ELECTROCHEMICAL AND CHEMICAL INTERCALATION
OF FLUORINE IN GRAPHITE IN THE KF2HF MELT

Tsuyoshi NAKAJIMA and Toru OGAWA
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University,
Sakyo-ku, Kyoto, 606, Japan

Nobuatsu WATANABE
Applied Science Research Institute,
49 Ooi-cho, Tanaka, Sakyo-ku, Kyoto, 606, Japan

ABSTRACT

Effect of a trace of water on graphite anode reaction has been investigated in the KF2HF melt at 100°C. Cyclic voltammetry shows that with increasing water content from 0.01% to 0.05%, anode potential for the formation of graphite oxide and graphite fluoride film on graphite electrode is shifted to a lower potential. This would be due to the increase in anode surface area by the decomposition of graphite oxide film, which is caused by the reaction with discharged fluorine.

When water content is ca. 0.05%, anode effect occurs in a short time, namely graphite fluoride having a low surface energy is easily formed on graphite. However, when it is 0.01%-0.02%, stage 4 intercalation compound of graphite, C\textsuperscript{+}HF\textsubscript{2} is prepared. Addition of 3-6 wt% LiF to the KF2HF melt gives stage 3 C\textsubscript{x}F\textsubscript{y}(HF)\textsubscript{x} without occurrence of anode effect.

INTRODUCTION

Fluorine gas is generally produced by electrolysis of KF2HF melt at 100°C. It is difficult due to anode effect to electrolyze KF2HF melt at a high current density. Anode effect is caused by a low surface energy of graphite fluoride film formed on carbon anode, i.e. the wettability of anode surface by electrolyte extremely decreases owing to the low surface energy of graphite fluoride film. Addition of a metal fluoride such as LiF having a low solubility to KF2HF melt is effective for preventing anode effect. However, the role of LiF suspended in the melt or impregnated in anode has not been clarified for a long time.

Recently we synthesized a new fluorine-graphite intercalation compound in the presence of a metal fluoride such as LiF, CuF\textsubscript{2} or AgF(1-3). The metal fluoride is considered to act as a catalyst for fluorine intercalation in graphite. Among metal fluorides examined, AgF shows the highest
catalytic ability because of the strong chemical interaction with fluorine and the low melting point. Based on the formation of fluorine-graphite intercalation compound, a new interpretation was proposed on the role of solid LiF(4). 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. Recent investigation on this problem has revealed that not only LiF but also a trace of water contained in the melt give serious effects to graphite anode reaction (5). In this paper, we report the effect of a trace of water on graphite anode reaction and intercalation of fluorine in graphite in the KF2HF melt.

EXPERIMENTAL

The electrolytic cell is made of polytetrafluoroethylene and polytrifluorochloroethylene. Working electrode and counter electrode are grafoil (graphite sheet, 35x6 mm) and nickel plate with a large surface area, respectively. Reference electrode is Pt wire. Fluorine evolution is made by cyclic voltammetry and galvanostatic electrolysis at 33 mAcm². The water content in the melt was estimated by the same method reported previously (5). After electrolysis, graphite anode was analyzed by X-ray diffractometry.

RESULTS AND DISCUSSION

1. Effect of a trace of water on the anode reaction

Fig. 1 shows the cyclic voltammograms for graphite anode in the KF2HF melts containing different amounts of water. All the voltammograms were obtained at first scan. It has been pointed out in a previous paper (5) that a small amount of water (less than 0.1%) significantly influences the fluorine evolution reaction on graphite anode. It is known that peak A corresponds to oxygen evolution reaction by electrolysis of water contained in the melt.

\[
\text{Peak A: } 2\text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}
\]  

With decreasing water content from 0.05% to 0.01%, the intensity of peak A decreases. Peak A disappears after 2nd scan because the wettability of anode by electrolyte decreases due to graphite fluoride prepared at 1st scan. Peaks B and C, however, move to higher potentials with decreasing water content. Peak B, observed as a shoulder in most cases, also disappears after 2nd scan. This has not been identified for a long time. When the water content is relatively large, anode effect immediately occurs, i.e. graphite fluoride is easily prepared on graphite anode (5).
It has been also found that graphite oxide is easily fluorinated to be graphite fluoride at 100-200°C because graphite oxide is more unstable than fluoride. From these facts, peak B would be the formation of graphite oxide on the anode surface.

