Synthesis and Characterization of Graphite Fluorides by Electrochemical Fluorination in Aqueous and Anhydrous Hydrogen Fluoride

H. Takenaka, M. Kawaguchi, M. Lerner, and N. Bartlett*

Department of Chemistry, University of California, Berkeley, CA 94720, and the Materials and Chemical Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, U.S.A.

The electrochemical oxidation of graphite in 50% aqueous hydrogen fluoride generates a second-stage graphite fluoride, $C_{14}F(HF)_y$, a relative of the graphite fluorides prepared and characterized by chemical or electrochemical fluorination of graphite in anhydrous hydrogen fluoride.

Earlier work on the electrochemical oxidation of graphite in aqueous electrolytes had indicated that graphite oxide was produced beyond a charge corresponding to $C_{24}{}^+A^-$.[1,2] More recently,[3,4] reversible intercalation of graphite in aqueous HF to a charge level corresponding to $C_{48}{}^+A^-$ has been proposed. In this work, highly charged materials produced by oxidation in 50% aqueous HF have been compared with those formed in anhydrous hydrogen fluoride.

Figure 1 shows the charge curve for the electrochemical oxidation of graphite both in aqueous electrolyte and in anh. HF/1M-NaF. The charge curves are similar at low charge values and each exhibits a long plateau at higher charging. This and the *X*-ray diffraction data for the various products indicated that the materials produced in the aqueous electrolyte were related to those formed in anhydrous HF.

Graphite is intercalated by elemental fluorine in the presence of liquid or gaseous HF at 20 °C[5,6] to produce a first-stage salt, $C_x{}^+F(HF)_y{}^-$ (third stage: $x = 24$; second stage: $x = 16$; $1 \leqslant y \leqslant 4.7$). These salts (see Table 1) evolve HF and the stage increases (from second to third, or first to second) under dynamic vacuum. The first-stage salts have an interlayer spacing near 6.4 Å, whereas for the higher stages the gallery height (*i.e.* spacing of the carbon layers enclosing the guest ions) is closer to 6.3 Å. Exposure of the salts to more fluorine eventually yields the first-stage graphite fluorides, $C_xF_{1-\delta}(HF)_\delta$ ($2 \leqslant x \leqslant 5$; $x/\delta \simeq 12$) in which fluorine is bound to carbon semi-ionically. The graphite fluorides, unlike the salts, remain first-stage on dynamic evacuation. As x decreases from 5 to 2 in $C_xF_{1-\delta}(HF)_\delta$, the gallery height of the vacuum-stable material increases from 5 to more than 6 Å. Simultaneously, as noted previously,[5,7] the bonding of the F to the carbon brings about a large decrease in conductivity.

The *X*-ray and gravimetric data (see Table 1) in association with the electrochemical work have established that the long, final plateau seen in the charge curve for the anhydrous electrolyte involves a transition from the first-stage graphite $C_{16}{}^+$ (with hydrofluoride anion) to the first-stage material in which the fluorine is bonded (semi-ionically) to the graphite, and which has the approximate composition $C_{5.5}F{\cdot}yHF$ (y being small in evacuated samples). Both products are indistinguishable from those produced from the action of elemental fluorine and anhydrous HF on graphite.

At the oxidation limit in aqueous HF (50%) a mixture of first ($c_0 \sim 5.7$ Å) and second ($c_0 \sim 9.1$ Å) stages was seen when the electrode was quickly removed from the electrolyte after charging; however, only the second stage was observed when reduction by the electrolyte and equilibration with it was permitted. Therefore, when materials stable in the aqueous electrolyte were desired, electrochemical oxidation was followed by equlibration in the electrolyte until the electrochemical potential of the graphite compound was stabilized, a process which generally required two or more days for highly-charged, low-stage compounds. The charge on the stable compound was determined coulometrically by slow (< 100 μA cm^{-2}) galvanostatic reduction in either aqueous or anhydrous HF. *X*-Ray diffraction study of the end products of reduction revealed only graphite (or high-stage compounds) and further electrochemical reduction even after several hours recovery time was minimal.

The highest charge stable in the aqueous electrolyte was

Table 1. Compositional and structural data for the products of chemical and electrochemical fluorination of graphite in anhydrous HF.

	Chemical fluorination		Electrochemical fluorination in anhydrous HF	
	in situ	Evacuated	*in situ*	Evacuated
Stage	2nd	3rd		
c_0/Å	9.61	12.98		
Composition	$C_{24}F(HF)_{2.5}$[a]	$C_{24}HF_2$		
Stage	1st	2nd	1st	2nd
c_0/Å	6.46	9.76	6.40	9.47
Composition	$C_{16}F(HF)_{4.3}$	$C_{16}HF_2$	$C_{16}F(HF)_{4.7}$[b]	$C_{16}HF_2$
Stage	1st	1st	1st	1st
c_0/Å	7.55	5.55	7.46	5.51
Composition	$C_{4.2}F(HF)_{1.5}$[c]	$C_{4.2}F(HF)_{0.4}$	$C_{5.5}F(HF)_{1.8}$	$C_{5.5}F(HF)_{0.6}$
Stage	1st	1st		
c_0/Å	6.70	6.17		
Composition	$C_{2.8}F(HF)_{0.4}$	$C_{2.8}F(HF)_{0.2}$		

[a] Calculated from gravimetric data. The evacuated hydrofluoride salts were vacuum-stable and assumed to contain only $HF_2{}^-$. [b] Calculated from coulometric data and the known unit cell volume. [c] Calculated from gravimetric data. The C : HF ratio was assumed, on the basis of previous analytical evidence, to be 12 : 1 after 24 h evacuation.

