

Surface free energy and chemical bonding of fluorine–graphite intercalation compounds

Tsuyoshi Nakajima and Mitsuhiro Touma

Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto (Japan)

Abstract

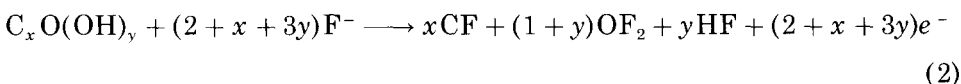
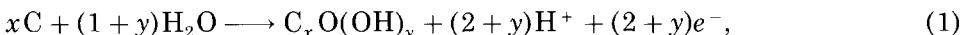
Surface free energy, electrical conductivity and charge transfer between carbon and fluorine have been obtained for the fluorine–graphite intercalation compound, C_xF , and the mechanism of anode effect prevention by C_xF is discussed. It has been found that C_xF has higher wettability by ionic $KF \cdot 2HF$ melt than not only graphite fluoride with a covalent C–F bond but also graphite itself. The electrical conductivity of C_xF is much higher than that of pristine pyrolytic graphite at stage II or higher. These properties of C_xF are brought about by electron transfer from carbon to fluorine, and give rise to favorable conditions at the carbon anode whilst carrying out the electrolysis of a $KF \cdot 2HF$ melt at a high current density.

Introduction

Fluorine gas is produced by the electrolysis of a $KF \cdot 2HF$ melt at $\sim 100^\circ C$. Some of the fluorine atoms discharged react with the carbon electrode, giving a thin covalently bonded graphite fluoride layer, although most of the discharged fluorine atoms combine with each other and leave the electrode surface as fluorine gas molecules. When the electrode surface is partially covered by a low surface energy graphite fluoride film, the wettability of the carbon anode by the melt is greatly decreased, which leads to the occurrence of the so-called anode effect.

It was recently found that the ionic fluorine–graphite intercalation compound formed in the graphite anode has an important role in preventing the anode effect. The following facts have been found [1, 2].

(1) When more than 0.05% water is present in the melt, the anode effect takes place quite easily, probably because of the immediate fluorination of the graphite oxide film which is previously found by the discharge of the water in the melt:



(2) When an insoluble fluoride such as LiF is present in a water-free melt, the ionic fluorine–graphite intercalation compound is quickly

formed at the graphite anode according to the following reactions, and no anode effect occurs



The reactions (3) and (4) provide $\text{C}_x\text{F}(\text{HF})_y$.

To continue the electrolysis of a $\text{KF} \cdot 2\text{HF}$ melt at a high current density for a long period without occurrence of the anode effect, it is essential to keep the melt dehydrated ($\text{H}_2\text{O} \leq 0.02\%$) and to prepare the fluorine-graphite intercalation compound at the carbon anode under the coexistence of an insoluble fluoride such as LiF . For this purpose, a LiF -impregnated carbon electrode was recently developed [3].

Thus the question arises as to why a fluorine-graphite intercalation compound prevents the occurrence of the anode effect. To clarify this problem, we measured the surface free energy, electrical conductivity and charge transfer of the fluorine-graphite intercalation compound C_xF , and discuss the mechanism of anode effect prevention by C_xF .

Experimental

Synthesis of C_xF samples

The C_xF samples were prepared at room temperature in the presence of a trace amount of HF . The experimental procedure is as follows. Highly Oriented Pyrolytic Graphite (HOPG, $5 \times 5 \times 0.4$ mm) and graphite sheet ($5 \times 35 \times 0.4$ mm) were put into a nickel reactor, which was evacuated by a rotary pump to 10^{-1} mmHg at 200°C for several hours. After the temperature of the reactor was decreased to room temperature under vacuum, high purity fluorine gas (Daikin Kogyo Company, 99.4–99.7%, N_2 0.3–0.6%, $\text{HF} < 0.01\%$) was introduced into the reactor. The reaction of fluorine gas with water molecules adsorbed on the internal wall of the reactor produces a trace amount of HF as a catalyst for fluorine intercalation in graphite (usually 0.1% to 0.4%). The reaction was conducted for several hours to several days. After fluorine gas was substituted by nitrogen or argon, C_xF samples were obtained.

The samples were analyzed by X-ray diffractometry and XPS. The stage number was determined from the repeat distance along the c -axis (I_c), and the composition from the weight increase.

