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A Study on Anode Effect in KF-2HF System. I. ESCA Spectra of Carbon and Graphite Anode Surfaces

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Synopsis. The ESCA spectra of carbon and graphite electrodes, used as an anode in the molten KF-2HF system at 100 °C, indicated that a $(CF)_n$ film was formed on the surface of the electrodes. This may give strong support to the assumption that the anode effect in molten KF-2HF is caused by the formation of $(CF)_n$ on the carbon and graphite electrodes.

Fluorine gas is produced by the electrolysis of molten KF-2HF by using a carbon anode. The electrolysis current density is in the range 0.1—0.18 A/cm^2,[1] since the anode effect takes place when the current density is higher than this, and electrolysis must be stopped. It is, therefore, necessary to study the anode effect to increase the operating current density. It has been claimed that the anode effect is caused by a decrease of the wettability of an anode surface with electrolyte, KF-2HF, owing to the formation of a $(CF)_n$ film which has very low surface energy.[2-7] The investigation confirmed this mechanism.

Experimental

Six kinds of carbon and graphite samples were prepared in the following manner. Five electrode samples were anodically polarized under various conditions and the surface of the other electrode was treated with fluorine gas.[8] Their ESCA spectra were obtained with a Du Pont 650 Electron Spectrometer. The cubic carbon and graphite electrodes which were covered with Teflon tape except for one side were fixed at the end of a brass rod coated with Teflon. A Pt rod was used as a reference electrode. The molten KF-2HF system was dehydrated by pre-electrolysis using a carbon electrode.

Results and Discussion

Figure 1 shows the ESCA spectra of the carbon 1s electron in the samples which were prepared as follows.

(A) Anodically polarized at 5 V *vs.* Pt for 30 min.

(B) Anodically polarized at 10 V *vs.* Pt for 30 min.

(C) Anodically polarized at a current density of 350 mA/cm^2, the circuit being opened immediately after onset of the anode effect.

(D) Anodically polarized at a constant current density of 350 mA/cm^2, and polarized further at 20 V *vs.* Pt for 5 min after onset of the anode effect.

(E) Conditions are the same as for (D) except for polarization of 30 min after onset of the anode effect.

(F) The carbon and graphite samples were directly treated with fluorine gas under the following conditions. (I) F_2 pressure; 200 mmHg, temp.; 450 °C, time; 2 hr. (II) F_2 pressure; 110 mmHg, temp.; 450 °C, time; 0.5 hr. $(CF)_n$ was formed on the surface of the samples.

(G) The original carbon and graphite samples.

When the carbon and graphite electrodes were polarized at various controlled potentials, the current densities

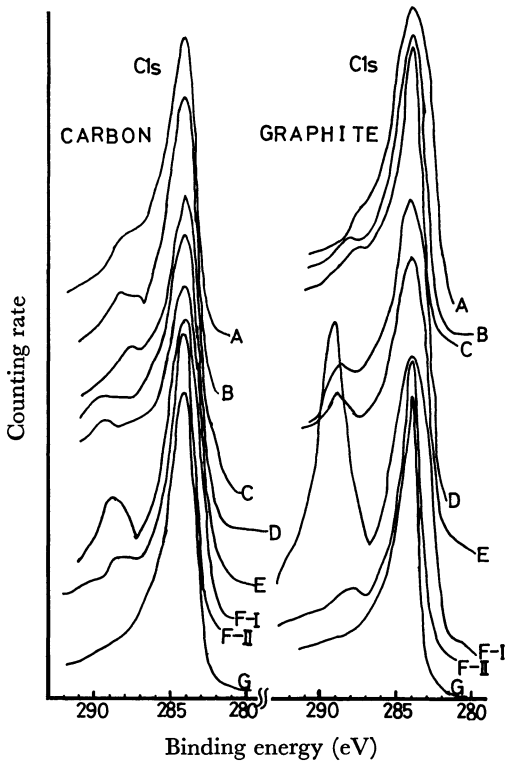

Fig. 1. ESCA spectra of carbon and graphite (C ls).

