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PREPARATION, STRUCTURE AND REDUCTION OF SOME GRAPHITE INTERCALATION COMPOUNDS

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SUMMARY

The structural features of several Fluorine-Graphite Intercalation Compounds (C_xF) and Vanadium fluoride-Graphite Intercalation Compound (C_xVF_6) have been determined by X-ray and electron diffraction measurements. The reduction of these compounds has been carried out in propylene carbonate by the carbon paste electrode technique. The results are compared with those obtained with graphite fluorides ; they are interpreted in relation to the structure, composition, and preparation mode of the different samples.

INTRODUCTION

The reaction of fluorine with carbon or graphite leads to the formation of different carbon-fluorine compounds, depending the temperature and the starting carbonaceous material [1-3]. If t > 630°C, only gaseous fluorocarbons are formed (CF_4, C_2F_6, ...). For 350 < t < 600°C, the reaction of F_2 with graphite leads to **graphite fluorides**, denoted $(C_xF)_n$, C_xF, or CF_x. The structures of poly (carbon monofluoride) $(CF)_n$ and poly (dicarbon monofluoride) $(C_2F)_n$ are well-known ; these insulating compounds have covalent bonds between fluorine and sp^3-hybridized carbon atoms. However, monocrystals are difficult to prepare and, in the formula C_xF, x represents the mean stoichiometric coefficient. Around 350°C, only C_2F is obtained, whereas CF is produced at 600°C ; for intermediary temperatures, a mixture of both graphite fluorides is obtained. Usually,

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graphitized petroleum coke is used for the manufacture of commercial graphite fluorides. The composition of the products depends not only on the temperature of the reaction but also on the temperature of graphitization of the coke.

Fluorine does not react directly with graphite below 300°C. If a catalyst is present, fluorine may be intercalated into the graphite lattice, forming 'nearly ionic bonds' [3] with the sp^2-hybridized carbon atoms. In these **Graphite Intercalation Compounds** (GIC), traces of catalyst molecules are sometimes present. For example, 'C_4F' prepared for the first time by Rüdorff in 1947 [4] belongs to this family of compounds because it must be prepared in the presence of HF and its exact formula is $C_xF(HF)_y$, with $2 < x < 5$ [5,6]. Other GIC's may be prepared at temperatures lower than 200°C in a reactor containing vapors of the fluorinated species to be intercalated, with or without an oxidative coreagent such as fluorine [7]. Recently, other GIC's have been synthesized in the presence of a non-volatile metal fluoride such as SnF_4, PbF_4 [7], LiF, CuF_2 [8,9], AlF_3, or MgF_2 [10]. The formula of these compounds is $C_xF(MF_z)_y$, in which z is the valency of the metal M ; it is sometimes abbreviated as "C_xF" in the literature, although they contain traces of the metal fluoride. In this paper, they will be denoted in italics 'C_xF', in order to distinguish them from the graphite fluorides. Some GIC's show higher electrical conductivity than the starting graphite.

Graphite fluorides have been proposed as cathodic materials in primary lithium batteries [11], and commercial cells are available [2]. The organic electrolyte is usually composed of acetonitrile, DMSO, γ-butyrolactone or propylene carbonate, in which a lithium salt (perchlorate or tetrafluoroborate) is added as supporting electrolyte. The presence of one of these salts in the solution enhances the performances of the battery because the insertion of Li^+ occurs during the discharge process [12]. The reduction of C_xF is easier when $LiClO_4$ is chosen rather than n Bu_4NClO_4 because of the difficult insertion of the bulky cations [13].

However, the performances of these batteries are limited for several reasons : first, graphite fluorides are non-conductors ; thus, they must be supported on a conducting phase such as graphite ; the energy density is thus lowered. Secondly, the rate of the electrochemical reduction of C_xF is very small ; the use of large active surface areas is necessary for obtaining a reasonable value of the discharge current [14]. Thirdly, the working voltage of a C_xF/Li cell is considerably lower than the theoretical value, due to a two step reduction mechanism including the formation of an intermediate compound Li_xCF_x and its further decomposition [15,16]. In addition, the discharge performances of these lithium batteries strongly depend on the crystallinity and composition of the cathodic material [1,16].

In order to avoid some of the problems met when using graphite fluorides, graphite intercalation compounds have been proposed recently as cathodic materials in lithium primary batteries [17].

