Fluoride Ion Conduction of Fluorine Intercalated Graphite C_xF

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(Received August 13, 1993)

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Fluorine intercalated graphite compounds C_xF with ionic or semi-ionic C-F bonding were prepared by direct fluorination of HOPG at 0°C or room temperature, and impedance measurements of these materials were carried out. Electrochemical intercalation and deintercalation of fluoride ions into graphite and from C_xF , respectively, were investigated using acetonitrile solutions containing tetramethyl ammonium fluoride salts. The results indicate that the fluoride ions in the graphite gallery have some mobility, and the electrochemical intercalation and deintercalation of fluoride ions are effected by applied potential gradient. These results suggest that C_xF are fluoride ion conducting solid state electrolytes.

KEYWORDS; *Fluorine intercalated graphite, Fluoride ion conduction, Solid state electrolyte*

1. Introduction

Fluoride ion conductors have many potential applications in batteries and other electrochemical devices and are of great interest. Crystalline fluoride ion conductor β -PbSnF₄, which has the highest conductivity known so far at room temperature (RT), exhibits conductivity 10^{-1} - 10^{-2} S/cm at 200°C¹⁾. Among the non-crystalline substances, on the other hand, 60ZrF₄·32BaF₂·8CsF glass has the fluoride ion conductivity of *ca.* 10^{-5} S/cm at 200°C²⁾. As for fluoride-graphite intercalation compounds (GICs), although their highly electrical conductivities have been well known³⁾, fluoride ion conductivities of the materials have not been known thus far. The fluorine intercalated graphite compounds (C_xF), with

ionic or semi-ionic C-F bonds, show excellent properties as a cathode material of lithium battery with anhydrous propylene carbonate (PC)-1M LiClO₄ electrolyte solution. Below the current density of 1A/m², these materials show extremely low overpotentials³⁾⁻⁵⁾ compared with conventional graphite fluoride cathode (CF)_n or (C₂F)_n with covalent C-F bonds. This property indicates that there are some differences in the discharge reaction mechanisms. In the conventional graphite fluorides, the chemical bonds between carbon and fluorine are covalent. The fluorine atoms are strongly bound to the carbon framework and they can not move within the gallery⁶⁾. The discharge reaction in the conventional graphite fluoride cathodes, therefore, proceeds through the diffusion of

solvated lithium ions between the layered structure of graphite fluoride. This leads to a high cathode overpotential⁷⁾. In the case of C_xF , however, the fluorine atoms are more weakly bound to the carbon framework, and as a result, the diffusion of fluoride ions within the gallery is possible. Accordingly, the discharge reaction seems to consist of the diffusion of fluoride ions from the bulk to the surface of the cathode and the following deintercalation. The present paper reports impedance analysis of C_xF , electrochemical oxidation of graphite and reduction of C_xF in the fluoride ion conductive solutions of tetramethyl ammonium fluorides⁸⁾. Based on the results, the fluoride ion conduction of C_xF is discussed.

2. Experimental

2.1 Synthesis and Characterization of C_xF

Highly Oriented Pyrolytic Graphite (HOPG: Union Carbide) as the host graphite was heat-treated for 3 days at 600°C. Ionic and semi-ionic C_xF were prepared by the direct fluorination of HOPG at either 0°C or RT for a few weeks. The ionic or semi-ionic character of C-F bonds in C_xF was investigated by X-ray photoelectron spectroscopy (XPS: Shimadzu ESCA 750 with Mg-K α radiation), and the structure of C_xF was determined by X-ray diffraction analysis (Shimadzu, XD-D1 with Cu-K α radiation). The compositions of these materials were determined by gravimetric analysis or XPS analysis.

