A Study on the Anode Effect in KF-2HF System. II. Difference in Anodic Behavior between Edge Plane and Layer-plane of Pyrolytic Graphite

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The anodic behavior of pyrolytic graphite has been studied by voltammetry and ESCA analysis in the molten KF–2HF system at 100 °C, attention being given to the difference in anodic behavior between the edge plane and layer-plane of the pyrolytic graphite. The polarization current obtained by a linear potential sweep experiment decreased rapidly with increasing potential after the onset of the anode effect. When the edge plane was used as a working electrode surface the current density was recovered on the subsequent sweep toward negative potentials, whereas the current density was hardly recovered on the layer-plane surface of the electrode. The difference in polarization behavior was interpreted on the basis of the difference in the rate of decomposition reaction of graphite fluoride, $(CF)_n$, formed on the electrode surface. ESCA spectra of the electrodes polarized at various potentials indicate that $(CF)_n$ was formed even at 2.0 V *vs.* Pt, below the fluorine evolution potential, on the edge plane of the pyrolytic graphite and that its amount did not increase appreciably with increasing potential. On the layer-plane, however, no formation of $(CF)_n$ was observed at 2 V *vs.* Pt, its amount increasing appreciably with potential at the potentials above 3 V *vs.* Pt.

The anodic behavior of graphite and carbon in molten fluorides is of importance since the cell operation during the course of electrolysis at high current density is remarkably restricted by the occurrence of anode effect.[1–3] In the preceding paper,[4] it was reported that the onset of the anode effect is due to a significant decrease in the wettability of the anode surface by the electrolyte caused by the formation of graphite fluoride, $(CF)_n$, having very low surface energy, and that the compound is formed even under normal electrolysis conditions. In the present investigation, the anodic behavior of the two distinct planes of pyrolytic graphite, edge plane and layer-plane, was studied by the potential sweep and potentiostatic methods, and by ESCA analysis of the electrodes polarized potentiostatically at various potentials and the electrodes after the anode effect.

The following reactions are considered to occur simultaneously on the anode surface.

1) Fluorine evolution

$$2F^- \longrightarrow F_2 + 2e^- \qquad (1)$$

2) Formation of $(CF)_n$ film

$$nF^- + nC \longrightarrow (CF)_n + ne^- \qquad (2)$$

3) Decomposition of $(CF)_n$ film

$$(CF)_n \longrightarrow C + CF_4,\ C_2F_6,\ etc. \qquad (3)$$

The results obtained were interpreted by considering the kinetic balance between the formation and the decomposition reaction of the $(CF)_n$ film on the anode surface.

Experimental

Voltammetry and preparation of the samples for ESCA analysis were carried out in the cell shown in Fig. 1. The cell was made of iron and its temperature was maintained at 100 °C in an oil bath. The wall of the cell was used as a cathode and the bottom of the cell was covered with a Teflon plate. The brass leads and all parts of the electrodes A, B, and C directly in contact with the vapor of hydrogen fluoride or KF–2HF melt were coated with Teflon. The molten KF–2HF was dehydrated by pre-electrolysis by using the carbon electrode C. The potentials of working electrode B were measured with respect to the reference electrode A of a Pt rod. The pyrolytic graphite used was supplied by Nihon Carbon Co., Ltd.. The pyrolytic graphite was heat-treated at 2200 °C for 1 h before use. Its crystallographic properties determined by X-ray analysis were as follows: lattice parameters a=2.457 Å and c=6.831 Å, crystallite size La (110)>1000 Å, crystallite height Lc (002)=240 Å, degree of crystalline alignment P (Franklin's P-value)*=0.84. The apparent density was 2.08 g/cm^3. The specific resistances parallel and perpendicular to the c axis were 0.52 and 3.9×10^{-5} ohm·cm, respectively. The layer-plan electrode was *ca.* 14 mm × *ca.* 9 mm and *ca.* 1 mm in thickness. The edge plane electrode was *ca.* 10 mm × 5 mm and *ca.* 6 mm in thickness. The apparent surface area was used for the calculation of current density. The surface of the edge plane electrode was polished with fine sandpaper Emery ♯600, the powder of graphite being removed by washing with distilled water.