Contact angle measurement and calculation of surface free energy of C_xF samples

Graphite sheet samples were employed for contact angle measurement. The liquids used were water, methylene iodide and formamide, whose polar and dispersion components of surface tensions are known [4, 5]. These three liquids were used in the present study to minimize the

experimental error. Contact angle measurements were performed at room temperature against a fresh surface of C_xF , which was obtained by cleavage of the graphite sheet sample with a sharp knife. Contact angles were measured 12 times for each sample, and the average value was obtained by omitting the largest and smallest ones.

The surface free energy of C_xF was calculated by use of the contact angle data in the following way. The Young–Dupre equation gives the relation between contact angle (θ), surface tension of liquid and solid (γ_l , γ_s) and interfacial tension between liquid and solid (γ_{sl}):

$$\gamma_s = \gamma_{sl} + \gamma_l \cos \theta. \quad (5)$$

The surface tension, γ , is divided into polar and dispersion components (γ^p , γ^d):

$$\gamma = \gamma^p + \gamma^d. \quad (6)$$

According to Fowkes, the interfacial tension, γ_{sl} , given by eqn. (7), is also a function of polar and dispersion components [4, 5]:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^d \cdot \gamma_l^d} - 2\sqrt{\gamma_s^p \cdot \gamma_l^p}. \quad (7)$$

By combining eqn. (5) with eqn. (7), we obtain eqn. (8):

$$1 + \cos \theta = 2\sqrt{\gamma_s^d \cdot \gamma_l^d}/\gamma_l + 2\sqrt{\gamma_s^p \cdot \gamma_l^p}/\gamma_l. \quad (8)$$

If we measure contact angles, using two liquids whose polar and dispersion components are known, we obtain the surface tension (surface free energy) of a solid material.

Electrical conductivity measurement

The in-plane electrical conductivity of HOPG samples was measured by a contactless Wien bridge at room temperature.

Reflectance measurement and calculation of Fermi energy and charge transfer per carbon or intercalated fluorine

Reflectance measurements were also carried out using the fresh surface of C_xF samples prepared from HOPG chips. The data were analyzed by the two-dimensional tight binding model proposed by Blinowski *et al.* [6]. The reflectance (R) is expressed as a function of plasma frequency (ω), Fermi energy (E_f) and free carrier scattering time (τ) for stages I and II acceptor-type graphite intercalation compounds. If Fermi energy (E_f) and free carrier scattering time (τ) are postulated, a theoretical $R(\omega) - h\omega$ curve is obtained. Fitting of the theoretical $R(\omega) - h\omega$ curve to the experimentally obtained one gives the most appropriate values of Fermi energy (E_f) and free carrier scattering time (τ). The charge transfer per carbon atom (f_c) or intercalated fluorine (f_m) is related to the Fermi energy and composition of C_xF by the equations:

$$f_c = (E_f/\gamma_0)^2/\sqrt{3\pi}, \quad (9)$$

$$f_m = xf_c. \quad (10)$$

where $x = x$ in $C_x F$ and γ_0 = the overlap integral between the electrons of adjacent carbons in the same carbon plane (2.9 eV).

Results and Discussion

Composition, stage and chemical bonding of $C_x F$ samples

Stage III, II and quasi-stage I compounds were obtained from both HOPG and graphite sheet. Table 1 shows the composition, stage number and c -axis repeat distance (I_c) of $C_x F$ samples prepared from HOPG chips. Stage I compounds of $C_{3.1} F$ to $C_{4.3} F$ containing a small amount of stage II phase gave a very strong (002) diffraction line with weak (001), (003) and (004) lines. The repeat distances calculated from these diffraction lines ranged from 10.48 to 11.38 Å. These large I_c values were attributed to the formation of a bi-intercalation phase where ionically and semi-ionically bonded fluorines are inserted in alternate carbon layers [7]. The composition of stage II was in the range $C_{3.9} F$ – $C_{10.6} F$ and that of stage III from $C_{9.5} F$ to $C_{12.6} F$. In stage III and most stage II compounds prepared from HOPG, the (004) and (003) diffraction lines had the highest intensity. This means that intercalated fluorine is oriented at the center of two carbon sheets, *i.e.* it has an almost ionic bond. On the other hand, the intensity of the (002) line gradually increased with increasing fluorine content, even at stage II, for the samples prepared from graphite sheet. The increase in the peak intensity of the (002) line indicates a deviation of the position of intercalated fluorine from the center of two carbon sheets, *i.e.* the increase in covalency of the C–F bonds. In the graphite sheet made of natural graphite, the diffusion of intercalated fluorine may be hindered due to the existence of more lattice defects than in HOPG. As a result, the carbon–fluorine bond would be further strengthened, *i.e.* from ionic to semi-ionic, without a structural change to stage I.

