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Surface Free Energies of Two Kinds of Graphite Fluorides, $(CF)_n$ and $(C_2F)_n$

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The surface free energies of two kinds of graphite fluorides, $(CF)_n$ and $(C_2F)_n$, were estimated from the contact angles of several liquids. The contact angles of water on flaky $(CF)_n$ and $(C_2F)_n$ were 117° and 116°, respectively, being slightly larger than that for poly(tetrafluoroethylene), while the values for tablets of powdery $(CF)_n$ and $(C_2F)_n$ were 143° and 141°, respectively, which indicates that powdery graphite fluoride is hardly wetted by water. From the contact angles obtained, the surface free energies were estimated to be *ca.* 18 mJ/m^2 for both flaky $(CF)_n$ and $(C_2F)_n$, *ca.* 2 mJ/m^2 for powdery $(CF)_n$ and *ca.* 3 mJ/m^2 for powdery $(C_2F)_n$. These differences depend on the surface conditions such as the packing of fluorine atoms, the roughness and porosity. From the contact angles for the tablets of $(CF)_n$–polyethylene mixtures, it is suggested that the anode effect in the fluorine or aluminium electrolysis takes place when the surface of carbon anode is partially covered by graphite fluoride.

During the electrolysis of molten KF·2HF or alumina in cryolite melt, it sometimes happens that the cell voltage suddenly increases with arc-discharging. This phenomenom is called the anode effect, on which a number of mechanisms have been reported by many investigators.[1,2]

Watanabe *et al.* proposed that the anode effect is attributed to the formation of graphite fluoride film on the surface of carbon electrode.[3–5] The formation of graphite fluoride on carbon anode surface extremely decreases the wettability of molten salt owing to its low surface free energy. On the basis of the mechanism, various experiments have been performed.[6–9] Graphite fluoride was detected on the surface of carbon anode after the anode effect from ESCA spectra.[10–11] Furthermore, during the studies on the relationship between composition and structure of graphite fluoride, it was found that a new compound, poly(dicarbon monofluoride), $(C_2F)_n$, is formed at a relatively low reaction temperature.[12] This compound might also be concerned with the anode effect besides $(CF)_n$.

The present study was carried out to clarify the roles of graphite fluorides on the anode effect. The extent of wetting between anode and electrolyte was evaluated physically from the surface free energies obtained from the contact angles of several liquids on two kinds of graphite fluorides at room temperature.

Experimental

Material. The following four samples of graphite fluorides were prepared. (1) Flaky poly(carbon monofluoride), $(CF)_n$ with F/C ratio of 1.0 was prepared by the direct fluorination of natural graphite (produced in Madagascar, purity: more than 99%) having a sieve size of 1.981—0.833 mm under F_2 pressure of 26664 Pa at 630 °C for 2 d. (2) Powdery $(CF)_n$ with F/C ratio of 1.1, prepared from petroleum coke of less than 37 μm, was supplied by Daikin Kogyo Co. Ltd. (3) Flaky poly(dicarbon monofluoride), $(C_2F)_n$ with F/C ratio of 0.65 was prepared by the fluorination of flaky natural graphite (1.981—0.833 mm) under F_2 pressure of 101325 Pa at 380 °C for 14 d. (4) Powdery $(C_2F)_n$ with F/C ratio of 0.65 was prepared by the fluorination of natural graphite of less than 37 μm under F_2 pressure of 101325 Pa at 380 °C for 3 d. All the samples were analyzed by X-ray diffractometry and their compositions were determined from elemental analysis of carbon and fluorine. For the purpose of comparison, flaky natural graphite with a sieve size of 1.981—0.833 mm, grafoil made by compressing exfoliated graphite from Union Carbide Corporation, poly(tetrafluoroethylene) (PTFE) supplied by Daikin Kogyo Co. Ltd. and polyethylene(PE) of E. Merck were used for the contact angle measurement.

Liquids used for the contact angle measurement were distilled water, reagent grade glycerol, formamide, 1,4-butanediol, hexadecane and 17% and 31% NaOH solutions.

