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Preparation of Graphite Intercalation Compound of Niobium Fluoride in Fluorine Atmosphere

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The 1st stage intercalation compound of graphite with niobium fluoride has been prepared in fluorine gas of 101 kPa. The composition is $C_{8-10}NbF_{6-7}$ with repeat distance of 0.818-0.834 nm. The highest electrical conductivity is 1.2 X 10^5 S cm^{-1} at stage 2+3.

Intercalation of niobium fluoride in graphite occurs in oxidative atmosphere. Melin and Herold[1)] reported the preparation of stage 2 $C_{16.6}NbF_5$ in chlorine or bromine atmosphere. Hamwi and Touzain[2)] prepared 1st stage $C_{8.3}NbF_{4.90}Cl_{0.17}$ under chlorine gas of 507 kPa. However, 1st stage $C_{8-10}NbF_{6-7}$ is synthesized with high reaction rate when intercalation is made in fluorine atmosphere. In this case, intercalated species is octahedral NbF_6^- anion except for the compound prepared under a low fluorine pressure. This paper deals with the preparation, structure and electrical conductivity of niobium fluoride-graphite intercalation compound(GIC).

Starting materials are natural graphite(NG, 295-833 μm), highly oriented pyrolytic graphite(HOPG) and Nb metal powder. Nb metal and graphite put in separate Ni boats are placed at the center of the reactor and between the center and flange of the reactor, respectively. The reactor is then evacuated by rotary and diffusion pumps with increasing the temperature from room temperature to 310 °C. The temperature of graphite is 160-210 °C. Intercalation of NbF_5 is made under fluorine gas of 10-101 kPa. Products were analyzed by X-ray diffraction, elemental analysis and ESCA, and electrical conductivity was measured by contactless Wien bridge.

Tables 1 and 2 show typical examples of the reaction conditions and analytical data for C_xNbF_y obtained in the present study. Stage 1 GIC is easily prepared in fluorine gas of 101 kPa. The repeat distance along c-axis is 0.818-0.834 nm and composition is $C_{8-10}NbF_{6-7}$. When a small amount of Nb metal is used, i.e. the vapor pressure of NbF_5 is low, a high stage GIC is formed even at 101 kPa of fluorine gas as shown in Table 2. On the other hand, a stage 2 or 3 GIC is generally obtained at low fluorine pressures of 30-10 kPa. In these GIC's, each X-ray diffraction line clearly splits into two peaks which indicate different GIC phases of a same stage. In an experiment performed with a high NbF_5 pressure and long reaction time, stage 1 GIC is prepared at 20 kPa.

The size of intercalated species(d_i) for stage 1 GIC is 0.483-0.499 nm along

Table 1. Reaction condition, X-ray data and composition of C_xNbF_y

Sample No.	Reaction conditions Temp/°C	P_{F_2}/kPa	Time/h	Stage	Ic/nm	di/nm	Composition C_xNbF_y
NG-1	200	101	18	1	0.823	0.488	$C_{9.6}NbF_{6.7}$ a)
NG-2	160	101	18	1	0.818	0.483	$C_{9.0}NbF_{6.2}$ a)
NG-3	200	101	33	1	0.818	0.483	$C_{8.0}NbF_{6.3}$ a)
HOPG-1	200	101	20	1	0.834	0.499	$C_{8.5}NbF_{6.0}$ b)
HOPG-2	200	30	19	2	{1.181 {1.165	{0.511 {0.495	$C_{23.1}NbF_{5.8}$ b)
HOPG-3	210	10	20	3	{1.515 {1.494	{0.510 {0.489	$C_{24.3}NbF_{5.5}$ b)

NG:Natural Graphite / HOPG:Highly Oriented Pyrolytic Graphite
a) from elemental analyses of C and F
b) from weight increase.