2.2 Impedance Measurements

The impedance measurements were carried out using Yokogawa Hewlett Packard 4194A Impedance/Gain Phase Analyzer in the frequency range 1kHz-15MHz with the oscillation level of 0.5 V at RT. Since C_xF is a good electrical conductor, the values of the impedance of C_xF are usually small and are greatly influenced by the contact noise impedance at the interface between electrode and material. Microelectrodes were employed successfully to investigate the impedance spectroscopy of the C_xF . Tungsten needles ($\phi=0.06$ mm) as the electrode were connected on both edges of the basal planes of C_xF , and the four-point method was employed (Fig. 1). Ionic and semi-ionic C_xF samples and pristine HOPG for comparison were analyzed. Equivalent circuits

Fig. 1 Electrode for impedance measurement.

Fig. 2 Cell assembly for electrochemical intercalation and deintercalation of fluoride ions into HOPG and from C_xF , respectively.

W: working electrode, C: counter electrode,
1: teflon cell, 2: Pt-wire, 3: Pt-mesh,
4: HOPG or C_xF , 5: electrolyte,

were assumed for the obtained impedance spectra Cole-Cole plots, and the optimum values of the components in the circuits were determined so as to reproduce the obtained Cole-Cole plots.

2.3 Electrochemical Intercalation and Deintercalation of Fluoride Ion

Fig. 2 shows the cell for electrochemical oxidation (intercalation) of HOPG and reduction (deintercalation) of C_xF . Hokuto Denko Potentiostat/Galvanostat HA-301 was used for galvanostatic electrolysis at current density of 1A/m² (*ac*-plane area).

In the experiment of the fluoride ion intercalation into the graphite, heat-treated HOPG was wrapped by Pt-mesh and used as the anode, and a Pt-mesh was also used as the counter electrode.

Fig. 3 Complex impedance plots of ionic $C_{12}F$ (a), semi-ionic C_8F (b) and HOPG(c) in the frequency range of 1kHz-15MHz.

The solid curves were obtained based on the equivalent circuit ((a) in **Fig. 4**) with optimum R_1 , R_2 and C_1 values given in **Table 1**. The dashed curves were graphical extrapolations of semicircles.

Two kinds of electrolytes were used for electrochemical preparation of C_xF . One of the electrolytes was 1M solution of $(CH_3)_4NF \cdot 2HF$ (Morita Chemicals) in acetonitrile (Wako Chemicals). The other electrolyte solution was 1M $(CH_3)_4NF \cdot 4HF$ -acetonitrile (Morita Chemicals).

In the electrochemical deintercalation of fluoride ion from C_xF , ionic C_xF was used as the cathode in the same way as above and the counter electrode was Pt-mesh. The electrolyte solution used was 1M $(CH_3)_4NF \cdot 2HF$ -acetonitrile.

After the electrolysis the samples were washed

Fig. 4 Equivalent circuits for the impedance plots of C_xF shown in **Fig. 3**.

with acetonitrile to eliminate the residual salt on the surface, and XPS and X-ray diffraction analyses were carried out.

3. Results and Discussion

3.1 Impedance Analysis of C_xF

In general the bulk impedance of uniform solid electrolyte is equalized by a parallel circuit of the bulk resistance and the geometrical capacitance. The complex impedance plots of such materials have a semicircular shape.

Fig. 3 shows the obtained impedance spectra of ionic $C_{12}F$, semi-ionic C_8F , and pristine HOPG for comparison. The complex impedance plots of C_xF are semicircular. In the case of HOPG, on the other hand, only a limited range of impedance originated from the interface between electrode and HOPG is observed. The equivalent circuit appropriate for these spectra of C_xF is shown in **Fig. 4(a)**. The optimum values of the components (C_1 , R_1 , R_2) in the analogue circuit in **Fig. 4(a)** are given in **Table 1**.

Table 1 Optimum values of components in the equivalent circuit((a) in Fig. 4).