Contact Angle Measurement. All the measurements were made at 30 °C using the CA-D type contact angle meter of Kyowa Kagaku Co. Ltd. For the flaky samples, the liquids were dropped onto them immediately after peeling off the thin layer with plastic adhesion tape. For the powdery samples, they were compressed and molded under a pressure of *ca.* 49 MPa to the tablets of 13 mm diameter and supplied for the contact angle measurement. The measurements for each sample were repeated 10 to 20 times and their average value was taken.

Results and Discussion

Surface Free Energy. Table 1 shows the contact angles of several liquids on each samples and water drops on the typical samples are shown in Fig. 1. It is of interest that water shows an extremely large contact angle on the tablet of graphite fluoride. The contact angles for PTFE and PE are in good agreement with the results measured by other investigators.[13–15] The data of water on natural graphite and grafoil are slightly larger than the values (60—86°) measured by others.[16–18] The difference of the data between natural graphite and grafoil would be attributed to the surface conditions such as the roughness and porosity. The large deviations in the data for flaky graphite fluorides might be due to the surface roughness and cracks made by fluorination, or/and the groups of $=CF_2$ and $-CF_3$ produced around the crack. Furthermore, the liquids with a surface tension lower than that of 1,4-butanediol penetrated into the flakes through the cracks. It was impossible to measure the contact angles of the liquids with a low surface tension such as hexadecane, since the powdery graphite fluorides were also too poor in cohesiveness

TABLE 1. CONTACT ANGLES FOR GRAPHITE FLUORIDES AND OTHER SAMPLES AT 30 °C

Sample	Liquids						
	31%NaOH soln	17%NaOH soln	Water	Glycerol	Formamide	1,4-Butanediol	Hexadecane
$(CF)_n$, flake	121±6	116±8	117±11	100±12	96±8	penetrate	penetrate
$(C_2F)_n$, flake	—	—	116±10	102±10	95±10	penetrate	penetrate
$(CF)_n$, tablet	146±3	139±2	143±3	151±2	128±3	103±2	penetrate
$(C_2F)_n$, tablet	—	—	141±6	145±7	129±9	—	penetrate
Graphite, flake	108±4	96±7	96±4	77±4	75±4	56±4	spread
Grafoil	110±2	101±5	95±2	91±2	81±2	65±3	spread
PTFE, tablet	118±3	114±3	109±3	105±2	95±1	86±2	44±1
PE, tablet	115±3	109±2	98±2	89±3	83±2	70±2	spread

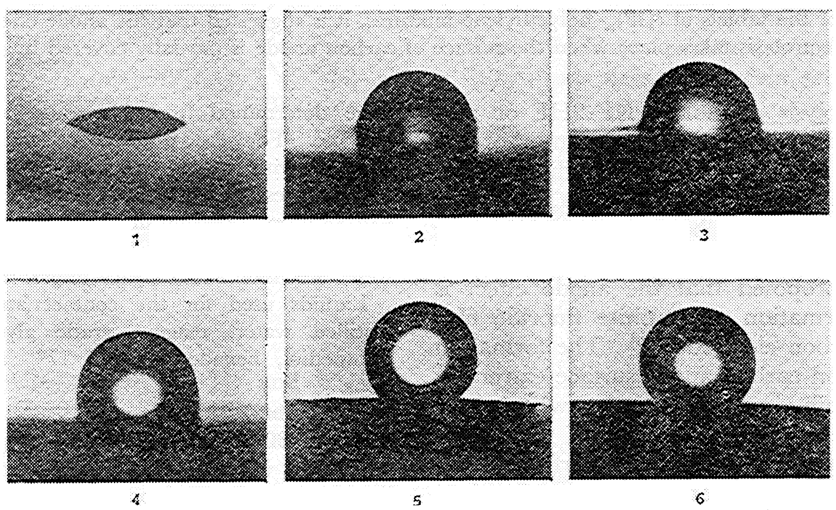

Fig. 1. Contact angles of water at 30 °C.
1. Glass, $\theta=27°$, 2. PE, $\theta=94°$, 3. Grafoil, $\theta=95°$, 4. PTFE, $\theta=109°$, 5. $(C_2F)_n$ tablet, $\theta=141°$, 6. $(CF)_n$ tablet, $\theta=143°$.

to make a tablet without pore.