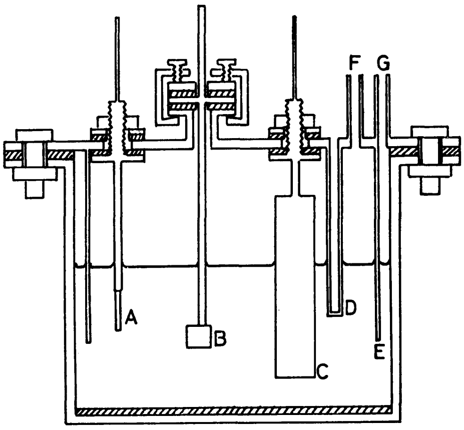

Fig. 1. Electrolytic cell.
A: Reference electrode (Pt), B: anode, C: carbon electrode for dehydration, D: well for thermometer, E: skirt, F: anode gas outlet, G: cathode gas outlet. The hatched parts are made of Teflon.

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* P-value was calculated by the equation

$$d(002) = 3.340 - 0.086(1-P^2),$$

where P is a ratio of the misoriented parts to the sum of the oriented and misoriented parts.

The electrodes were connected with the brass leads by winding fine copper wire on to them. Only one face of the pyrolytic graphite, the edge plane or the layer-plane, was used as a working electrode surface, the other faces being covered with Teflon tape. The edge plane electrodes polarized at various potentials were washed with anhydrous hydrogen fluoride in order to remove KF–2HF before ESCA analysis.

Results and Discussion

Polarization Curves. Figure 2 shows a polarization curve obtained by sweeping potential 1—10 V *vs.* Pt for the layer-plane electrode. Three peaks were observed on the *I*—*V* curve. An explanation for these peaks was given in a previous paper[5] in which the anodic behavior of carbon, graphite, and glassy carbon electrodes was dealt with. The first peak corresponds to the discharge reaction of trace water in the electrolyte and the second and third peaks to the discharge reaction of fluoride ion. Current density decreased rapidly at 5 V due to the onset of the anode effect. Restoration of the current density was hardly observed on the subsequent sweep from 10 to 3 V. The observed current density was as small as 2 mA/cm^2, when the anode potential was swept again from 3.5 to 10 V at the same sweep rate. Thus it is indicated that if $(CF)_n$ film is once formed on the layer-plane of pyrolytic graphite by reaction (2), the anode surface is hardly restored.

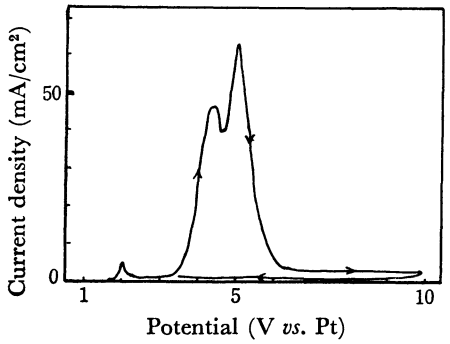

Fig. 2. *I*—*V* curve (potential sweep) in KF–2HF at 100 °C. Anode: layer-plane of pyrolytic graphite, sweep rate: 12.5 mV/s.

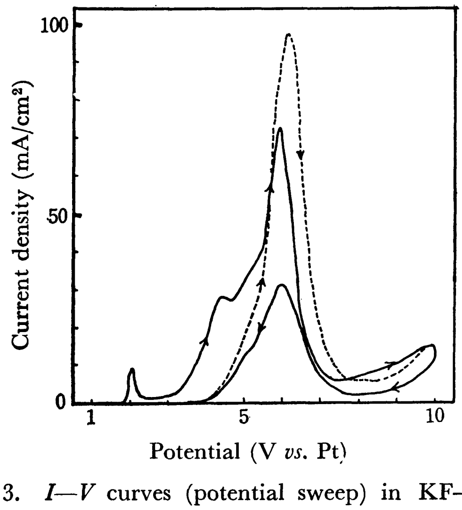

Fig. 3. *I*—*V* curves (potential sweep) in KF–2HF at 100 °C. Anode: edge plane of pyrolytic graphite, sweep rate: 12.5 mV/s.
——: First sweep, ------: second sweep.