Table 2. Electrochemical, gravimetric, and *X*-ray analysis of the products of oxidation in 50% aqueous HF.

$-Q$ applied[a]/ C per mmol carbon	Stoicheiometry by discharge[b]	*E*/V at 24 h	*X*-Ray data	
			in situ	After evacuation
1.42	$C_{137}{}^+$	+1.4		
2.01	$C_{64}{}^+$	+1.4	High stage	High stage
3.57	$C_{68}{}^+$	+1.4		
7.14	$C_{64}{}^+$	+1.3		
12.5	$C_{27}{}^+$	+1.3	$c = 9.9$ Å	
16.7—25.0	$C_{14}{}^+$	+1.3	$c = 9.53$ Å	$c = 9.15$ Å
>25	$C_{14}{}^+$	+0.6		$c = 9.15$ Å

[a] The charge applied to the cell does not accurately reflect the charge on carbon. In addition to slow chemical reduction of the anode by the electrolyte, electrolyte oxidation becomes significant above 1.6 V. [b] As determined coulometrically by galvanostatic discharge in aqueous or anhydrous HF after equilibration in the aqueous HF electrolyte.

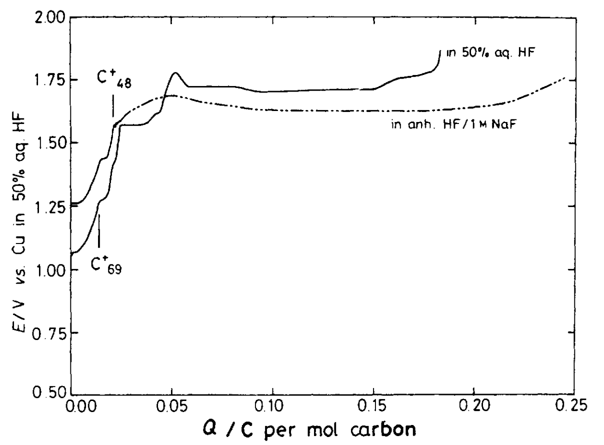

Figure 1. Galvanostatic oxidation of graphite in 50% aqueous HF and anh. HF/1M-NaF. The curves are normalized to the same potential scale. Charge rate is approximately $-150\ \mu A\ cm^{-2}$. Oxygen evolution is observed to be a competing oxidation process in the aqueous electrolyte at potentials above +1.6 V. The broken line denotes the region where coulometry does not indicate the charge on carbon.

found to be appropriate for $C_{14}F$ (see Table 2). After removal of volatile material from this product, the black, air-stable material exhibited a sharp diffraction pattern with a *c*-axis repeat of 9.15 Å. Chemical analyses† indicated that the predominant intercalating species was fluoride and not oxide.

The small gallery height, the persistence of second-stage character on evacuation, and the relatively low conductivity‡ suggest that the $C_{14}F$ produced in the aqueous electrolyte involves F bound to carbon. It appears to be a novel relative of the first-stage graphite fluorides produced by fluorination in anhydrous HF.

In the electrochemical syntheses, the working electrode (apparent surface area 2 cm^2) was formed by mixing 15—70 mg of SP1 graphite (Union Carbide spectroscopic powder) into a solution of cyclohexane with 3—20% binder (ethylene propylene terpolymers; Exxon Chemicals) and painting the resulting slurry onto Pt mesh. Freshly cleaned Cu rod and Cu or Pt wire served as the reference and the counter electrode respectively. The electrodes were sealed into 3/8 inch FEP tubing and connected *via* compression fittings to a Kel-F union cross. In the anhydrous system, NaF (200 mg) was added and the cells were evacuated before anhydrous HF was condensed (*ca.* 5 ml). In the aqueous system, 50% aqueous HF (Fischer Scientific) was used and the cells were left open to air.

Electrochemical experiments were performed with a PAR M273 potentiostat/galvanostat. *X*-Ray powder diffraction data were obtained by the Debye-Scherrer method with a GE Precision camera of 45 cm circumference using Ni-filtered Cu-K_α radiation.

We acknowledge the support of the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

Received, 14th May 1987; Com. 650

References

1 M. J. Bottomley, G. S. Parry, A. R. Ubbelohde, and D. A. Young, *J. Chem. Soc.*, 1963, 5674.
2 H. P. Boehm, M. Eckel, and W. Scholz, *Z. Anorg. Allg. Chem.*, 1967, **353**, 236.
3 F. Beck and H. Krohn, *Synth. Metals,* 1983, **7**, 193.
4 F. Beck, H. Krohn, and W. Kaiser, *J. Electroanal. Chem.*, 1984, **165**, 93.
5 T. Mallouk and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 1983, 103.
6 T. Mallouk, B. L. Hawkins, M. P. Conrad, K. Zilm, G. E. Maciel, and N. Bartlett, *Philos. Trans. R. Soc. London, A*, 1985, **314**, 179.
7 T. Mallouk, Ph.D. Thesis, 1983, University of California, Berkeley, California.

---

† Oxygen analysis of the material depended on the extremely favourable reaction of PF_5 with oxygen-containing species to form POF_3. Based on POF_3 evolution after reaction with PF_5 and displacement by BF_3, oxygen comprises less than 33 mol % of the intercalant present.

‡ The conductivity per carbon sheet (measured by a four-probe apparatus) is close to that of graphite ($k/k_g = \sigma/\sigma_g \times c/3.35$ Å $=$ 0.8—1), as compared with k/k_g of at least 1.6 for the second-stage ionic salt and at most 0.3 for the most conductive first-stage graphite fluoride.