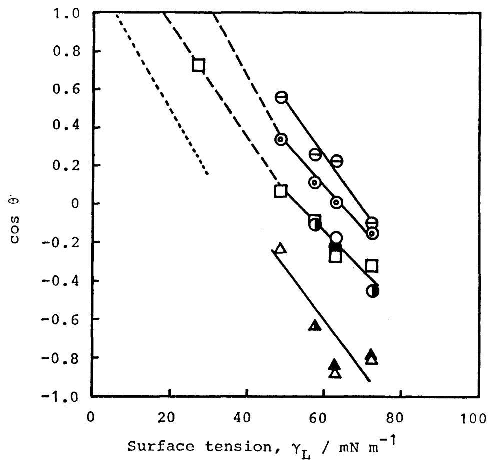

Fig. 2. Zisman plots for $(CF)_n$, $(C_2F)_n$, graphite, PTFE, and PE.
○ $(CF)_n$, flake, ●: $(C_2F)_n$, flake, △: $(CF)_n$, tablet, ▲: $(C_2F)_n$, tablet, ⊖: graphite, □: PTFE, ◎: PE, ……: perfluorolauric acid monolayer.

It was attempted to estimate the critical surface tensions, γ_c, from the Zisman plots in Fig. 2 using the data in Table 1. In Fig. 2, the surface tensions of the liquids, γ_L, at 20 °C were adopted because the values at 30 °C were not available. The difference in the data between 20 °C and 30 °C would be negligibly small, being less than 2 mN/m.[19] The critical surface tension is determined from a point where the extrapolated line of Zisman plot intersects the abscissa of $\cos\theta=1$, which is approximately equal to the surface free energy. As shown by the dashed lines in Fig. 2, the critical surface tensions of PTFE and PE are 18 and 31 mN/m, respectively.[20] It is also known that the Zisman plot consists of two lines for nonpolar and polar liquids. Although graphite fluorides could not be measured for the nonpolar liquids in this work, if the samples without crack and pore were prepared, their Zisman plots for the nonpolar liquids would give a line with a slope similar to the dashed line for PTFE. Accordingly, it is suggested that the critical surface tensions for flaky graphite fluorides, $(CF)_n$ and $(C_2F)_n$ are nearly equal to that of PTFE. As shown in Fig. 3, two kinds of graphite fluorides have different structures, however, the packings of fluorine atoms on the basal plane are equal to each other, being ca. 1.9×10^{19} F/m^2 (The packing for PTFE is calculated to be ca. 3.2×10^{19} F/m^2 along the long chain and ca. 1.0×10^{19} F/m^2 at the chain edge.[21]). It is therefore reasonable that

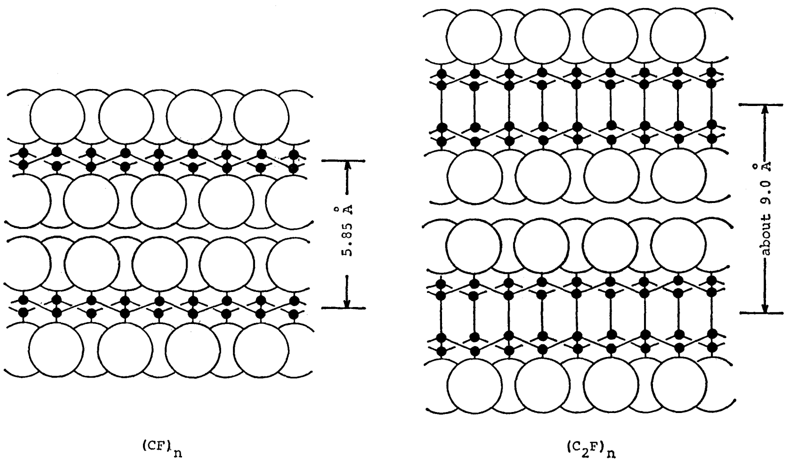

Fig. 3. Crystal structures of $(CF)_n$ and $(C_2F)_n$.
●: Carbon atom, ○: fluorine atom.

two kinds of flake samples have the same surface free energy.

