CARBON ANODE REACTION AND INTERCALATION COMPOUNDS IN FLUORIDE MELT

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ABSTRACT

The large overpotential on carbon anode in fluoride melt is due to a strong chemical interaction of discharged fluorine with carbon, which provides graphite fluoride film having an extremely low surface energy. When carbon anode is somewhat covered by thin graphite fluoride film, the wettability of anode by electrolyte decreases and anode effect occurs. Graphite fluoride film is directly detected by ESCA. Graphitization of carbon anode significantly affects the critical current density for anode effect. Namely amorphous carbon gives a higher critical current density than high quality graphite because graphite fluoride film easily decomposes to fluorocarbon gases. Recent investigation has revealed that a small amount of water contained in KF2HF melt gives serious effect to the formation of graphite fluoride film on carbon anode. The effect of LiF addition to the melt first appears when water content is less than 0.02%. The role of LiF is the catalytic action for fluorine intercalation in graphite to give a highly conductive intercalation compound.

INTRODUCTION

The study on the mechanism of anode effect in fluoride melts had already started at the end of 19th century, being concerned with the electrolytic production of aluminum metal in cryolite melt. The first theory was that a high resistivity film was formed on the carbon anode by discharge of fluoride ion(1). This is similar to the passivative state of metal, which was supported for 20 years. However, it was found in 1916 that voltage increase is not so high as that experimentally observed when calculated from the resistivity of the film. Second theory was that gas film was formed between electrode and electrolyte by vaporization of molten salt due to to abnormal generation of Joule heat(2). This
view had an advantage that anode effect was understandable from charged gas bubbles, surface tension of molten salt, viscosity, density and so on.

The authors proposed a new interpretation on the basis of the studies on wettability of carbon electrode by electrolyte (3) and overpotential in fluorine evolution reaction (4). Carbon anode reactions including anode effect are understood by the formation and properties of graphite intercalation compound on the anode surface. This paper summarizes carbon anode reactions in KF2HF melt.

RESULTS AND DISCUSSION

1. Overpotential for the discharge reaction of fluoride ion on carbon electrode

Two kinds of overpotentials are always observed on carbon anode reaction in KF2HF melt (Fig. 1). One increases rapidly as soon as the circuit is closed ($\eta_0$), but another increases slowly with time ($\eta_8$). Tafel equation is applicable at a current density less than 2 Adm$^{-2}$ where $\eta_0$ is under 1 V (Fig. 2). However, $\eta_8$ varies with time and reaches such a high potential at which anode effect occurs as the current density increases. Fig. 2 shows that $\eta_8$ obeys the Tafel relation, however, $\eta_0$ is strongly dependent on the crystallinity of carbon electrode, i.e. being different between carbon and graphite electrodes. Fig. 3 is the variation of cell voltage and a contact angle of electrolyte on anode as a function of time. Variation of the contact angle is very large compared with that of cell voltage. This phenomenon is interpreted as follows. Discharge of fluoride ion on carbon electrode is given by equation (1).

$$HF_2^− \rightarrow \frac{1}{2}F_2 + HF + e \quad (1)$$

$$nC + nHF_2^− \rightarrow (CF)_n + nHF + ne \quad (2)$$

However, (CF)$_n$ film formation proceeds at the same time by the reaction of discharged fluorine with carbon. If this film has a low surface energy, it becomes gradually difficult that carbon electrode is wetted by electrolyte. With increasing contact angle, a real current density also significantly increases, which would facilitate the reaction of discharged fluorine with carbon. The low surface energy of (CF)$_n$ is demonstrated by contact angle measurement of (CF)$_n$ prepared by direct fluorination of graphite at a high temperature (Table 1). Fig. 4 is a cyclic voltammogram of carbon electrode in KF2HF melt containing a small amount of water. The solid line indicates the first scan, in which peak B shows the discharge of OH$^-$ ion (oxygen evolution) and peak F is the discharge of F$^-$ ion (fluorine evolution). The
dashed line is the second scan, in which the peak corresponding to oxygen evolution disappears and only fluorine evolution is observed. A shoulder D is observed only in the first scan. This has not been clarified for a long time. However, a recent study suggests that peak D corresponds to the formation of graphite oxide film, which is decomposed by the attack of fluorine. If a low surface energy film is partly formed on the anode after first scan, the surface energy of anode might be decreased. This would result in the difficulty in water adsorption on anode surface. However, the adsorption of fluoride ion is possible because of the lower surface tension of HF than water. A large overpotential observed on carboneous anode is thus understood by postulating a low surface energy film on anode. Anode effect is considered to be such a state that anode potential extremely increases with decrease in the wettability of anode by electrolyte. The film on carbon anode cannot be detected by X-ray diffraction probably because it is too thin to be detected. (CF) film is confirmed by ESCA measurement. Fig. 5 shows ESCA spectra of pyrolytic graphite anode which is obtained immediately after anode effect. C 1s peak around 288-289 eV indicates C-F covalent bond and another peak at 284.3 eV corresponds to C-C bond of graphite.