The aim of the present paper is to present the method of preparation, the structure, and the electrochemical behaviour of several GIC's, and to compare the results with those obtained with graphite fluorides.

EXPERIMENTAL

The layered structure of several samples has been observed with a JEOL JEM 100 CX II Electron Microscope equipped with a JEOL scanning attachment STEM-SEM (ASID 4D). An energy dispersive X-ray detector LINK AN 10000 (with a Si(Li) ultrathin window) was used for qualitative and quantitative determination of the amount of intercalated species (vanadium fluoride). Electron diffraction patterns of the samples were obtained with a JEOL JEM 100 CX II high resolution Transmission Electron Microscope.

For our electrochemical experiments, we have used the carbon paste electrode technique, which allows the study of insoluble and insulating compounds drowned in a conductive carbon paste [18,19]. The electrolyte is a molecular solution of $LiClO_4$ in propylene carbonate because of its large electroactivity domain.

Graphite fluoride samples

Commercial poly (dicarbon monofluoride) (Sample 1) and poly (carbon monofluoride) (Samples 3-6) have been studied. Another sample was synthesized on a laboratory scale : poly (carbon monofluoride) (Sample 2, prepared by Professor Watanabe, Kyoto).

We give hereafter details for the preparation of the compounds :

- Sample (1) : $x = 1.54$ (Cefbon-DM®, Central Glass), prepared from petroleum coke. Its decomposition temperature lies between 400 and 450°C.

- Sample (2) : $x = 0.97$, prepared by direct fluorination of flaky natural graphite, at 600°C, under an atmosphere of a fluorine-argon mixture (1:1). Its decomposition temperature is above 610°C.

- Sample (3) : x = 0.91 (Cefbon-CM®, Central Glass), prepared from artificial graphite powder (decomposition temperature : $450 < t_d < 500°C$).
- Sample (4) : x = 0.91 (Alfa Ventron ref. 88548).
- Sample (5) : x = 0.91 (Foracarb®, Atochem).
- Sample (6) : x = 0.885 (Daikin Kogyo), prepared from petroleum coke.

The composition of these compounds was determined from elemental analysis. For example, for Sample (6) : (found, C : 35.68 %, F : 63.2 %; calcd, C : 35.87 %, F : 64.13 %).

The experimental procedure and the results from the electron diffraction patterns of some of the graphite fluorides (1-3) are given in ref. [13]. Only crystalline compounds (such as Sample 2) show well-defined patterns from which the crystallographic parameters can be deduced ; commercial graphite fluorides usually present diffuse lines. For example, the crystallinity of Sample (6), prepared from petroleum coke, is not high. Very broad (100) and (110) diffraction rings were observed in the electron diffraction pattern. Indexed patterns are shown in Table 1.

Disintegration of all of these carbon-fluorine compounds under the electron beam occurs with varying rapidity.

Graphite Intercalation Compounds

Three GIC's were prepared, their composition being determined from the weight increase.

Two fluorine-graphite intercalation compounds (C_xF), denoted Sample (7) and Sample (8) hereafter, were prepared at room temperature from natural graphite (147-295 μm) in the presence of silver fluoride. The preparative method has been reported previously [3] :

- Sample (7) : x = 6.6.
- Sample (8) : x = 14.7.

A vanadium fluoride-graphite intercalation compound (C_xVF_6) was prepared from natural graphite (147-295 μm) and metallic vanadium in a fluorine atmosphere at 200°C [20]. At this temperature, the fluorination of metallic vanadium to VF_5 and the intercalation of VF_5 and fluorine into graphite occurs successively. The composition of the product is :

- Sample (9) : x = 14.1 ($C_{14.1}VF_6$).

The stability of this compound towards the electron beam was confirmed by the invariability of its vanadium content deduced from X-ray spectra, performed at the beginning and at the end of the experiment.

The structural features such as stage number and lattice parameters were determined by X-ray and electron diffraction measurements. The layered structures of these compounds were also observed by scanning electron microscopy (SEM). In Fig. 1 some results obtained with Sample (9) are presented.

Other chemicals

- Solvent : propylene carbonate for synthesis MERCK
- Supporting electrolyte : lithium perchlorate (purum) FLUKA
- The reference electrode contains lithium nitrate and sodium iodide R.P. RHONE-POULENC (PROLABO)
- The working electrode contains JOHNSON MATTHEY graphite powder (non-pelletable, Grade II).