Table 2. Reaction condition and X-ray data of C_xNbF_y prepared from HOPG

Sample No.	Wt.ratio Sample:Metal	Reaction conditions Temp/°C	P_{F_2}/kPa	Time/h	Stage	Ic/nm	di/nm
HOPG-1	1 : 25	200	101	20	1	0.834	0.499
HOPG-4	1 : 20	200	20	45	1	0.824	0.488
HOPG-5	1 : 1	190	101	26	3+4	1.450 1.787	0.444 0.446
HOPG-3	1 : 1	210	10	20	3	{1.515 {1.494	{0.510 {0.489

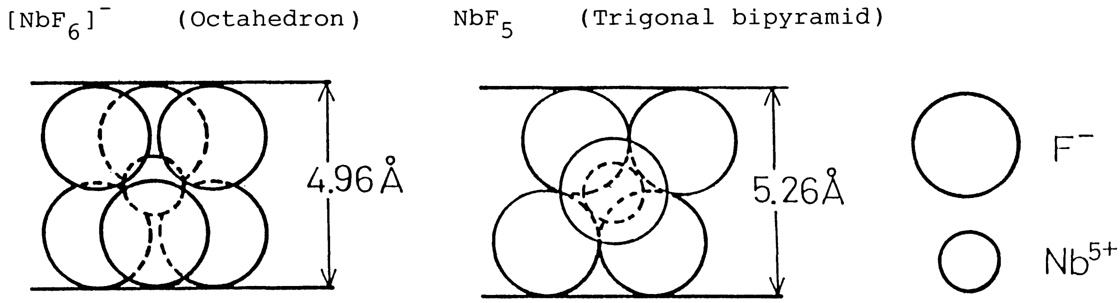

Fig.1. Geometry of NbF_6^- and NbF_5. Calculated on the assumption that ionic radii are 0.133 nm for F^- and 0.066 nm for Nb^{5+}, respectively.

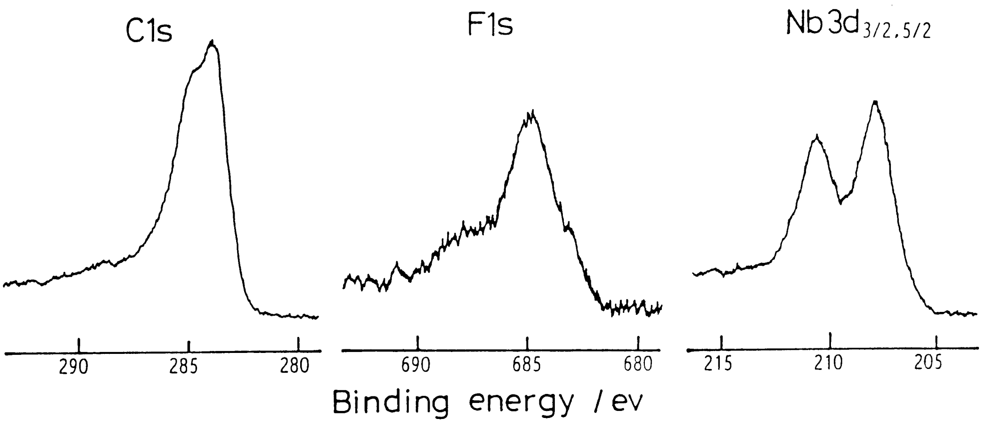

Fig.2. ESCA spectra of C_xNbF_y prepared from HOPG.