The combination of Young's and Fowkes's equations for the interfacial tension[22,23] leads the relation between the contact angle and the surface free energy in the solid–liquid system depending only on the dispersion force.

$$\cos\theta = -1+2(\gamma_s^d\cdot\gamma_l^d)^{1/2}/\gamma_L,$$

where θ is contact angle, γ_s^d and δ_l^d are the surface free energies of solid and liquid, respectively, and γ_L is the surface tension of liquid. The calculations for water, glycerol and formamide gave the average surface free energies of *ca.* 18 mJ/m^2 for flaky $(CF)_n$, *ca.* 18 mJ/m^2 for flaky $(C_2F)_n$, *ca.* 2 mJ/m^2 for powdery $(CF)_n$, *ca.* 3 mJ/m^2 for powdery $(C_2F)_n$, *ca.* 20 mJ/m^2 for PTFE and *ca.* 33 mJ/m^2 for PE. (*cf.* published data: 19.5 mJ/m^2 for PTFE and 35.0 mJ/m^2 for PE.[23]) The surface free energies of two powdery graphite fluorides are much lower than those of the flakes, being nearly equal to that of perfluorolauric acid monolayer having the group of $-CF_3$ on the surface (γ_c=6 mN/m).[24] This might be attributable to the group of $-CF_3$ or $=CF_2$ on the edge plane of graphite fluoride crystallite as shown in Fig. 4. The surface free energy of graphite fluoride would depend on the ratio of the basal and edge planes on the surface of graphite fluoride particle.

Relation between Surface Free Energy and Anode Effect. Both of the basal and edge planes of graphite crystallite would be present at random on the surface of actual carbon electrode. Powdery graphite fluoride is preferred to investigate influence of surface covering by graphite fluoride on the anode effect or the contact angle. Since it was difficult to make a tablet from graphite and graphite fluoride because of their poor cohesiveness, PE having the surface free energy analogous to that of graphite was used as a binder on preparing a tablet.

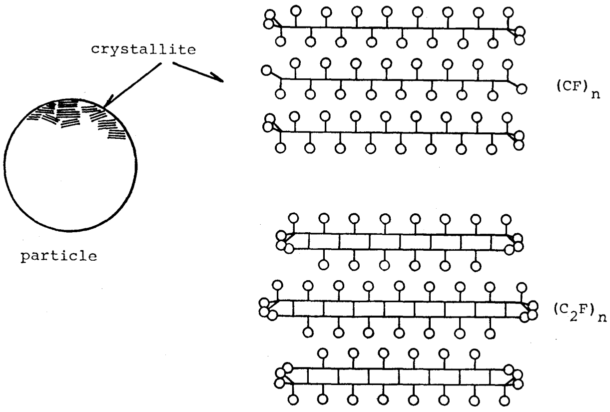

Fig. 4. Illustration of particle and crystallite of graphite fluoride.

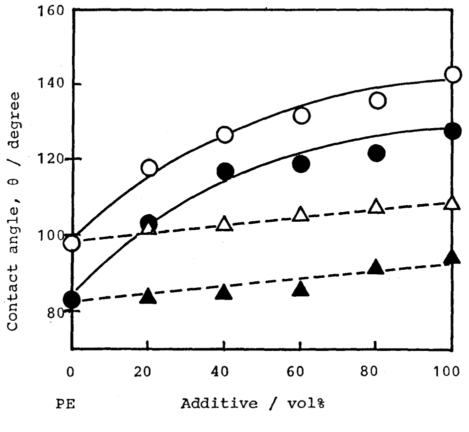

Fig. 5. Effect of additive content in the tablet on contact angle.
○: $(CF)_n$–water, ●: $(CF)_n$ formamide, △: PTFE–water, ▲: PTFE–formamide.