Electrochemical apparatus

Experiments were carried out at 25°C in the polypropylene cell described in ref.[13], fitted with a carbon paste working electrode, an auxiliary platinum electrode, and a Ag/AgI reference electrode. The latter is maintained in a special compartment containing a saturated NaI solution in propylene carbonate. It is separated from the main compartment of the cell by a PVDF junction [13,21].

The working electrode is a Teflon cup containing an electron collector (vitreous carbon rod) and the carbon paste, *i.e.* a mixture of solid electroactive compound C_xF or GIC (0.02 g) and graphite powder (0.1 g) wetted by a few drops of the propylene carbonate solution. Silica powder is placed over the paste in order to avoid mixing with the electrolyte. A potential scan in the range + 1 V and - 2.5 V is performed at a very low sweep rate (v = 0.02 mV/s) with a PAR 273 potentiostat. The I-V curves are plotted on a XY recorder.

STRUCTURE OF THE INTERCALATION COMPOUNDS

The C_xF compounds obtained were stage 4 (Sample 8 : $C_{14.7}F$), and stage 2 (Sample 7 : $C_{6.6}F$). The results for $C_{14.7}F$ by X-ray and electron diffraction are summarized in Tables 2a and 2b. The electron diffraction

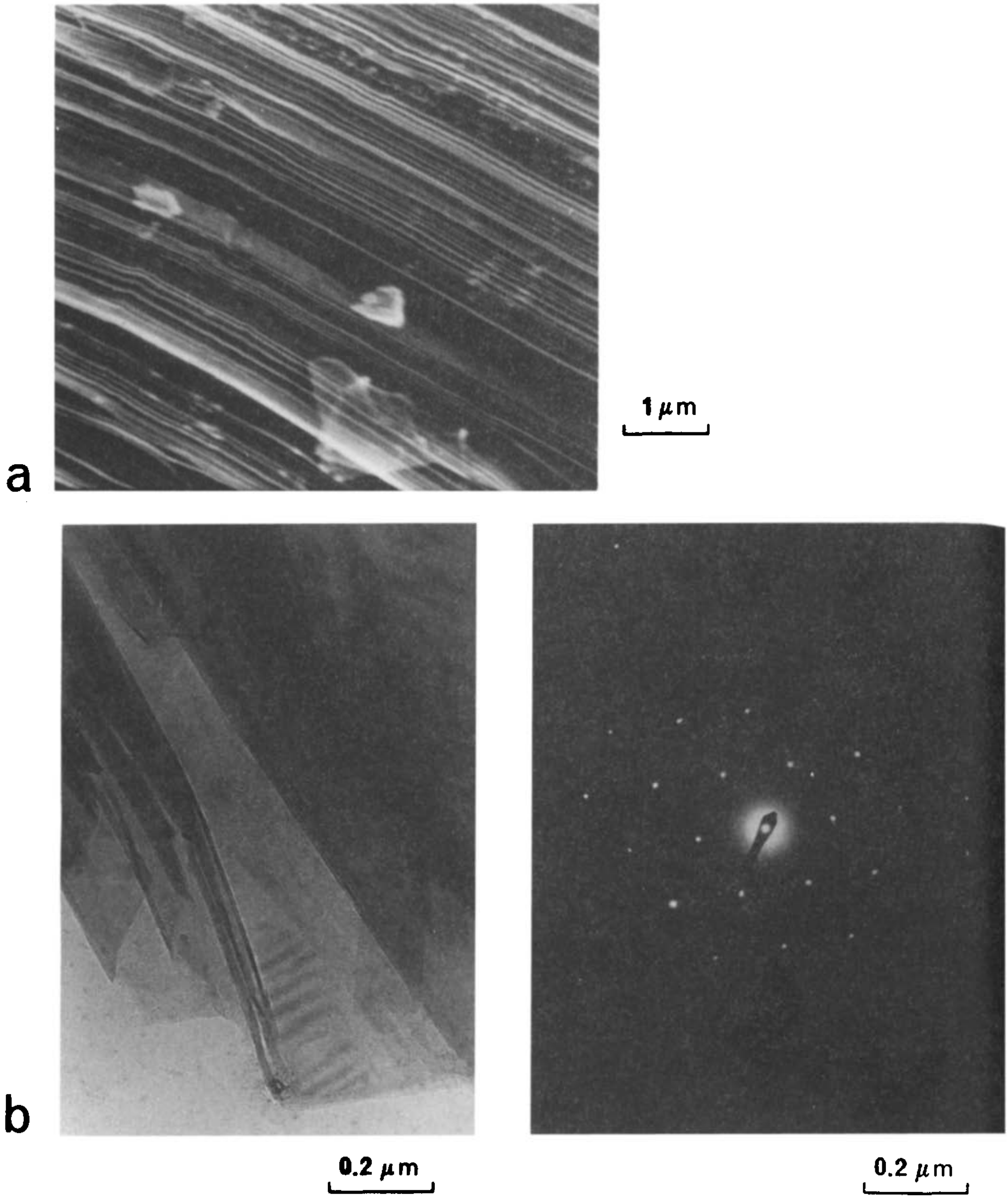

Fig. 1. Study of the GIC : $C_{14.1}VF_6$ (Sample 9)
(a) S.E.M. micrograph;
(b) T.E.M. micrograph;
(c) Electron diffraction pattern.

