—Communication—

Fluorine Intercalation in Graphite in Molten Salt and Anhydrous Liquid Hydrogen Fluoride

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Received February 4, 1993; Accepted March 19, 1993

1 INTRODUCTION

Recently it was found that fluorine-graphite intercalation compounds [C_xF , $C_xF(HF)_y$ or C_xHF_2] have a very important role in the electrolytic production of fluorine gas using $KF \cdot 2HF$ melt^{1),2)}. When graphite fluoride film with covalent C-F bond is formed at the surface of carbon anode, a so-called anode effect easily takes place. On the contrary, the ionic fluorine-graphite intercalation compound formed around the surface of carbon anode enables the continuous electrolysis at a high current density because of its high surface free energy and electrical conductivity³⁾. It is thus important to clarify the fluorine intercalation in graphite in the solution containing HF. In this paper, we report the electrochemical and chemical intercalation of fluorine in graphite in molten salt and anhydrous liquid HF.

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Key Words: Fluorine, Intercalation,
Graphite

2 EXPERIMENTAL

Electrochemical intercalation of fluorine was made by galvanostatic method in molten $KF \cdot 2HF$ at ca. 100°C. Electrolytic bath was prepared by the reaction of $KF \cdot HF$ salt with HF gas in a PTFE electrolytic cell, which was placed in a glove box filled with dry nitrogen gas during the experiment. A trace of water contained in the $KF \cdot 2HF$ melt was removed by preelectrolysis using carbon anode. The working electrode was graphite sheet, the potential of which was monitored by Pt reference electrode. The counter electrode was Ni plate with a large surface area. Anodic polarization of graphite sheet electrode was performed at a current density of 0.3 to 0.8 mA cm⁻². Fluorine intercalation was also performed by flowing fluorine gas into anhydrous liquid HF containing a small amount of MoF_6 (~0.01 mol/mol-carbon) and natural graphite powder (<37μm, 50-100mg). Fluorine gas was allowed to flow for 3 to 7 days at 8°C or 18°C. Liquid HF was gradually removed from Teflon PFA reaction tube during fluorine gas flow. The reaction tube was evacuated for 12 hours after the reaction to remove HF completely.

The products were analyzed by

X-ray diffractometry (Diffractometer and Debye-Scherrer methods). The stage number and lattice parameters were determined by X-ray data. The composition was determined by elemental analysis of carbon and fluorine.

3 RESULTS AND DISCUSSION

3.1 Fluorine intercalation in molten $\text{KF} \cdot 2\text{HF}$

Fluorine intercalation was studied by electrochemical polarization of graphite sheet in molten $\text{KF} \cdot 2\text{HF}$. Fig.1 shows the cyclic voltammogram for a graphite sheet, obtained in a well dehydrated melt. When a carbonaceous electrode is anodically polarized, a small current is usually observed around 1.5–2 V vs Pt. It is known that the current around 1.5–2 V increases with increasing water content in the melt. This means that the discharge of water in the melt occurs in this potential range. Recently it was suggested that the electrochemical intercalation of HF_2^- in graphite started around 1.5–2 V⁴⁾, where the reversible oxidation and reduction currents were observed for carbon electrode.

We have taken the X-ray diffraction patterns of graphite sheet anodes which have been polarized to 3 V and 8 V at a scan rate of 30 mV s^{-1} . The graphite anodes polarized to 3 V and 8 V have indicated the formation of stage 5 or 6 C_xHF_2 and stage 4 C_xHF_2 , respectively.

To study the electrochemical intercalation of fluorine more thoroughly, the galvanostatic method has been applied to graphite sheet electrode in a well dehydrat-

Fig.1 A cyclic voltammogram obtained in a well dehydrated $\text{KF} \cdot 2\text{HF}$ melt.

Fig.2 Variation of anode potential during galvanostatic polarization at 0.3 mA cm^{-2} .

ed melt. Fig.2 shows a typical anode potential curve obtained at 0.3 mA cm^{-2} as a function of quantity of electricity. The potential curve has three plateaus at ca. 1.6 V, 2.5 V and 3.8 V with a small one at ca. 3.4 V. Fig.3 is the X-ray diffraction patterns of graphite sheet and those polarized to 2.6 V. At the first plateau in the range of 1.5 V to 1.7 V, stage 7 to stage 5 compounds were observed with (002) and (004) diffraction lines of unreacted graphite. After 10 C cm^{-2} , the second plateau appeared at ca. 2.5 V, where stage 4 compound was observed. When the quantity of electricity exceeded 30 C cm^{-2} , the potential increased