Figure 3 shows the polarization curves obtained by the potential sweep method for the edge plane electrode. On the first sweep from 1 to 10 V, the polarization curve for the edge plane electrode was similar to that for the layer-plane electrode. However, in contrast to the case for the layer-plane electrode, the restoration of current was observed on the subsequent sweep toward negative potentials, the peak current density on the second sweep toward positive potentials (a dotted line) being comparable to the third peak on the first sweep. The restoration in current indicates that the decomposition of $(CF)_n$ takes place much faster on the edge plane than on the layer-plane.

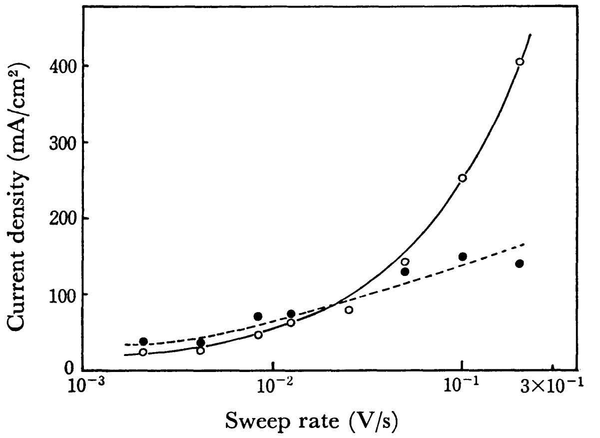

Fig. 4. Dependence of peak current densities on sweep rate.
○: Layer-plane of pyrolytic graphite,
●: edge plane of pyrolytic graphite.

The third peak current density in the polarization curve on the first sweep toward positive potential depends upon the rates of reactions (2) and (3). The peak current densities are plotted against the sweep rate for both layer-plane and edge plane electrodes in Fig. 4. The peak current density increased noticeably with increasing sweep rate for the layer-plane electrode, while it increased only slightly for the edge plane electrode. It is supposed in general that the peak current density becomes less dependent on the sweep rate with an increase in the rate of deactivation of electrode surface, since the relatively fast deactivation reaction of electrode surface with respect to the sweep rate leads to a nearly steady-state condition of the electrode surface irrespective of the sweep rate. Thus, it might be suggested that the rate of deactivation of the anode surface, which depends upon the difference in rates between reactions (2) and (3), is smaller at the layer-plane electrode than at the edge plane electrode, if it is assumed that the potential dependence of the current density due to the fluorine evolution reaction (1) at both the plane is equal to each other.

When the layer-plane and edge plane electrodes were polarized potentiostatically at various potentials, the current densities reached stationary values within 30

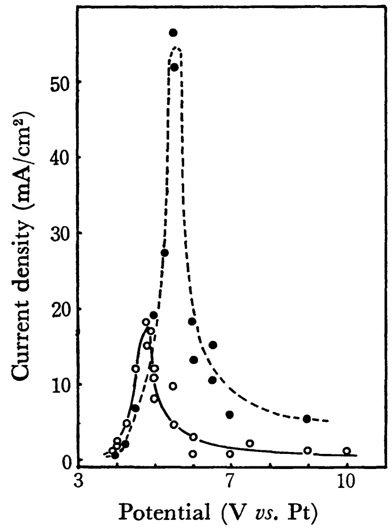

Fig. 5. *I*—*V* curves (potentiostatic) in KF-2HF at 100 °C.
○: Layer-plane of pyrolytic graphite,
●: edge plane of pyrolytic graphite.

min. These values are plotted against potentials in Fig. 5. Maximum current densities are observed at 4.8 V and 5.5 V for the layer-plane and edge plane, respectively. Since the maximum current densities are observed at 5.5 V for carbon and graphite,[4] it seems that the critical current densities at graphite and carbon anodes are attributable to those at their edge plane.