2. Several factors influencing anode effect
Occurrence of anode effect is strongly affected by crystallinity of carbon anode and fluoride additives. Fig. 6 is the critical current density (the highest current density just before anode effect happens) as a function of graphitization degree of carbon anode. Critical current density remarkably decreases when graphitization degree exceeds 50%. This is more clearly observed in the melt containing NiF₂. Amorphous carbon reacts more easily with fluorine than high quality graphite. However, since the reaction of amorphous carbon with discharged fluorine proceeds more faster than graphite, it produces fluorocarbons such as CF₄ and C₂F₆, giving new carbon surface with high roughness. On the other hand, the reaction of graphite with fluorine gives a more stable (CF) film. This is similar to the behavior of layer plane and edge plane of pyrolytic graphite as shown in Fig. 5.

3. Effect of a trace of water and solid LiF on anode effect
LiF is often added to the electrolyte so that fluorine evolution may be continued at a high current density. The solubility of LiF in KF2HF melt is 0.6-0.8 wt% at 100 °C. The addition of LiF over the solubility gives a colloidal solution of KF2HF melt, in which the increase in the electrolytic current is first observed. The impregnation of LiF in carbon electrode is more effective than the addition of LiF to the melt for preventing the anode effect. This is
shown in Fig.7, which suggests that solid LiF acts at anode/electrolyte interface.

The following explanation was proposed concerning the role of LiF suspended in KF2HF melt. Fluorine gas bubbles having a negative charge are strongly attracted to anode surface by anodic polarization. LiF particles having a positive charge are adsorbed onto the surface of fluorine gas bubbles at anode/electrolyte interface. Neutralization of the charges facilitates the separation of gas bubbles from anode surface(5). Based on this interpretation, it was attempted to measure the potential of LiF particles in liquid hydrogen fluoride. However, no potential was detected by such an experiment(6).

Recently, a new fluorine-graphite intercalation compound was successfully synthesized in the presence of metal fluoride such as LiF, CuF, or AgF(7-9). It shows high electrical conductivity and stability. The intercalated fluorine has a nearly ionic bond with graphite, and the carbon layer is still plane after intercalation of fluorine. Based on the formation of fluorine-graphite intercalation compound in the presence of LiF, a new proposal was given on the role of solid LiF suspended in KF2HF melt or impregnated in carbon electrode(10). It is that the occurrence of anode effect may be suppressed by the formation of graphite intercalation compound (GIC) which gives a high electrical conductivity to carbon anode and ensures the wettability of anode surface by electrolyte.

Fig.8 is the variation of anode potential under various conditions as a function of quantity of electricity. When water content in KF2HF melt is relatively large, that is, ca. 0.05%, anode effect occurs in a short time compared with the case that water content is less than 0.02%, almost independently of whether LiF is added to the melt or not. Anode effect occurs only slightly later in the melt containing 3 wt% LiF. However, when water content is less than 0.02%, the effect of LiF added to the melt distinctly appears as shown in Fig.8. In this case, it is required that addition of LiF is made after water content is decreased to less than 0.02% by preelectrolysis. When preelectrolysis is done after addition of LiF to the melt, LiF give no effect on the suppression of anode effect probably because water in the melt is adsorbed by LiF particles. This is supported from the fact that water content decreases from 0.05% to 0.03% by addition of 3 wt% LiF.

Fig.9 shows the GIC and graphite fluoride film formed during electrolysis under various conditions. In the melt containing ca. 0.05% H2O, GIC is not formed but graphite fluoride film is easily prepared and anode effect occurs by a small quantity of electricity.
\[ xC + 2OH^- \rightarrow C_xO{\text{graphite oxide film}} + H_2O + 2e \quad (3) \]

\[ C_xO + 3F^- \rightarrow C_xF{\text{graphite fluoride film}} + COF_2 + 3e \quad (4) \]

However, when water content is less than 0.02%, stage 6 and 4 GIC’s are formed even in the melt without LiF, giving 23.7 Å and 16.2 Å as the repeat distance. Since no LiF is contained in the melt, this would be due to the electrochemical intercalation of HF_2 into graphite.