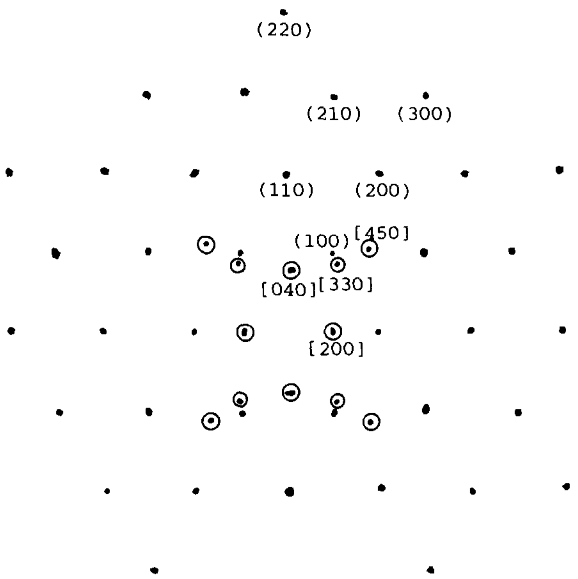

Fig. 2. **Electron diffraction pattern of stage 4, $C_{14.7}F$**
(hkℓ) and [hkℓ] in this figure are shown in Tables 2a and 2b, respectively. Circled spots are from intercalated fluorines and others are from graphite lattice. The [640] line in Table 2b is a very weak ring, therefore it is not written in this figure.

TABLE 1

Indexed result for graphite fluoride $CF_{0.885}$ (Sample 6)

No	Intensity	$1/d^2$(obsd)	$1/d^2$(calcd)	hkℓ
1	m	0.0219	0.0219	002
2	m	0.218	0.216	100
3	w	0.693	0.650	110

Hexagonal, a_0=2.48 Å, c_0=6.75 Å
(00ℓ):from X-ray diffraction, (hk0):from electron diffraction
m:medium, w:weak

TABLE 2a

Indexed result for graphite lattice of stage 4, $C_{14.7}F$ by X-ray and electron diffraction

No	Intensity	1/d^2(obsd)	1/d^2(calcd)	hkℓ
1	m	0.0614	0.0626	004
2	vs	0.0986	0.0978	005
3	s	0.2215	0.2215	100
4	vw	0.3170	0.3167	009
5	w	0.3951	0.3911	0010
6	m	0.6730	0.6642	110
7	w	0.8934	0.8850	200
8	w	1.594	1.551	210
9	w	2.029	1.993	300
10	w	2.723	2.657	220

Hexagonal, $a_0=b_0=2.454$ Å, $c_0=15.991$ Å

(00ℓ):from X-ray diffraction, (hk0):from electron diffraction

TABLE 2b

Indexed result for intercalated fluorines of stage 4, $C_{14.7}F$ by electron diffraction

No	Intensity	1/d^2(obsd)	1/d^2(calcd)	hkℓ
1	s	0.0544	0.0553	200
2	m	0.1082	0.1062	040
3	s	0.1913	0.1842	330
4	m	0.3853	0.3873	450
5	vw	0.5809	0.6041	640