	C_1 / F	R_1 / Ω	R_2 / Ω
$C_{12}F$	2.8×10^{-10}	38.0	3.7
CaF	5.3×10^{-10}	15.4	8.4

The frequency simulations based on these values for the circuit were carried out and the results are shown in Fig. 3 by solid lines. The fits were satisfactory indicating the complex impedance plots of C_xF can be equalized by this analogue circuit in the experimental frequency range. When the observed plots are assumed to have originated from the bulk impedance of C_xF , the physical interpretation of the components in the circuit of Fig. 4(a) is the following: components R_1 and C_1 , respectively, are the bulk resistance and the geometrical capacitance, and R_2 is the interfacial charge transfer resistance between electrode and material. In this interpretation, it can be not explained why the observed impedances of C_xF are larger than that of HOPG which has lower or the same electron conductivity compared with the C_xF used in this experiments.

Another interpretation can be suggested; the observed semicircular plots have originated from the interfacial impedance of electrode and materials. This interpretation leads to the assumption that another semicircle exists at higher frequency range, where the measurement was not carried out in this study. The equivalent circuit, in this case, is shown in Fig. 4(b), and the physical interpretation of the components in this circuit is the following: the parallel made of R_1 and C_1 , which are the interfacial charge transfer resistance and the electric double-layer capacitance, is the cause of the observed semicircular plots, and components R_2 and C_2 , respectively, are the bulk resistance and the geometrical capacitance of C_xF . The larger impedance of C_xF compared to HOPG can be accounted for by the influence of the C-F covalent bonds, which may exist at the surface of the C_xF materials.

Either of the interpretations suggests that these C_xF are mixed conduction solid electrolytes of fluoride ion. The fluoride ions in the graphite

gallery obtain mobility by potential gradient.

3.2 Electrochemical Intercalation and Deintercalation of Fluoride Ion

3.2.1 Electrochemical Intercalation of Fluoride Ion Into Graphite

Electrochemical syntheses of C_xF were attempted using $1M (CH_3)_4NF \cdot 4HF$ -acetonitrile electrolyte. The XPS analysis of HOPG anode after electrochemical oxidations indicated the existence of fluoride ions in the graphite gallery. X-ray diffraction patterns of these materials, however, were not able to be indexed.

On the other hand, in the experiment using $1M (CH_3)_4NF \cdot 4HF$ -acetonitrile electrolyte solution at the current density of $1A/m^2$, the oxidized HOPG gave a clear X-ray diffraction pattern shown in Fig. 5. The pattern indicates that a fluoride-GIC was prepared electrochemically, its stage number being 5 and d_i , which is the size of intercalate, $2.7 \text{ \AA}$. Some of the diffraction lines indicated the existence of higher-stage compounds. The XPS measurements of

Fig. 5 (00l) X-ray diffraction profiles of stage-5 $C_{18}F$ obtained by the electrochemical intercalation in $1M (CH_3)_4NF \cdot 4HF$ -acetonitrile solution. a: the diffraction line of polyvinylchloride film used for the sample protection from moist air, b: higher stage compounds.

Fig. 6 (001) X-ray diffraction profiles of stage-2 $C_{5.5}F$ (a) prepared by direct fluorination of HOPG and stage-4 $C_{10}F$ (b) obtained by the electrochemical reduction of $C_{5.5}F$.

the compound show that the bulk C-F bonding nature is ionic, with semi-ionic and covalent bonds at the surface of the material. The composition of prepared material determined by XPS is $C_{18}F$ whereas that from coulometry is $C_{10}F$, indicating the current efficiency of *ca.* 56%. The open circuit voltage of this electrolysis cell was about 0V, and the voltage increased to 2V as soon as the electrolysis had started. The stepwise potential increase according to the change in stage number, which is reported in the case of electrochemical preparation of sulfate-graphite intercalation compounds⁹⁾, was not observed in this experiment.

This result suggests that the fluoride ions can be intercalated into the graphite layers electrochemically and the following diffusion of fluoride ions in the graphite gallery occurs. The electrochemical synthesis of C_xF in 50% aqueous hydrogen fluoride and 1M NaF-anhydrous HF solutions have already been reported¹⁰⁾. The results of our experiments show that electrochemical synthesis of C_xF is also possible in the electrolyte solutions without using HF solutions. The electrochemical stability and the

fluoride ion conductivity of electrolytes¹¹⁾ may influence the electrochemical synthesis of C_xF .