\[ nC + HF_2^- \rightarrow C_n^+HF_2^- + e \quad (5) \]

The repeat distance \( d \) of this GIC is expressed as follows as a function of stage number, \( n \).

\[ d(C) = 6.05 + 3.35(n - 1) \quad (6) \]

When LiF is added to the melt containing a trace of water less than 0.02%, the lower stage GIC (stage 3) is formed without occurrence of anode effect. This would be due to the intercalation of fluorine in graphite by the catalytic action of solid LiF in addition to the electrochemical intercalation of HF_2.

\[ nC + mF \overset{\text{LiF}}{\rightarrow} C_n^+F_m^- \quad (7) \]

As the product is a mixture of \( C_n^+HF_2^- \) and \( C_n^+F_m^- \), it is described as \( C_xF(HF)_y \).

There are two roles of solid LiF in KF2HF melt. One is the adsorption of water in the melt which contains a relatively large amount of water. Water-adsorbed LiF particles have no function to suppress the occurrence of anode effect. The film of adsorbed water on LiF particles would prevent the interaction of fluorine with LiF. LiF should be added to the melt after water content is decreased by preelectrolysis. When water content in KF2HF melt is less than 0.02%, water adsorption by suspended LiF can be neglected because the peak ratios for oxygen and fluorine evolution in cyclic voltammograms are the same before and after addition of LiF to the melt.

Another effect is the intercalation of fluorine in graphite as indicated in equation (7). This appears when water content is small, less than 0.02%. The reaction (7) occurs together with the electrochemical intercalation of HF_2 in graphite, giving a lower stage GIC than that formed in the melt without LiF. The formation of GIC having a high electrical conductivity would ensure the sufficient wettability of anode by KF2HF melt.
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Fig.1 Overpotentials of carbon anode

![Graph showing overpotential vs. time for graphite, carbon, and platinum anodes.](image)

**Overpotential**

**Graphite**

**Carbon**

**Platinum**

**Time**

**Fig.2 Relation between overpotential and current density**

- Graphite, ○: carbon

![Graph showing the relation between overpotential and current density for graphite and carbon.](image)

**Overpotential**

**Current density**

**Time**
Fig. 3 Change in cell voltage and contact angle as a function of time.

Fig. 4 Polarization curves of carbon anode in KF2HF melt at 100°C.
Fig. 5 ESCA spectra of pyrolytic graphite anodes immediately after the anode effect.
I: Layer-plane,
II: edge plane.

Table 1 Surface Free Energies Obtained from Contact Angles

| Solid                              | $\gamma_3$ / erg cm$^{-2}$ | Surface Composition          |
|-----------------------------------|----------------------------|------------------------------|
| Graphite fluoride, [CF]$_6$        | 6±3                        | $\geq$CF for basal plane; $\geq$CF$_2$, $-\text{CF}_3$ for edge plane |
| Perfluorododecanoic acid (on Pt)   | 10.4                       | $-\text{CF}_3$               |
| Poly(hexafluoropropylene)         | 18.0                       | $-\text{CF}_3$, $>\text{CF}_2$, $>\text{CF}$ |
| Poly(tetrafluoroethylene)         | 19.5                       | $>\text{CF}_3$               |

$^a1 \text{ erg} = 10^{-7} \text{ J.}$
Fig. 6 Effect of graphitization degree on critical current density

Fig. 7 Effect of LiF added to KF2HF melt and impregnated in carbon electrode

- ○: added to KF2HF, ●: impregnated in electrode
Fig. 8 Variation of anode potential with electrolysis
A, $\text{H}_2\text{O} \leq 0.05\%$, LiF: 0 wt%, B, $\text{H}_2\text{O} \leq 0.05\%$, LiF: 3 wt%,
C, $\text{H}_2\text{O} < 0.02\%$, LiF: 0 wt%, D, $\text{H}_2\text{O} < 0.02\%$, LiF: 3-6 wt%

Fig. 9 Stage number of GIC formed in grafoil anode
A, $\text{H}_2\text{O} \leq 0.02\%$, LiF: 0 wt%, B, $\text{H}_2\text{O} \leq 0.02\%$, LiF: 3-6 wt%,
C, $\text{H}_2\text{O} \leq 0.05\%$, LiF: 0 wt%, D, $\text{H}_2\text{O} \leq 0.05\%$, LiF: 3 wt%
G: graphite, CF: graphite fluoride film,
A.E.: anode effect