Orthorhombic, $a_0=8.502$ Å, $b_0=12.270$ Å

m:medium, s:strong, w:weak, vs:very strong, vw:very weak

pattern of $C_{14.7}F$ is shown in Fig. 2. The electron diffractogram shows two sets of diffraction spots indicating the crystal lattices of graphite and intercalated species. The indexed result for the graphite lattice is given in Table 2a together with the (00ℓ) lines, and that for intercalated fluorines in Table 2b. The diffraction spots from the crystal lattice of intercalated fluorines have twofold symmetry while those from the graphite lattice have sixfold symmetry. This suggests that the crystal lattice made by intercalated fluorines belongs to an orthorhombic system. If an intercalated species is randomly oriented between carbon layers, diffraction lines for the intercalated species disappear and only (hk0) lines for a graphite lattice are observed. The graphite lattice of $C_{14.7}F$ has been indexed on a hexagonal system. The lattice parameter (a_0 = 2.454 Å) is smaller than that of graphite itself (a_g = 2.462 Å) due to the bonding with highly electronegative fluorine atoms. The (00ℓ) lines indicate that $C_{14.7}F$ is a stage 4 compound (I_c = 15.991 Å) and the apparent size of intercalated fluorine is 2.59 Å which is almost equal to the diameter of fluoride ion. The intercalated species would be situated at the center of two carbon sheets because the (005) diffraction line has the highest intensity. The calculation of the intensity of the diffraction lines shows that the (n + 1) line is the strongest when an intercalated species is arranged just at the center of two carbon sheets. On the other hand, the diffraction spots indicating the regular arrangement of intercalated fluorines have been indexed on the orthorhombic system. The lattice parameters for in-plane orientation of fluorines are a_0 = 8.502 Å and b_0 = 12.270 Å (Table 2b). It is clear from Tables 2a and 2b that the new superlattice made by combining the graphite lattice with that of intercalated fluorines has a big orthorhombic unit cell as shown in Fig. 3. The lattice parameters of stage 4, $C_{14.7}F$ are therefore a = 8.502 Å, b = 15.991 Å and c = 12.270 Å (twofold axes of rotation are taken as <u>a</u> and <u>b</u> axes). These are represented in Fig. 3 which shows a possible in-plane orientation of intercalated fluorines. This structure has 2 twofold axes of rotation (<u>a</u> and <u>b</u>-axes, <u>b</u>-axis is perpendicular to the carbon plane), and 1 twofold axis of rotary inversion (<u>c</u>-axis) if carbon layers take a A/ABAB/BABA/A---- stacking (/: intercalated layer). When the stacking sequence of carbon layers is A/ABAB/BABA/A----, the lattice parameter b should be 15.991 × 2 Å.

The composition of the structure model in Figure 3 is expressed as $C_{3.3n}F$ (n : stage number). When n is 4, this gives $C_{13.2}F$ close to the experimental value.

