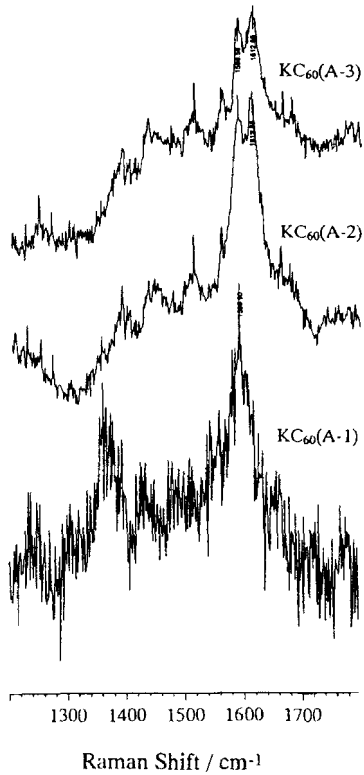

FIGURE 6 Raman spectra of KC_{60}s prepared from A-1, A-2 and A-3.

structure at 1586 and 1612 cm^{-1}. Peaks at 1356 cm^{-1} (A-2) and 1358 cm^{-1} (A-3) , observed for the host materials, are disappeared in the spectra of KC_{60}s. In contrast, no splitting was observed for KC_{60} (A-1). Those facts suggest that potassium metals exist in the interlayer spaces for KC_{60}s (A-2, A-3), but not for KC_{60} (A-1), in agreement with the observations of the resistivity described above.

Tanaike et al. studied the host effect in the intercalation of alkali metal and tetrahydrofuran into various carbon materials, and found that the stage 1 compound is formed if the parameter of graphitization degree of carbon materials, $P_1 > 0.2$ and random stage structure if $P_1 < 0.2$[5] , where P_1 is a parameter indicating the graphitization degree of a carbon material and corresponds to the volume fraction of graphitic structure in a carbon material. To compare the present results with their observations, L_c values should be used instead of P_1 values (because P_1 values of A-1, A-2 and A-3 are not known). The critical point ($P_1 = 0.2$) can be expressed as $L_c = 40$ nm, by reference to their specimen[5]. The result that only A-1(L_c = 11 nm) does not allow the intercalation of potassium looks reasonable.

The ESR spectra of the host material (A-3) and derived KC_{60} are shown in Fig. 7, where the spectra of the standard (Mn^{2+}) are also given. Significant resonance shift by the intercalation of potassium is observed. The calculated g values are plotted against temperature in Fig. 8. The g value of the host material increases with decreasing temperature, in agreement with the reported data for various carbon materials[6]. On the other hand, g value of KC_{60} is independent of temperature and the absolute value (2.002) is close to that of K-GICs prepared from HOPG[7].

It can be considered that the variation in g value is caused by the intercalation

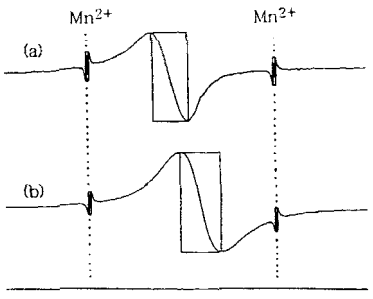

FIGURE 7 ESR spectra of host carbon material (A-3) and derived KC_{60}.

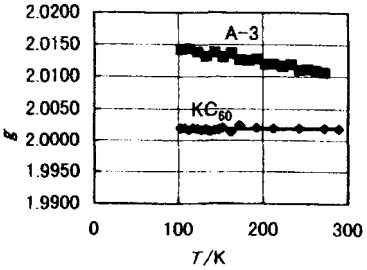

FIGURE 8 Temperature dependence of g value of host carbon material (A-3)and derived KC_{60}.

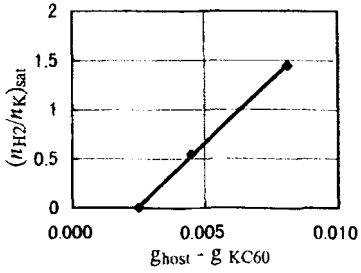

FIGURE 9 $(n_{H2}/n_K)_{sat}$ of KC_{60} plotted as a function of the magnitude of the variation of g value, $(g_{host} - g_{KC60})$.

of potassium and is a measure of the charge transfer. A plot of the sorbed amount of hydrogen, $(H_2/K)_{sat}$, against the magnitude of the variation of g value, $(g_{host} - g_{KC60})$, shows a linear relationship as seen in Fig. 9. Although reproducebility of the relation must be examined with other carbon materials, it is suggested that the ESR parameter is possibly useful to predicting the hydrogen sorption behavior, i.e. to probing the nanospaces of alkali-metal intercalated carbon materials.

4. CONCLUSIONS

The hydrogen-sorption isotherms of KC_{60}, prepared from artificial graphites (A-1, A-2 and A-3) with different graphitization degree, at 77K were determined. In addition, electrical resistivity, magnetoresistance, ESR and Raman spectra of the host materials and derived KC_{60}s were also determined. The sorbed amount of H_2 at saturation, $(n_{H2}/n_K)_{sat}$, was 0, 0.55 and 1.43 for KC_{60}s derived from A-1(d_{002}= 0.342 nm; Lc = 11 nm), A-2 (d_{002}= 0.3377 nm; Lc = 43 nm) and A-3 (d_{002}= 0.3361 nm; Lc = 70 nm), respectively.

The resistivity of KC_{60} was smaller than that of host material. The resistivity ratio of KC_{60} to host material at room temperature, $\rho(KC_{60})/\rho$ (host), was 0.8, 0.20 and 0.17 for A-1, A-2 and A-3, respectively. The values for A-2 and A-3 were close to the literature value (0.15) of HOPG. The semiconductive temperature dependence of the resistivity was observed for KC_{60} (A-1), in contrast to the metallic character of KC_{60}s (A-2 and A-3).

Raman spectra of KC_{60}s prepared from A-2 and A-3 showed doublet structure characteristic for graphite intercalation compounds with stage n > 2. However no splitting was observed for KC_{60} (A-1). Those facts suggest that potassium exists in the interlayer spaces for KC_{60}s (A-2, A-3), but not for KC_{60} (A-1), in agreement with the observations of the resistivity described above.

The ESR spectra of the host material and derived KC_{60}s were measured. Significant resonance shift by the intercalation of potassium was observed. Relationship of g value and hydrogen-sorption behavior was discussed.

Acknowledgements
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References

[1] K. Watanabe, M. Soma, T. Onishi and K. Tamaru, *Nature Phys. Sci.*, **233,** 161 (1971).

[2] N. Akuzawa and Y. Takahashi, *TANSO,* **1995** [No.170] 295 (in Japanese).

[3] E. McRae, D. Billaud, J. F. Mareche and A. Herold, *Physica B,* **99,** 541(1980).

[4] M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys.*, **30,** 139 (1981).

[5] O. Tanaike and M. Inagaki, *Carbon,* **35**, 831 (1997).

[6] K. Matsubara, *TANSO,* **1998** [No.181] 41 (in Japanese).

[7] P. Lauginic, H. Estrade, J. Conard, D. Guerard, P. Lagrange and M. EL. Makrini, *Physica B*, **99**, 514(1980).