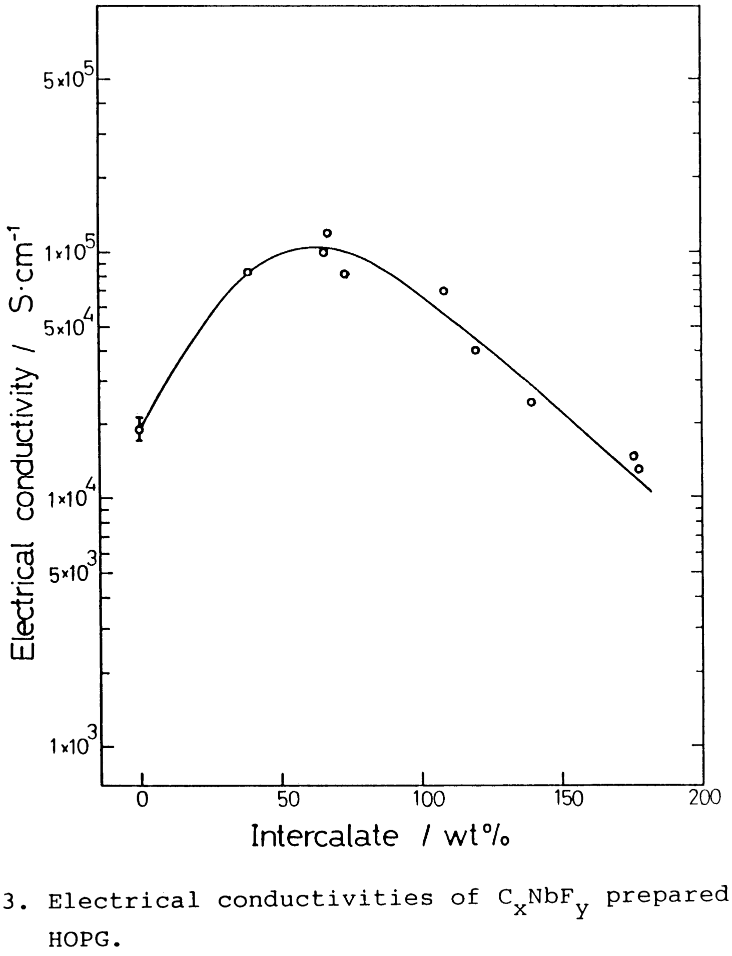

Fig.3. Electrical conductivities of C_xNbF_y prepared from HOPG.

c-axis. Stage 2 and 3 GIC's contain a different phase whose d_i is 0.510-0.511 nm. There are two possible intercalates in C_xNbF_y, i.e. NbF_6^- and NbF_5. Figure 1 illustrates the intercalated models for NbF_6^- and NbF_5. NbF_5 has larger dimension than NbF_6^-. THe intercalate size of 0.510-0.511 nm is well consistent with 0.508 nm reported previously for the GIC's of NbF_5.[1,2] It is furthermore demonstrated from the intensity calculation for X-ray diffraction lines that the configuration shown in Fig.1 is the most appropriate though both of NbF_6^- and NbF_5 can take different configurations between carbon layers. It is therefore determined that the intercalated species of stage 1 GIC is NbF_6^-, and stage 2 and 3 GIC's involve another phase in which NbF_5 is mainly intercalated in addition to C_mNbF_6 phase. This is consistent with the results of elemental analysis. Excess fluorine in $C_{8-10}NbF_{6-7}$, detected by elemental analysis, may be derived from surface C-F layers because GIC is prepared in fluorine atmosphere at 160-210 °C. As the decomposition of stage 2 or 3 GIC proceeds, the diffraction line indicating C_mNbF_6 phase increases its intensity compared with that for C_nNbF_5 phase, which shows that the decomposition of C_nNbF_5 is faster than that of C_mNbF_6.

A mixture of stage 3+4 shown in Table 2 has a smaller d_i than others. This is observed only for the GIC prepared under low NbF_5 pressure and 101 kPa fluorine gas. It is due to the nestling[3] of fluoride ions of NbF_6^- into benzene rings of carbon layers above and below the intercalated NbF_6^-. The nestling effect decreases the apparent size of intercalated fluoride, d_i by 0.04 nm.

Figure 2 shows the typical ESCA spectra of C_xNbF_y. C_{1s} spectrum has two peaks at 284.7 eV and 283.8 eV. The latter indicates GIC phase and the former corresponds to graphite itself which would arise from the decomposition of GIC surface. F_{1s} spectrum gives one peak at 684.8 eV, which is almost the same binding energy as that for fluoride ion of other metal fluorides. When GIC is a mixture of C_mNbF_6 and C_nNbF_5, F_{1s} spectrum does not split into two peaks. This may be because the binding energies of F_{1s} electron in NbF_6^- and NbF_5 are similar to each other.

Figure 3 shows the electrical conductivity of C_xNbF_y prepared from HOPG as a function of amount of intercalate. A mixture of stage 2+3 gives the highest conductivity of 1.2×10^5 S cm^{-1} which is 7 times that of pristine HOPG. It is lower than the highest conductivity of C_xTiF_y, 2.4×10^5 S cm^{-1}, previously reported.[4] NbF_5 is more stronger Lewis acid than TiF_4 because NbF_5 easily makes stage 1 GIC while stage 2 GIC is normally prepared by TiF_4. Therefore charge transfer coefficient would be larger in C_xNbF_y than in C_xTiF_y. Probably because a strong electrostatic force between charged carbon and fluoride decreases mobility of carriers, the highest conductivity of C_xNbF_y is lower than that for C_xTiF_y.

References

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