The effect of the surface covering by graphite fluoride on the contact angles is shown in Fig. 5, together with the result of PTFE–PE system. In the latter, the contact angles increased linearly with increasing content of PTFE, which satisfied the following equation;[25]

$$\cos\theta_{\mathrm{mix}} = f_A\cdot\cos\theta_A + f_B\cdot\cos\theta_B,$$

where θ is contact angle, f is volume percentage of composite, A or B, and $f_A+f_B=1$. On the other hand, $(CF)_n$–PE mixture dosen't obey this relation, which would be due to the low surface free energy

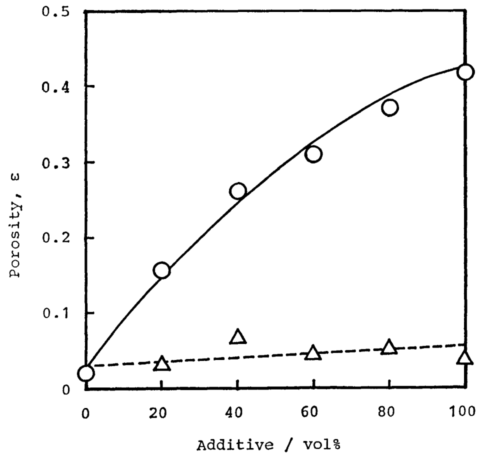

Fig. 6. Plots of porosity *vs.* additive content of $(CF)_n$– and PTFE–PE tablets pressed at *ca.* 49 MPa. Additive: ○: $(CF)_n$, △: PTFE.

of graphite fluoride or the surface roughness or porosity of the tablet. Wenzel[26] found that when a true contact angle is larger than 90°, a larger contact angle than the true one is observed by the surface roughness, and Ito *et al.*[27] also reported the similar effect by the porosity. The porosity of $(CF)_n$–PE tablet calculated from the weight and size of tablet and the density of mixture increases with the content of $(CF)_n$ as shown in Fig. 6. In this case, the effect increasing a contact angle by porosity or roughness and another effect decreasing a contact angle by penetration of liquid through the pore would give some change to the contact angle. If a tablet having the smooth surface like that of PTFE–PE system is made, the true contact angle would be measured. In case of the tablet composed of only $(CF)_n$, no tablet with the porosity less than 0.4 could be made even under the pressure of *ca.* 490 MPa.

Although this problem still remains, it was attempted to discuss the effect of the surface covering by graphite fluoride on the anode effect on the basis of the data in Fig. 5 and the contact angles of 17 and 31% NaOH solutions with high surface tensions. The cosine of contact angle *vs.* surface tension of liquid is plotted in Fig. 7. The contact angle of molten cryolite having the surface tension of 134 mN/m at 1000 °C is reported to be in the range of *ca.* 130 to 140° on natural graphite.[1] It is likely that the contact angle increases with increasing surface tension of liquid as shown in the solid line for natural graphite in Fig. 7. In the range of $(CF)_n$ content of more than 60% for $(CF)_n$–PE system, the contact angles seem to reach constant in spite of increase in the surface tensions of liquids, which would be due to the limit of the experimental method used in this study. If a liquid behaves like a rigid sphere, its contact angle would be measured accurately up to 180°. In practice, it is known that the contact angle of mercury on PTFE is *ca.* 150° which is the critical value for wetting in contact angle measurement by sessile drop method. Thus, the contact angle for $(CF)_n$–PE tablet would vary with the surface tension of liquid as shown by the dotted lines in Fig. 7.