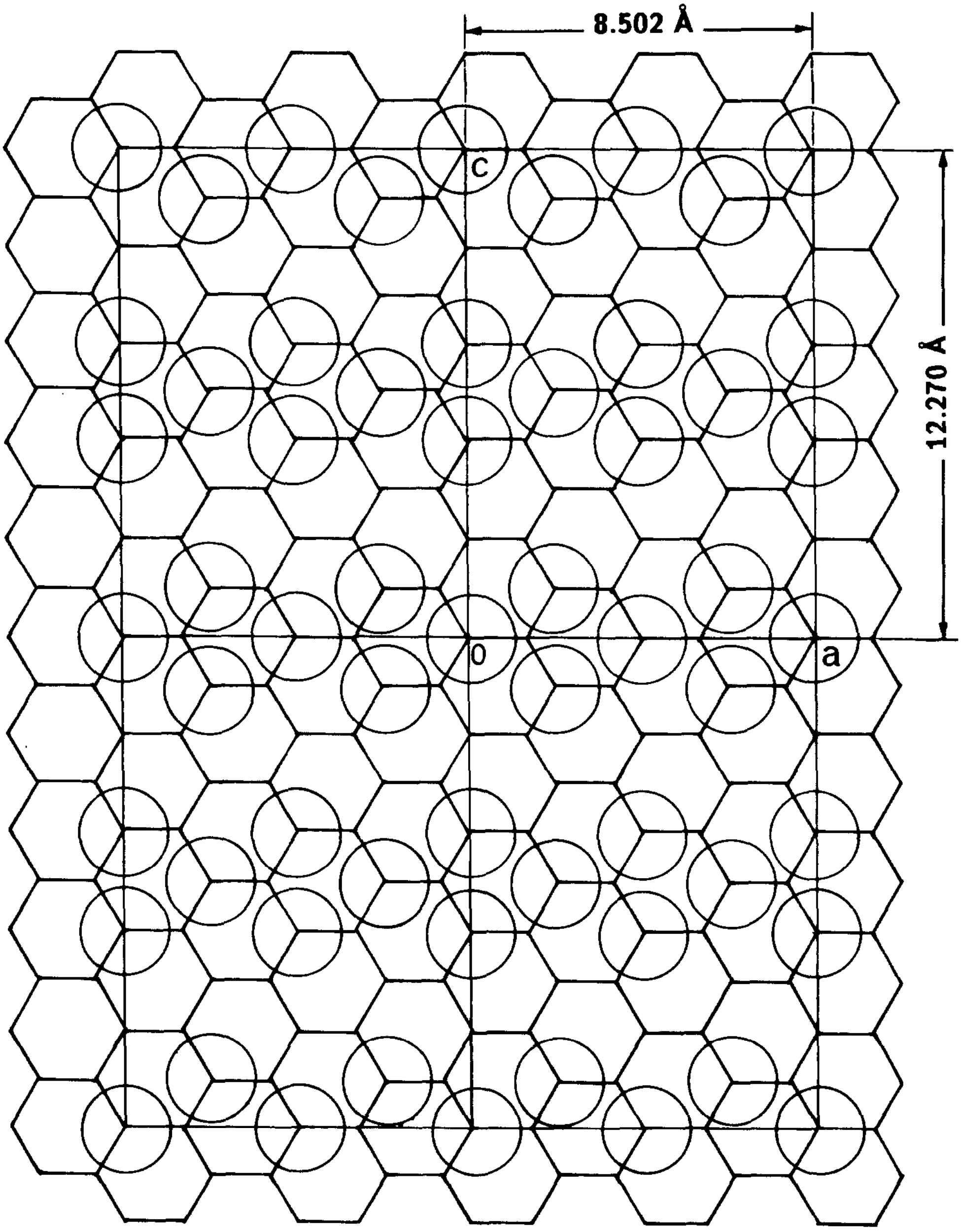

Fig. 3. A possible structure of stage 4, $C_{14.7}F$
Orthorhombic, a = 8.502 Å, c = 12.270 Å, b = 15.991 Å.

The regular arrangement of intercalated fluorines was not found in the electron diffraction pattern of stage 2, $C_{6.6}F$, in which only the diffraction spots corresponding to the graphite lattice were observed. However, two different repeat distances along the c-axis were obtained (I_c = 8.85 Å and 9.40 Å). This suggests that $C_{6.6}F$ consists of two phases. In a phase with 9.40 Å as the repeat distance along the c-axis, the apparent size of intercalated fluorine (2.70 Å) is equal to the diameter of fluoride ion, and the fluoride ions would be arranged at the center of two carbon sheets because the (003) diffraction line has the highest intensity. In the other phase, the apparent size of fluorine, however, is a smaller value, 2.15 Å, and the (002) line is the strongest. This may have arisen from the deviation of the position of fluorines from the center of two carbon sheets because of an increase in the chemical bond between fluorine and carbon of one carbon sheet. The indexed result is shown in Table 3.

In the diffraction pattern of stage 2, $C_{14.1}VF_6$, only the diffraction spots indicating graphite lattice were observed. This means that the VF_6^- anions are randomly distributed in a graphite gallery, which coincides with the result obtained by Debye-Scherrer methods. Table 4 shows the indexed result.

ELECTROCHEMICAL BEHAVIOUR OF THE SAMPLES

Preliminary experiments have shown that the residual current is very weak in the potential range of CF_x reduction. The cathodic peak observed at - 1.2 V, when the carbon paste does not contain any electroactive carbon-fluorine compound, is attributed to the reduction of water (curve (0) in Fig. 4). In Fig. 4 the reduction peaks for Samples 4-9 are also presented.

Table 5 summarizes the peak characteristics E_p, I_p and Q_{exp} of all the tested samples. I_p is the intensity and E_p the potential of the reduction peaks, and Q_{exp} the experimental charge required for the reduction process, deduced from the voltammograms. This may be compared with the theoretical charge Q_{th} which is needed for the complete reduction of the compound.