Peak B: \[ xC + 2OH^- \rightarrow C_xO \text{ (graphite oxide film)} + H_2O + 2e \]  

Graphite oxide has a covalent bond as well as graphite fluoride, therefore it is an electric insulator. After peak B, since fluorine evolution occurs vigorously, graphite oxide is attacked by discharged fluorine, which would give the anode more active and larger surface than that of pristine graphite. This facilitates the reaction of graphite anode with discharged fluorine, i.e. the formation of graphite fluoride film. Thus the following reactions would occur between peak B and peak C.

\[ F^- \rightarrow \frac{1}{2}F_2 + e \]  
\[ C_xO + 2F^- \rightarrow x'C + COF_2 + 2e \]  
\[ x'C + F^- \rightarrow C_xF \text{ (graphite fluoride film)} + e \]

Therefore with increasing water content, the formation of graphite oxide and graphite fluoride are both accelerated. This would be the reason why the peaks B and C are shifted to higher potentials with decreasing water content.

2. Intercalation of fluorine in graphite

When water content in the melt is ca. 0.05%, anode effect occurs in a short time, i.e. anode surface is covered with graphite fluoride at least to some extent without formation of ionic intercalation compound of graphite. This is almost the same even when LiF is added to the melt(4). However, with decreasing water content, GIC having an ionic bond is prepared electrochemically while the formation of graphite fluoride becomes difficult.

\[ nC + HF_2^- \rightarrow C_n^+HF^-_2 + e \]

Fig.2 is the X-ray diffraction patterns of pristine grafoil and GIC’s prepared in KF2HF melt containing 0.01-0.02% water. GIC formed was a mixture of stage 4-6 till 100 C.cm\(^{-2}\)(Fig.2 (C) (D)), after which stage 4 GIC was observed until anode effect occurred(Fig.2 (E) (F)), though the crystallinity of GIC increased as shown in the figure. On the other hand, when LiF was added to the melt by 3-6 wt%, intercalation of fluorine was considerably accelerated without occurrence of anode effect. This is due to the
catalytic intercalation of fluorine in graphite by solid LiF suspended in the melt as reported previously (5).

\[ nC + F + LiF \rightarrow nF^- \]  \hspace{1cm} (7)

GIC of stage 4+5 was first formed and stage number remained 4 till 1000 C cm\(^{-2}\). When quantity of electricity reached 3000 C cm\(^{-2}\), stage 3 GIC became a main component. Fig. 3 (G) shows the typical stage 3 GIC obtained at 4000 C cm\(^{-2}\).

REFERENCES

1. T. Nakajima, M. Kawaguchi and N. Watanabe, Synthetic Metals, 7, 117 (1983)
2. T. Nakajima, I, Kameda, M. Endo and N. Watanabe, Carbon, 24, 343 (1986)
3. T. Nakajima, T. Ino, N. Watanabe and H. Takenaka, sumitted to Carbon
4. N. Watanabe, Proceedings of First International Symposium on Molten Salt Chemistry and Technology, p.21, Kyoto, Japan (1983)
5. T. Nakajima, T. Ogawa and N. Watanabe, J. Electrochem. Soc., 134, 8 (1987)
Fig. 1  Cyclic voltammograms for graphite anode in KF2HF melt

Water content: (a) 0.05%, (b) 0.03%,
(c) 0.01%

Scan rate: 10 mV/sec
(A) graphite

(B) graphite

(C) stage 4-6
Fig. 2  Change in X-ray diffraction patterns obtained in the melt containing 0.01-0.02% water as a function of quantity of electricity

Quantity of electricity (C·cm$^{-2}$): (A) 0, (B) 20, (C) 60, (D) 100, (E) 200, (F) 380
(A) graphite
high stage

(B) stage 4 + 5
$\lambda_c = 16.40 \text{ Å, } 19.74 \text{ Å}$

(C) stage 4
$\lambda_c = 16.21 \text{ Å}$

(D) stage 4
$\lambda_c = 16.20 \text{ Å}$
Fig. 3 Change in X-ray diffraction patterns obtained in the melt containing 0.01 - 0.02% water and 3-6 wt% LiF as a function of quantity of electricity

Quantity of electricity (C·cm⁻²): (A) 20, (B) 60, (C) 100, (D) 200, (E) 400, (F) 1000, (G) 4000