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Preparation of Graphite Intercalation Compound of Vanadium Fluoride in Fluorine Atmosphere

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Graphite intercalation compound(GIC) of vanadium fluoride has been prepared in fluorine atmosphere. The GIC's prepared were stage 1-8 compounds with composition, $C_{8.4-79.5}VF_{5.8-6.0}$. The size of intercalated VF_6^-(d_i) decreased from 0.533 nm to 0.415 nm with increasing x in C_xVF_6. The compounds with small d_i's showed high stability in air.

Intercalation of vanadium fluoride in graphite occurs in oxidative atmosphere. Nikonorov et al.$^{1)}$ attempted the preparation of vanadium pentafluoride-GIC under ClF_5 gas and obtained a mixture of vanadium pentafluoride-GIC and graphite fluoride($C_{51.6}VF_{18.3}$) at 237-277 °C. However, stage 1-8 compounds represented by C_xVF_6 have been easily prepared at 180-220 °C under fluorine gas of 10-101 kPa. In this paper we report the preparation, structure and electrical conductivity of vanadium fluoride-GIC.

Host materials of GIC are highly oriented pyrolytic graphite(HOPG) and natural graphite(NG). Vanadium fluoride is prepared by fluorinating V metal powder at 200 °C and successively supplied for the intercalation reaction in the same reactor. The preparative method of GIC is the same as reported previously.$^{2)}$ Analyses of GIC's were made by X-ray diffraction, elemental analysis and ESCA. The electrical conductivity was measured by contactless Wien bridge.

Table 1 shows typical examples of the reaction conditions and analytical data for C_xVF_y obtained in the present study. The intercalated species is determined to be a VF_6^- anion by elemental analysis of carbon, fluorine and vanadium. Only stage 2 compound was obtained from NG, however, HOPG gave stage 1-8 compounds. The stage number strongly depends on the amount of V metal powder i.e. the vapor pressure of VF_5. The higher the VF_5 pressure is, the lower stage compound is obtained. It is noted that intercalate size, which is calculated from repeat distance along c-axis, takes various values, that is, stage 1: 0.520-0.533 nm, stage 2: 0.415-0.466 nm, and stage 4-8: 0.418-0.433 nm. This suggests that the intercalated VF_6^- takes different configurations between carbon layers in the different stages. The geometrical calculation of intercalated species and intensity calculation of X-ray diffraction lines support the following assignment. In stage 1 GIC and a mixture of stage 1 and 2 GIC's, 4 fluoride ions of octahedral VF_6^- are in contact with carbon layers just above and below the intercalated VF_6^-, and other 2 fluoride ions are situated at the center between carbon layers. This configuration of VF_6^- needs

Table 1. Reaction conditions, X-ray data and composition of C_xVF_y

Host	Time	P_{F_2}	Amount of V	Stage	I_c	d_i	Composition
		kPa	mg		nm	nm	
HOPG	4 d	101	200	1	0.860	0.525	$C_{10.6}VF_6$ a)
HOPG	2 h	10	50	2	1.167	0.459	$C_{19.9}VF_6$ a)
HOPG	2 h	10	10	2	1.134	0.426	$C_{29.3}VF_6$ a)
HOPG	2 h	101	10	4	1.760	0.418	$C_{52.9}VF_6$ a)
HOPG	2 h	10	5	5	2.110	0.433	$C_{62.2}VF_6$ a)
HOPG	2 h	10	5	8	3.103	0.420	$C_{79.5}VF_6$ a)
NG	1 d	101	80	2	1.112	0.441	$C_{28.9}VF_{5.9}$ b)
NG	1 d	101	80	2	1.103	0.432	$C_{29.5}VF_{5.8}$ b)

NG : Natural Graphite / HOPG : Highly Oriented Pyrolytic Graphite

a) Calculated from weight increase.

b) Calculated from elemental analyses of C, F, and V.