XPS spectra show the nature of chemical bond between carbon and fluorine. C_{1s} peaks appeared at 284.1 eV in both stage I, $C_{3.0} F$ and stage II, $C_{9.4} F$, indicating the existence of carbon atoms ionically bonded to

TABLE 1

Composition, stage number and c -axis repeat distance (I_c) of $C_x F$ prepared from HOPG

Composition range	Stage	I_c range (Å)
$C_{3.1} F$ – $C_{4.3} F$	I + (II) ^a	10.48–11.38 ^b
$C_{3.9} F$ – $C_{5.8} F$	II + (I) ^a	9.29–9.46 ^b
$C_{6.0} F$ – $C_{10.6} F$	II	9.23–9.45
$C_{9.5} F$ – $C_{12.6} F$	III	12.55–12.72

^aMinor phase.

^b I_c values of minor phases are not given.

fluorine and without direct chemical interaction with fluorine. In addition to the strong peak at 284.1 eV, the stage I compound has a small peak at 286.7 eV indicating carbon atoms semi-ionically bonded to fluorine. Corresponding to the C_{1s} peaks, F_{1s} spectra showed peaks at 685.2 eV and 686.0 eV in stage II and I compounds, respectively. The F_{1s} spectrum gives only one peak for each stage, however the binding energy is slightly larger in the stage I phase because of the existence of a semi-ionic C–F bond. This may be because of the high electronegativity of fluorine.

Surface free energy

The data for the contact angle against graphite sheet, $C_{5.3}F$ and graphite fluoride with C–F covalent bonds, $(CF_{0.74})_n$, are given in Table 2. Methylene iodide penetrated into graphite fluoride sheet. Therefore the surface free energy of graphite fluoride was calculated from contact angles of water and formamide. Table 3 shows the surface free energies

TABLE 2

Contact angles on graphite sheet, C_xF , and graphite fluoride

Sample	Contact angle (°)		
	Water	Methylene iodide	Formamide
Graphite	93.6	34.3	69.2
$C_{5.3}F$	70.6	43.1	44.8
$(CF_{0.74})_n$	112.3	Penetrated	87.9

TABLE 3

Surface free energies of graphite sheet, C_xF and graphite fluoride obtained from contact angles

Sample	Liquid ^a	Surface free energy/mJ m ⁻²		
		Dispersion component	Polar component	Total
Graphite	W–MI	43.0	0.237	43.2
	W–FA	44.0	0.189	44.2
	MI–FA	42.8	0.313	43.1
	Average	43.3	0.246	43.5
$C_{5.3}F$	W–MI	42.1	6.99	48.6
	W–FA	31.8	9.64	41.4
	MI–FA	30.5	13.05	43.6
	Average	34.8	9.89	44.5
$(CF_{0.74})_n$	W–FA	22.7	0.00267	22.7

^aW = Water, MI = Methylene iodide, FA = Formamide.

calculated from contact angle data. The surface free energy of $C_{5.3}F$ is almost equal to that of graphite sheet. However, the polar component of $C_{5.3}F$ is clearly much larger than that for graphite sheet. This suggests that $C_{5.3}F$ shows higher wettability by ionic substances, *e.g.* $KF \cdot 2HF$ melt, than graphite sheet itself. On the other hand, graphite fluoride has a much lower surface free energy than the others. The value of surface free energy is close to that of polytetrafluoroethylene (PTFE), 20 mJ m^{-2} , and its polar component is negligible. C_xF with ionic and semi-ionic C-F bonds has higher hydrophilicity than not only graphite fluoride but also graphite sheet while graphite fluoride with C-F covalent bonding shows such strong hydrophobicity as to cause the anode effect in fluorine evolution reaction.