It is often noticed with the carbon paste electrode technique that the reduction yield Q_{exp}/Q_{th} is never equal to unity because of the slow diffusion of the species in the solid phase and because of the geometry of the working electrode. The yield of the reduction of CF_x in batteries is of

TABLE 3

Indexed result for stage 2, $C_{6.6}F$

No	Intensity	$1/d^2$(obsd)	$1/d^2$(calcd)	hkℓ
1	w	0.0132	0.0128	001*
2	vs	0.0501	0.0510	002*
3	vs	0.1015	0.1018	003
4	vw	0.2004	0.2042	004*
5	s	0.2215	0.2219	100
6	w	0.4088	0.4073	006
7	s	0.6664	0.6653	110
8	m	0.8934	0.8866	200
9	w	1.582	1.553	210
10	w	2.018	1.995	300
11	w	2.723	2.661	220

Hexagonal, a_0=2.452 Å, c_0=8.853 Å(*), c_0=9.401 Å

(00ℓ):from X-ray diffraction, (hk0):from electron diffraction

m:medium, s:strong, w:weak, vs:very strong, vw:very weak

TABLE 4

Indexed result for stage 2, $C_{14.1}VF_6$

No	Intensity	$1/d^2$(obsd)	$1/d^2$(calcd)	hkℓ
1	w	0.0314	0.0315	002
2	vs	0.0723	0.0709	003
3	s	0.1256	0.1261	004
4	s	0.2240	0.2219	100
5	w	0.2805	0.2838	006
6	s	0.6599	0.6653	110
7	m	0.8934	0.8866	200
8	w	1.563	1.553	210
9	w	1.995	1.995	300

Hexagonal, a_0=2.452 Å, c_0=11.264 Å

(00ℓ):from X-ray diffraction, (hk0):from electron diffraction

m:medium, s:strong, w:weak, vs:very strong

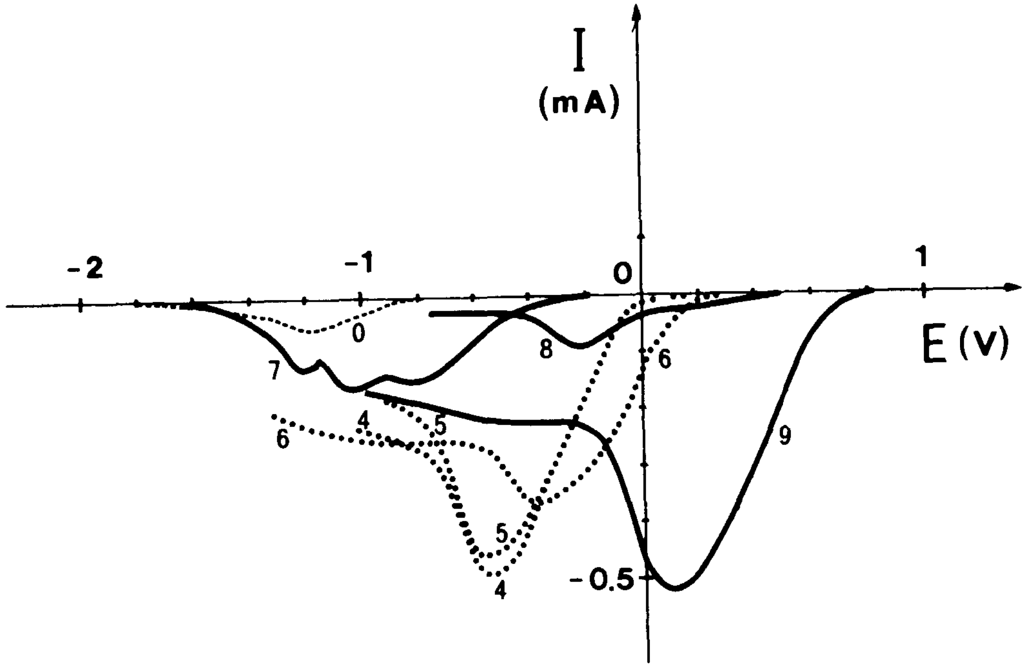

Fig. 4 Electrochemical behaviour (reduction) of Samples 4-9

Carbon paste technique ; v = 0.04 mV/s ; reference electrode Ag/AgI ; electrolyte : $LiClO_4$ M in propylene carbonate.