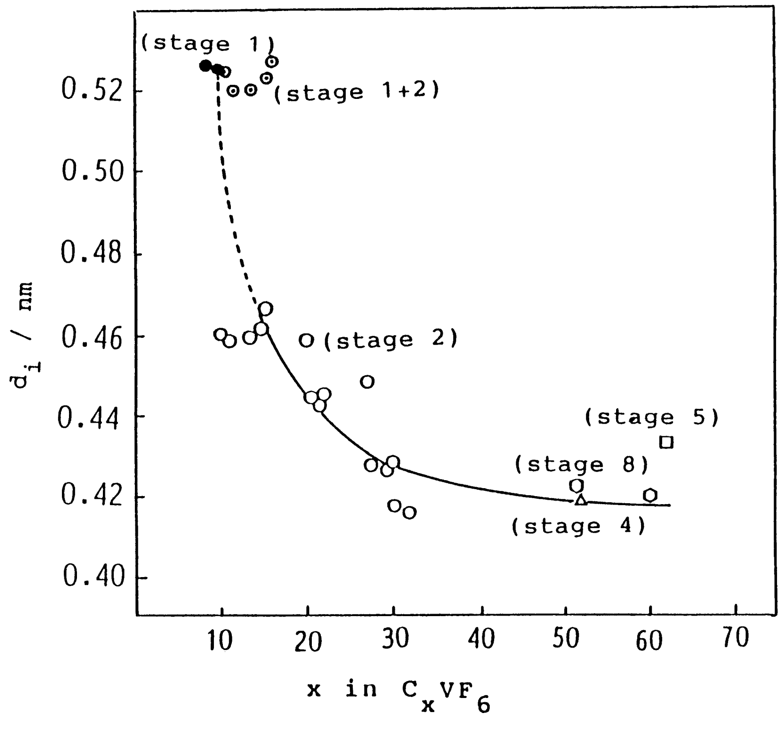

Fig.1.

The relationship between intercalate size d_i and the carbon content of the samples (The values of x were calculated based on weight increase.).

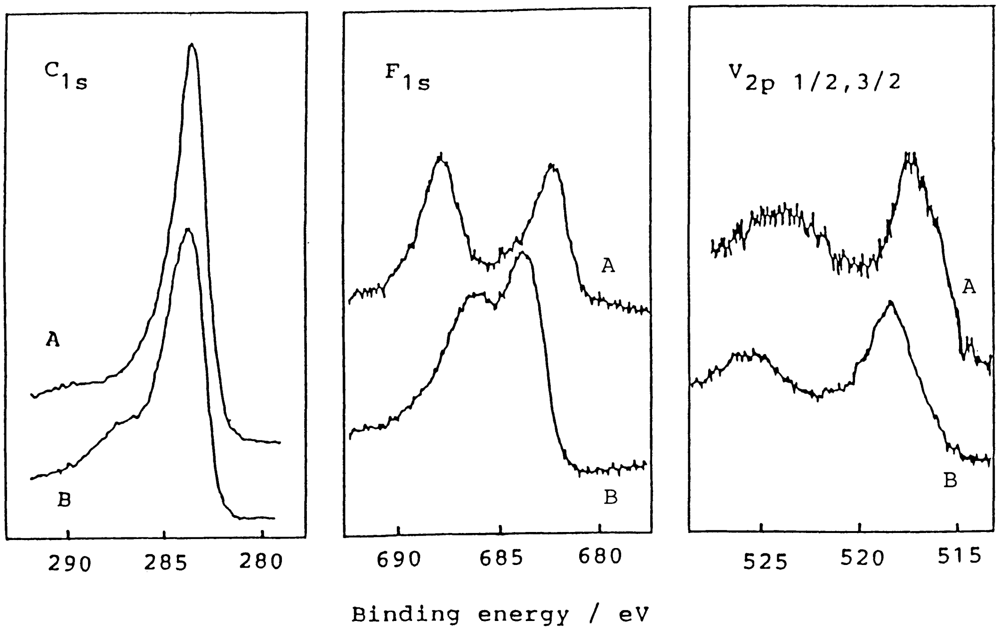

Fig.2.
ESCA spectra of C_xVF_y prepared from HOPG. A:$C_{27.4}VF_6$(stage 2)
B:$C_{10.1}VF_6$(stage 1).