3.2.2 Electrochemical Deintercalation of Fluoride Ion

Electrochemical deintercalation of fluoride ions from C_xF , *i.e.*, electrochemical reduction of the material in $(CH_3)_4NF \cdot 2HF$ -acetonitrile solution was performed. The open circuit voltage was about 1.7V, and the voltage decreased gradually and stabilized at about -2V as the electrochemical reaction proceeded. In this experiment 75% deintercalation of fluoride ions in the material was achieved. The X-ray diffraction pattern of this material after electrochemical reaction is shown in **Fig. 6(b)**, together with that of ionic $C_{5.5}F$ before electrolysis (a). The structural change has occurred through the electrolysis, with the stage number increasing from 2 to 4. The composition of the substance after reduction became $C_{10}F$ by XPS, and the current efficiency was *ca.* 61%. These results indicate the electrochemical deintercalation of fluoride ions from the graphite gallery of C_xF .

The electrochemical intercalation and deintercalation of fluoride ions into graphite and from C_xF involving the change in staging and compositions indicate that graphite and C_xF are fluoride ion conductive devices and that the construction of rocking-chair-type secondary battery is possible.

4. Summary

The fluoride ions of ionic and semi-ionic C_xF gain mobility as potential gradient is applied, since they are not bound to carbon atoms in contrast with those in covalent graphite fluorides. Electrochemical intercalation and deintercalation of fluoride ions have been also confirmed. Our present results indicate that ionic and semi-ionic C_xF are fluoride ion conducting solid electrolytes.

In the discharge reaction of C_xF as a cathode material of the lithium battery, fluoride ion conduction of C_xF plays a role in the reaction mechanism, and the polarization character of these batteries differs from the conventional graphite fluoride cathode.

5. Acknowledgement

The authors are indebted to the Ministry of Education, Science and Culture of Japan for financial support by Grant-in-Aid for Scientific Research No. 05650840. We also wish to thank Mr. Y. Takeuchi and Miss. A. Komamura of Shinko Electric Industries Co., Ltd. for their help on impedance measurements. One of the authors (FO) also thanks Research Foundation for Electrotechnology of Chubu for support.

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1. 日時: 平成5年9月24日(金)
2. 場所: 弘済会館
3. 提出資料:

117-226-A-1 貴金属超微粒子分散炭素の調製とマトリックス炭素の高比表面積化 (九工試)児玉昌也, 本田英昌 117-226-A-2 単結晶 ZrC の酸化における炭素の析出と酸化層の微構造観察 (北大・工)嶋田志郎, 西佐古将, 稲垣道夫 117-226-A-3 酸化処理した熱分解黒鉛表面の構造変化 (北大・工)中原雅則, 真田雄三 117-226-A-4 DRIFT/TPD Study of Surface Oxygen Complexes Formed in Carbon Gasification with Oxygen (Tohoku University) T. Kyotani, Q.-L. Zhuang and A. Tomita 117-226-A-5 フィルム内部からの N_2 ガス放出による黒鉛化ポリイミドフィルムの破裂	(資環研)羽鳥浩章, 山田能生, 白石 稔 117-226-B-1 熱分解カーボンの微細組織のSEM観察 (武蔵工大)吉田 明, 菱山幸有 117-226-B-2 グラファイトウイスカーのリチウム吸蔵反応に与える生成プロセスの影響 (大工研)辰巳国昭, Karim Zaghib, 澤田吉裕 (日機装(株))阿部浩史, 大崎 孝 117-226-C-1 高炉用コークスの高温における耐熱特性 (茨城大工)佐藤千之助, 酒井直孝 (豊橋技科大)鈴木隆之 (NKK)板垣省三, 三谷成康 117-226-C-2 Development of self-mending type oxidation protection of furan resin-derived carbon by Ta-compounds addition (Tokyo Institute of Technology) Ei-ichi Yasuda, Sei-Main Park, Takashi Akatsu and Yasuhiro Tanabe
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