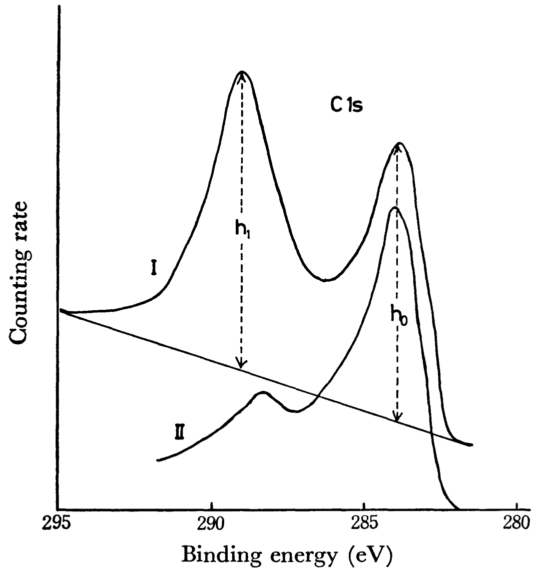

Fig. 6. ESCA spectra of pyrolytic graphite anodes immediately after the anode effect.
I: Layer-plane,
II: edge plane.

ESCA Spectra. When the layer-plane and edge plane electrodes were polarized at a constant current density of 400 mA/cm^2, the anode effect took place within 10 s and the circuit was opened immediately after the onset of the anode effect. Figure 6 shows the ESCA spectra of the carbon 1s electron for the above samples. The peak at 284 eV corresponds to the binding energy of the carbon 1s electron for the carbon which has only the C–C bond. The peak at 288.5 eV corresponds to the one for the carbon atom with the C–F bond.[4] The height of the peaks at 284 eV and 288.5 eV is denoted by h_0 and h_1, respectively.

In order to investigate the potential dependence of the amount of $(CF)_n$ on the anode surface, the ESCA spectra of the fluorine 1s electron as well as carbon 1s electron were obtained for the layer-plane and edge plane electrodes polarized potentiostacitally at various potentials for 30 min. The height of the peaks at 688

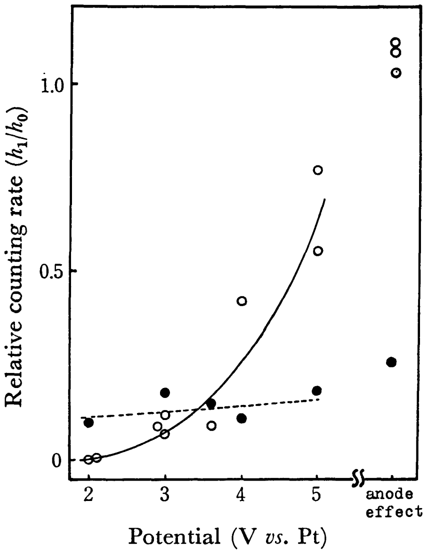

Fig. 7. Potential dependence of ESCA spectra. C 1s (288.5 eV).
○: Layer-plane of pyrolytic graphite,
●: edge plane of pyrolytic graphite.

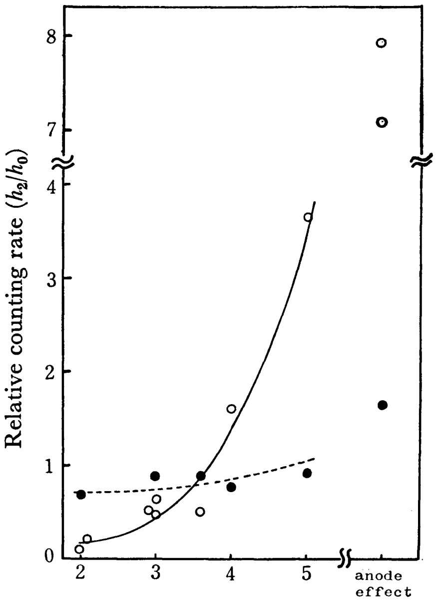

Fig. 8. Potential dependence of ESCA spectra. F 1s (688 eV).
○: Layer-plane of pyrolytic graphite,
●: edge plane of pyrolytic graphite.