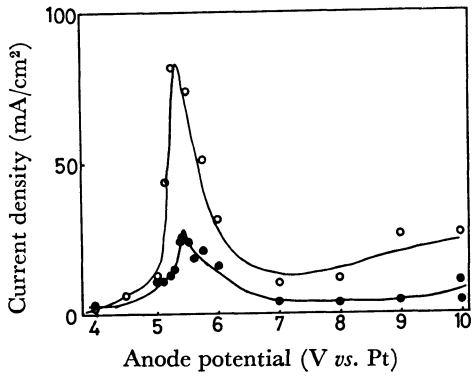

Fig. 2. Polarization curves (potentiostatic).
○: Carbon, ●: Graphite.

reached stationary values. Figure 2 shows the relation of these values against their potentials; electrode (A) was prepared under conditions of normal electrolysis, (B) under conditions of the anode effect. The latter conditions, however, are milder than those of (D) and (E). Anodic polarization of carbon and graphite electrodes with a constant current density of 350 mA/cm^2 gave rise to the anode effect within five seconds. The spectra of the original carbon and graphite samples (G) indicated

only one peak at 284 eV. This peak may correspond to the binding energy of the carbon 1s electron in cases where the carbon atom has the C–C bond. On the other hand, the spectra of samples (F) fluorinated by fluorine gas indicated two peaks at 284 and 289 eV. The peak at 289 eV may be assigned to the binding energy of the carbon 1s electron in cases where the carbon atom has the C–F bond. If the carbon atom is combined with the fluorine atom which is the most electro-negative element, the chemical shift of the binding energy of the carbon 1s electron must be large and positive. The spectra of samples (A), (B), (C), (D), and (E) indicated the same peaks as those of sample (F), that is, at 284 eV and 289 eV (the latter became a shoulder or appeared to slightly approach the peak at 284 eV as it was much smaller than this peak). Consequently, it was proved that the $(CF)_n$ film was formed on the surface of the carbon and graphite anodes not only during the anode effect but also under normal electrolysis conditions. From the results described above, it can be considered that the following reactions may occur on the anode surface, when the molten KF-2HF is electrolyzed by using the carbon or graphite anode.

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

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

When a $(CF)_n$ compound is formed on the anode surface during the evolution of fluorine, the wettability of the anode surface with the molten KF-2HF decreases markedly because of the very low surface energy of the $(CF)_n$ compound and the carbon and graphite surfaces do not come directly into contact with the electrolyte. If a large part of the anode surface is covered with the $(CF)_n$ conpound, the anode reaction does not proceed and only a small arc current flows through the interface at the anode under higher voltages. This is called the anode effect. However, since the following reaction (Eq. (3)) is considered to take place simultaneously, the net formation reaction rate of $(CF)_n$ during the fluorine evolution reaction depends upon the reaction rates of Eqs. (2) and (3).

The decomposition reaction of the $(CF)_n$ film.

$$(CF)_n \longrightarrow C + CF_4 + C_2F_6, \textit{ etc.} \quad (3)$$

In conclusion, the previous explanation that the cause of the anode effect is the formation of a compound which has a very low surface energy on the carbon and graphite electrodes has been confirmed experimentally by ESCA analysis.

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References

1) A. J. Rudge, "Industrial Electrochemical Processes," ed. by A. T. Kuhn, Elsevier Publishing Company, Amsterdam-London-New York (1971), p. 47.
2) N. Watanabe and M. Ishii, *Denki-Kagaku*, **29**, 364 (1961).
3) N. Watanabe and T. Asaue, *ibid.*, **39**, 123 (1971).
4) N. Watanabe, M. Ishii, and S. Yoshizawa, *J. Electrochem. Soc. Japan*, **29**, 177 (1961).
5) N. Watanabe, M. Ishii, and S. Yoshizawa, *ibid.*, **29**, 180 (1961).
6) N. Watanabe, M. Inoue, and S. Yoshizawa, *Denki-Kagaku*, **31**, 698 (1963).
7) M. Nishimura, A. Tasaka, K. Nakanishi, and N. Watanabe, *ibid.*, **38**, 294 (1970).
8) N. Watanabe and M. Takashima, *Kogyo Kagaku Zasshi*, **74**, 1788 (1971).