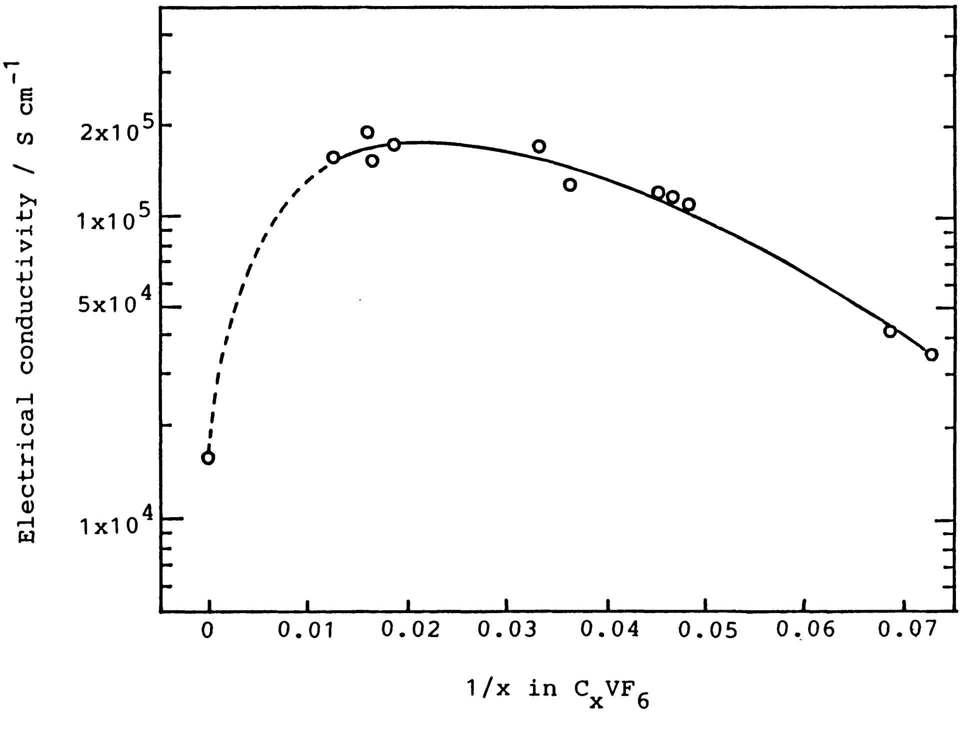

Fig.3.
Electrical conductivities of C_xVF_y prepared from HOPG.

0.532 nm along c-axis, which is well consistent with the observed value, 0.525 nm(d_i) in Table 1. These GIC's may be formed to avoid the increasing repulsion of VF_6^- anions with increase in the in-plane density of VF_6^-.

Stage 2 and other higher stage GIC's take more stable configuration that all 6 fluoride ions of octahedral VF_6^- interact with carbon layers. In this model, the size of intercalated VF_6^-(d_i) is calculated to be 0.483 nm along c-axis. However, the observed d_i values range from 0.466 nm to 0.415 nm which are smaller than the calculated value. This is attributed to the nestling[3)] of fluoride ions of VF_6^- into benzene rings of carbon layers. The nestling effect decreases the apparent size of intercalated fluoride, d_i by ca. 0.04 nm in stage 1 GIC. In case of the higher stage GIC, the decrease in d_i reaches ca. 0.06 nm.[3)] Figure 1 shows the d_i values as a function of x in C_xVF_6. The d_i decreases with increasing x, i.e. with decreasing VF_6^- in the GIC. As the decrease of in-plane density of VF_6^- decreases the repulsion among VF_6^- anions intercalated between carbon layers, the more deeper nestling of VF_6^- into benzene rings occurs. This model is also consistent with ESCA spectra for stage 1 and 2 GIC's having different d_i values. Stage 2 GIC with small d_i, 0.427 nm gave F_{1s} peak at a lower energy position, 682.2 eV than stage 1 GIC whose F_{1s} binding energy was 683.8 eV close to that for the hexafluoride anion. This indicates that a fluoride ion is more strongly reduced in the stage 2 than in the stage 1. The V_{2p} peaks appeared at 517.4 and 524.4 eV for stage 2 GIC (A), and 518.5 and 525.5 eV for the stage 1 (B), from which it is found that vanadium metal of stage 2 GIC is not so oxidized as that for the stage 1. The result of ESCA measurement suggests that fluoride ions interact more strongly with carbons in stage 2 GIC than in the stage 1. The structure and chemical bond of C_xVF_6 mentioned above are closely related with the stability in air. The intercalated model suggests that stage 1 GIC is unstable compared with the other stages. In fact, stage 1 C_xVF_6 decomposed to the stage 2 in 1 week after preparation. Stage 2 GIC having ca. 0.460 nm as intercalate size, d_i, is more stable than the stage 1, starting to decompose to a higher stage after 4 weeks. Stage 2 or other higher stage GIC with a small d_i of 0.415-0.430 nm shows high stability in air. Almost no change in the X-ray diffraction pattern was observed for 7 months after preparation.

Figure 3 shows the in-plane electrical conductivity of C_xVF_y prepared from HOPG as a function of amount of intercalate. The conductivity increased rapidly with increasing intercalate. The highest electrical conductivity was obtained at a stage 5 compound $C_{62.2}VF_6$, being 1.97×10^5 S cm^{-1} which is 12 times that of pristine HOPG (1.7×10^4 S cm^{-1}). Afterwards the conductivity gradually decreased. The decrease in conductivity of GIC's with compositions of $C_{60-80}VF_6$ was only 3-13% after exposure to air for 8 months.

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