4, 5, 6 : Graphite fluoride samples

7, 8, 9 : GIC

0 : Residual current

TABLE 5

Peak characteristics of some graphite fluorides (Samples 1-6) and GIC s (Samples 7-9) ; carbon paste technique

Sample	$\|I_p\|$ (mA)	E_p (V)	Q_{exp} (C)	Q_{exp}/Q_{th}	Ref.
1	0.555	-0.30	17.0	0.38	[13]
2	0.575	-0.75	12.0	0.19	[13]
3	0.480	-0.20	16.5	0.26	[13]
4	0.490	-0.54	16.2	0.26	This work
5	0.445	-0.58	13.7	0.21	This work
6	0.360	-0.38	13.8	0.21	This work
7	0.180	-1.02	6.6	0.34	This work
8	0.080	-0.22	2.4	0.07	This work
9	0.490	+0.07	20.4	20.4/5.78(m+1)	This work

course higher ; in this work, the ability of the compounds to be reduced is deduced from the comparison of the ratios Q_{exp}/Q_{th}.

Graphite fluorides

The electrochemical behaviour of Samples 1-3 has been investigated previously by the same experimental technique [13]. The results are given in Table 5 for comparison.

The potential E_p depends on the crystallinity of the compound and on its ability to be reduced easily. It was mentioned in ref. [13] that the reduction of well-defined crystalline samples (Sample 2) occurs at lower potentials because they are less reactive than the other samples ; they are characterized by higher decomposition temperatures.

Samples (3), (4) and (5) have the same composition (x = 0.91). The reduction peaks for Samples (4) and (5) coincide, but Sample (3) gives rise to a peak shifted towards less negative potentials, indicating a more reactive compound. These results confirm that the stoichiometric coefficient x is not the only parameter to be considered in order to forecast the reactivity of a C_xF (x is only the average). If the sample consists of a broad statistical distribution of x values, the reduction peak will be broad (Sample 6); if this distribution is not centered on one mean value but several, the reduction peak may present shoulders.

Graphite Intercalation Compounds

The reduction peak of Sample (7) is characterized by two shoulders. One of them (- 1.2 V) is attributed to the contribution of the traces of water contained in the electrolyte. The second may be interpreted by the non-homogeneity of the sample (see above), in agreement with the results of electron and X-ray diffraction patterns. Each distinct phase gives rise to its own reduction peak.

However, it is quite surprising to obtain such low values of E_p with GIC ; the present values seem to indicate an increase of the chemical bond between fluorine and carbon.

The potential E_p for Sample (8) is higher than the values obtained with graphite fluorides, as is expected for a GIC. The ratio Q_{exp}/Q_{th} is very low for this compound, but the results are inaccurate in this case, because of the very small value of Q (the amount of electroactive compound is limited by the dimension of the working electrode).

The reduction peak obtained with Sample (9) is characterized by a positive value of E_p and a large value of Q_{exp}. These results suggest that the reduction of both the C_xF and the intercalated VF_5 occurs.

$Q_{th}' = 5.78$ C are required for the complete reduction of the C_xF, according to :

$$C_{14.1}F + e^- \rightarrow 14.1\ C^* + F^-$$

$Q_{th}'' = 5.78$ m coulombs are required for the reduction of the vanadium species to a lower fluoride according to :

$$C_{14.1}VF_6 + m\ e^- \rightarrow C_{14.1}VF_{6-m} + m\ F^-$$

As Q_{th} is always greater than Q_{exp} with the carbon paste electrode technique, $5.78\ (m + 1) > 20.4$; one may deduce from our experiments that $m \geq 3$.

The shoulder at - 0.5 V on the voltammogram probably corresponds to the last step of the reduction of vanadium species or to the reduction of intercalated fluorine species.

CONCLUSION

A study of the electrochemical behaviour of GIC's is necessary before using them in batteries. In this work, several compounds have been synthesized. Their structures have been deduced from X-ray and electron diffraction patterns. Our electrochemical experiments, performed in propylene carbonate by the carbon paste electrode technique, lead to several conclusions :

- the electrochemical behavior of the GIC's depends strongly on their mode of preparation
- when both fluorine and a volatile fluoride are intercalated, the reduction process may include the reduction of this fluoride. One may turn this result to advantage in order to increase the energy density of batteries.

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