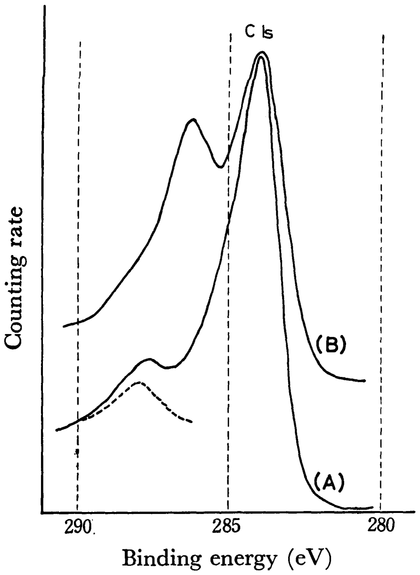

Fig. 9. ESCA spectra of anode surfaces.
(A): Edge plane of pyrolytic graphite polarized at 2.0 V *vs.* Pt in KF-2HF at 100 °C.
(B): Graphite polarized at constant current density of 500 mA/cm^2 in 2M-H_2SO_4 at room temperature.

eV corresponding to the binding energy of F 1s electron is represented by h_2. The ratios h_1/h_0 and h_2/h_0 plotted against potentials are illustrated in Figs. 7 and 8, respectively.

The equilibrium potential of reaction (1) is 3.4 V *vs.* Pt in KF–2HF at 100 °C.[6] A peak was observed at 288.5 eV in the carbon 1s spectra for the edge plane electrode polarized at 2 V, at a more negative potential than 3.4 V. The following experiments were carried out in order to confirm the view that the peak at 288.5 eV observed for the edge plane electrode polarized at 2 V is attributable to the C–F bond, but not to the C–O bond formed by the discharge reaction of the trace water.

Sample A: the edge plane electrode polarized at 2.0 V for 30 min at 100 °C in KF–2HF.

Sample B: the graphite anodically polarized at constant current density of 500 mA/cm^2 in 2M-H_2SO_4, for 10 min at room temperature.

Figure 9 shows the ESCA spectra of C 1s electron for samples A and B. A peak was observed at 286 eV for sample B, which is identical with that for the graphite oxide in the binding energy.[7] Since the peak at 288.5 eV for sample A is attributable to the C–F bond, but not to the C–O bond, it becomes apparent that reaction (2) proceeds at a more negative potential than the equilibrium potential of reaction (1).

The same tendency is shown in Fig. 7 as in Fig. 8. It is thus evident that the peak at 288.5 eV is associated with the carbon bound with fluorine atom. No detectable amount of $(CF)_n$ exists on the layer-plane electrode polarized at 2 V in Fig. 7, but the amount of $(CF)_n$ increases noticeably as the potential becomes higher than 2 V. On the other hand, a considerable amount of $(CF)_n$ is detected on the edge plane electrode polarized at 2 V, above which the amount of $(CF)_n$ increases slightly with increasing potential.

The values of h_1/h_0 for the layer plane electrode are much larger than those for the edge plane under the conditions of the anode effect, which is in line with the view that the rate of the decomposition of the $(CF)_n$ film is larger on the edge plane than on the layer-plane.

It is concluded that the amount of $(CF)_n$ formed on the surface of carbon and graphite anode increases with an increase in the polarization potential and that the restoration of current at these electrodes during the polarization toward negative potentials after the onset of anode effect is attributed to the fast decomposition reaction of the $(CF)_n$ film on the portions of these electrodes where the edge plane is in contact with the electrolyte.

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