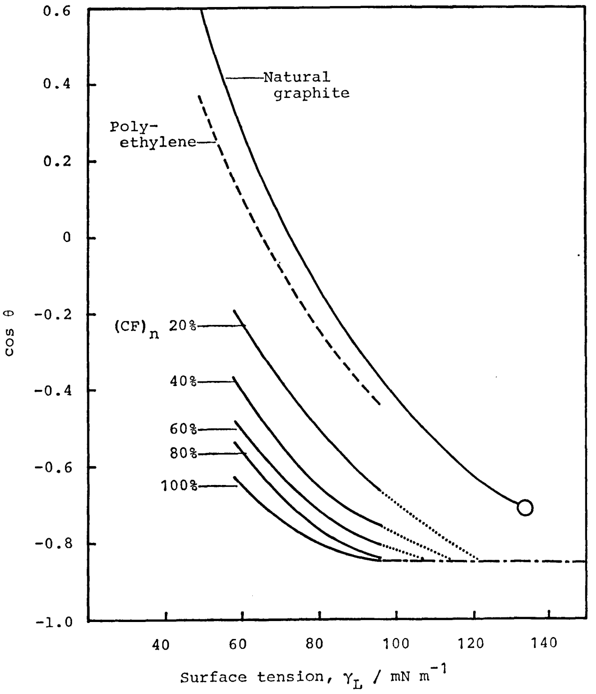

Fig. 7. Influence of $(CF)_n$ surface covering upon contact angle.
%: Vol% of $(CF)_n$ in $(CF)_n$–PE tablet. ○: contact angle of cryolite melt on natural graphite.

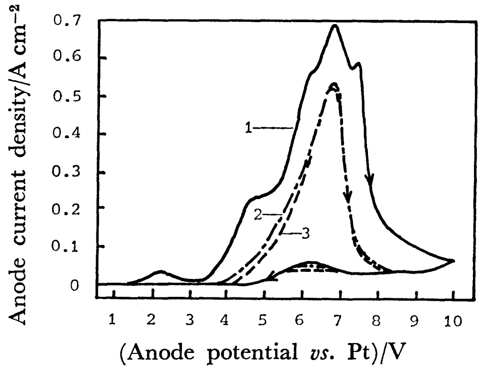

Fig. 8. Potential-sweep diagram for carbon anode in KF·2HF melt.
Sweep rate: 0.2V/s. 1: 1st sweep, 2: 2nd sweep, 3: 3rd sweep.

It is assumed that the anode effect occurs when the contact angle of molten salt on carbon anode reaches the critical value shown in Fig. 7. If the wettability of anode surface is determined by the relation between the surface tension of molten salt and the property of anode surface, the anode effect in the aluminium electrolysis is expected to occur at the surface covering of 10 to 20% by graphite fluoride on the basis of above surface tension of molten cryolite. Likewise, the anode effect in the fluorine electrolysis is expected to occur at the surface covering of 60 to 80% by graphite fluoride since the surface tension of molten KF·2HF is reported to be *ca.* 100 mN/m at 100 °C.[6]

Figure 8 shows the current-potential curves for carbon anode in molten KF·2HF.[5] In the first sweep,

OH^- ion is first discharged owing to its low discharge potential and through the discharge of F^- ion, the anode effect occurs when anode surface is covered by graphite fluoride to some extent. The second and third sweeps indicate that the anode surface partially covered by graphite fluoride remaining without decomposition is not wetted by the species including OH^- ion but wetted by the species including F^- ion, which means that the surface tension of the species including OH^- ion is higher than that of the species including F^- ion. If water exists as a molecule in molten $KF \cdot 2HF$, it should be easily adsorbed by carbon anode prior to molten $KF \cdot 2HF$ because of its low surface tension, *ca.* 60 mN/m at 100 °C. This is in conflict with the above experimental result. The wettability of anode surface under electrolysis would be dominated by other species different from the bulk species of molten $KF \cdot 2HF$ or water itself.

In order to estimate accurately the anode surface covering by graphite fluoride at the onset of anode effect, the surface tension of the dominant species present in the vicinity of anode surface must be evaluated, taking into account the other factors such as the roughness of anode surface, temperature, polarizing effect by electric current and composition of molten salt.

From the results obtained in this work, it is inferred that the partial covering of anode surface by graphite fluoride can easily cause the anode effect in the system having substantially poor wettability between carbon electrode and melt as in the case of aluminium electrolysis.

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