Fig.3 X-ray diffraction patterns of graphite sheet anodes as a function of quantity of electricity. (a)graphite, (b)stage 7, $I_c=26.15 \text{ \AA}$, $Q=2.16 \text{ C}$, $E=1.60 \text{ V}$, (c)stage 6, $I_c=22.73 \text{ \AA}$, $Q=3.24 \text{ C}$, $E=1.49 \text{ V}$, (d) stage 5, $I_c=19.35 \text{ \AA}$, $Q=4.32 \text{ C}$, $E=1.52 \text{ V}$, (e)stage 4, $I_c=16.01 \text{ \AA}$, $Q=18.90 \text{ C}$, $E=2.58 \text{ V}$.

again, reaching the third plateau at ca. 3.8 V through the small one at ca. 3.4 V. Fluorine gas evolution started at ca. 3.8 V. The electrochemically prepared stage 7 to 4 compounds are unstable because the intercalated species is HF_2^- anion. The $(00n+1)$ diffraction lines (n :stage number) were always the strongest as shown in Fig.3.

This indicates that the intercalated fluorine is situated at the center of two carbon sheets, which is in agreement with the intercalation of HF_2^- anion in graphite. After fluorine gas evolution commenced at ca. 3.8 V, the C_xHF_2 layer formed around the surface area of graphite sheet was destroyed by the vigorous reaction with discharged fluorine atoms. In fact, the surface of graphite sheet was changed to the porous one, and only (002) and (004) diffraction lines of graphite itself were detected for the graphite anode polarized to 3.8 V. When the current density was increased from 0.3 mA cm^{-2} to 0.5 or 0.8 mA cm^{-2} , the lowest stage number of the intercalation compound was still 4.

3.2 Fluorine intercalation in anhydrous liquid HF

The lowest stage number of C_xHF_2 was 4 when fluorine intercalation was made by anodic polarization in molten salt. The lower stage compounds, for example, the stage 1 or 2 were not obtained. This would be mainly due to the high intercalation temperature of ca. 100°C . A low temperature is thermodynamically favorable for the intercalation reaction because it accompanies the entropy decrease. With increasing temperature, the deintercalation rate is increased. When fluorine intercalation is carried out in anhydrous liquid HF, C_xHF_2 is formed at first and HF is gradually desolvated as liquid HF is removed by fluorine gas flow.

The composition and X-ray data

Table 1 Composition and X-ray data of stage 1 CxF samples prepared in anhydrous liquid HF

Sample	Composition	a_0 / Å	I_c / Å	Intensity ^{a)}
1 ^{b)}	C _{2.0} F	2.473	13.21 12.48	vs s
2 ^{c)}	C _{2.0} F	2.473	12.39 10.44	s w
3 ^{c)}	C _{2.3} F	2.472	12.56 5.87	s vs
4 ^{d)}	C _{2.1} F	2.471	12.02	s
5 ^{c)}	C _{2.3} F	2.471	12.83 5.99	vs s
6 ^{c)}	C _{2.4} F	2.470	12.28 10.74	vs s
7 ^{e)}	C _{2.0} F	2.468	13.12 10.38	s w

a) Intensity of X-ray diffraction peak, s: strong, w: weak, v: very, b) F₂ flow for 5 days after removal of anhydrous liquid HF, c) F₂ flow for 1 day after removal of anhydrous liquid HF, d) F₂ flow for 3 days after removal of anhydrous liquid HF, e) Fluorination procedure c) was repeated 4 times.

are given in Table 1. The products were all stage 1 compounds with composition of C_{2.0}F to C_{2.4}F. The large c-axis repeat distances (I_c =10.4~12.5 Å) indicate the existence of stage 1 phase in which almost ionically bonded fluorine atoms and covalently bonded ones are inserted in every other carbon layer⁵⁾. The larger I_c values than 13 Å of samples 1 and 7 in Table 1 might be due to the existence of HF molecules between carbon layers. Another phase with a smaller I_c value ($\approx$ 6 Å) is stage 1 phase in which almost ionically bonded fluorine atoms would exist between two carbon sheets. The a-axis lattice parameter, a_0 is increased to 2.470~2.473 Å, which is clearly larger values than that of graphite itself, 2.462 Å. This is attributed to the formation of C-F covalent

bond in stage 1 phase.

Thus graphite is highly fluorinated in anhydrous liquid HF at low temperatures. Two reasons should be pointed out for the results obtained. Low temperatures are thermodynamically preferred for the intercalation reaction as already mentioned. The other reason is the higher activity of HF in case of anhydrous liquid HF. Intercalation rate of HF₂ in graphite is increased with increasing activity of HF in the reaction system.

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