Electrical conductivity

Figure 1 shows the in-plane electrical conductivity of C_xF samples prepared from HOPG, measured at room temperature. The conductivity of the host HOPG chips were in the range of 0.7×10^4 to $1.8 \times 10^4 \text{ S cm}^{-1}$. At first the electrical conductivity increases rapidly with increasing fluorine intercalation, due to an increase in the number of positive holes created by electron transfer from carbon to fluorine. After reaching the maximum, the conductivity decreases due to a decrease in the mobility of the carrier, which is scattered by lattice vibration. Furthermore, electron localization results from the increase in the covalency of the C-F bond, particularly at stage I. Therefore the electrical conductivity is much higher than that of pristine HOPG at stage II or higher, but almost equal to or less than that of host HOPG at stage I.

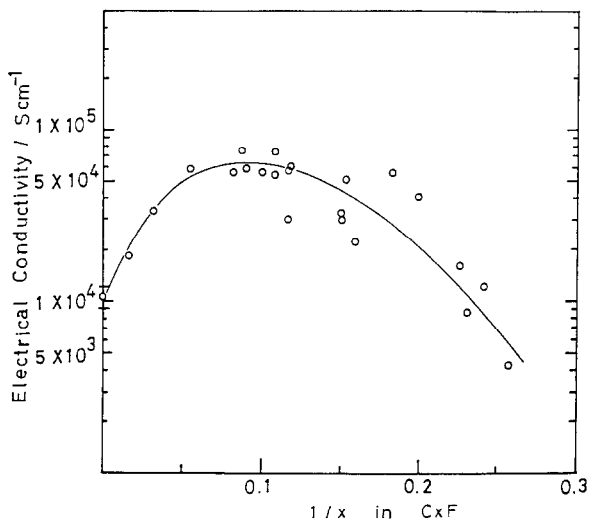


Fig. 1. Room temperature electrical conductivity of C_xF prepared from HOPG.

Charge transfer between carbon and fluorine

Figure 2 shows a typical reflectance spectrum obtained for stage II, $C_{7.48}F$, in which open circles indicate the experimentally obtained reflectance; and solid line fitting curve is calculated from a Blinowski model. Fermi energy, E_f and free carrier scattering time, τ , were obtained by fitting a theoretical curve to the experimental data. The charge transfer per carbon atom or per intercalated fluorine was calculated using eqns. (9) and (10). These data are all summarized in Table 4. Ohana *et al.* [8] measured the reflectance of stage III, $C_{9.0}F$ to stages I and II, $C_{3.3}F$, and calculated the Fermi energy and charge transfer of stage II samples of $C_{8.4}F$ to $C_{4.0}F$, based on the Blinowski model. The Fermi energy increased from 0.97 eV to 1.01 eV with increasing fluorine content from $C_{8.4}F$ to $C_{6.0}F$, and decreased from 1.01 eV to 0.87 eV with further increase in the fluorine content from $C_{6.0}F$ to $C_{4.0}F$. According to this change, the charge transfer per carbon atom, f_c , showed a maximum value, 0.021, for $C_{6.0}F$. However, we obtained somewhat different results. The difference may be attributed to the synthetic conditions of C_xF and host materials. All the parameters, E_f , f_c and f_m showed a trend to decrease with increasing fluorine content from stage II, $C_{10.62}F$ to stage I, $C_{3.05}F$. Stage I compounds in particular clearly gave smaller values than those of the stage II. The Fermi energy ranges from 0.92 to 0.80 eV at stage II, and from 0.80 to 0.75 eV at stage I. The charge transfer between carbon and fluorine is 0.018 to 0.014 per carbon atom and 0.184 to 0.093 per fluorine atom at stage II. At stage I, f_c and f_m are smaller values, in the ranges 0.014–0.012 and 0.059–0.041, respectively. In acceptor-type intercalation compounds of graphite, E_f and f_c generally increase with increasing intercalated species, accompanying the decrease in Fermi level [9]. This means that electron transfer from carbon to an intercalated species increases with increasing

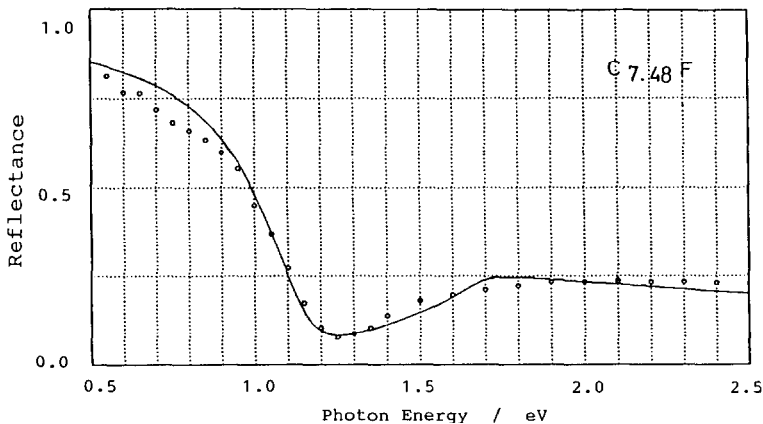


Fig. 2. Reflectance curve for stage II, $C_{7.48}F$; (○): experimentally obtained reflectance; (—): curve fit calculated by the Blinowski model.

TABLE 4

Parameters^a obtained by the fitting of the experimental reflectance data to a Blinowski model

Sample	Stage	E_f (eV)	$\tau(10^{-14})$ (s)	f_c	f_m
C _{3.05} F	I	0.780	1.15	0.0133	0.041
C _{4.00} F	I	0.750	1.10	0.0116	0.046
C _{4.05} F	I	0.780	1.20	0.0133	0.054
C _{4.25} F	I	0.795	1.60	0.0138	0.059
C _{5.97} F	II	0.845	2.55	0.0156	0.093
C _{6.48} F	II	0.820	1.60	0.0147	0.095
C _{6.68} F	II	0.800	1.70	0.0140	0.094
C _{6.69} F	II	0.890	3.60	0.0173	0.116
C _{6.73} F	II	0.900	3.40	0.0177	0.119
C _{7.48} F	II	0.840	1.90	0.0154	0.115
C _{8.21} F	II	0.820	1.75	0.0147	0.121
C _{8.52} F	II	0.880	3.30	0.0169	0.144
C _{8.58} F	II	0.915	2.50	0.0183	0.157
C _{8.59} F	II	0.890	3.25	0.0173	0.149
C _{8.62} F	II	0.870	2.50	0.0165	0.142
C _{8.87} F	II	0.850	1.90	0.0158	0.140
C _{9.29} F	II	0.875	1.60	0.0167	0.155
C _{9.49} F	II	0.870	2.10	0.0165	0.157
C _{10.62} F	II	0.890	2.45	0.0173	0.184

^a E_f = Fermi energy, τ = free carrier scattering time, f_c = charge transfer per carbon atom, f_m = charge transfer per intercalated fluorine.

intercalation or with decreasing stage number. The reverse tendency in E_f and f_c of C_xF would be explained in terms of the change of chemical bond, *i.e.* the decrease in E_f and f_c values with increasing fluorine content would be attributed to the increase in covalency of the C-F bond as indicated by XPS and X-ray diffraction data.

Mechanism of anode effect prevention by C_xF

To avoid anode effect in electrolytic production of fluorine gas, a C_xF type compound with ionic bonds should be prepared around the surface of the carbon anode at the beginning of electrolysis. Contact angle measurement has indicated that C_xF has higher wettability by ionic $KF \cdot 2HF$ melt than graphite fluoride with covalent C-F bonds and graphite itself. The polar component of the surface free energy of C_xF is larger than that of graphite sheet. This would be brought about by electron transfer from carbon to intercalated fluorine, *i.e.* the nature of the C-F bond in C_xF is almost ionic at stage II or higher, and semi-ionic at stage I.

The $C_xF(HF)_y$ prepared in a graphite sheet electrode during electrolysis is stage IV or III [1, 2]. The electrical conductivity data obtained in the present study strongly suggest that the $C_xF(HF)_y$ formed in a graphite

anode has much higher conductivity than host graphite. This gives a further reason for the anode to continue electrolysis without occurrence of the anode effect, because graphite fluoride with covalent bonding is an electric insulator.

C_xF with ionic bonding is not directly converted to graphite fluoride having covalent bonds by high temperature treatment in a fluorine atmosphere or electrochemical polarization. For example, when C_xF is heated in fluorine gas with increasing temperature, it decomposes to expanded graphite and fluorocarbons such as CF_4 and C_2F_6 at temperatures over $100^\circ C$.

For these reasons, C_xF -type compounds would prevent the anode effect occurrence and enable continuous electrolysis at a high current density.

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