Lawrence Berkeley National Laboratory

Recent Work

Title

THE SYNTHESIS AND CHARACTERIZATION OF GRAPHITE FLUORIDES BY ELECTROCHEMICAL FLUORINATION IN AQUEOUS AND ANHYDROUS HYDROGEN FLUORIDE

Permalink

<https://escholarship.org/uc/item/91w5d61x>

Author

Takenaka, H.

Publication Date

1987-07-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Submitted to Chemical Communications

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

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

July 1987

RECEIVED
LAWRENCE
BERKELEY LABORATORY

SEP 18 1987

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.*

LBL-23061

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

The 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 Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

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

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

Figure 1 shows the charge curve for the electrochemical oxidation of graphite in both the aqueous electrolyte and AHF/1 M NaF. The charge curves are similar at low charge values and each ex-

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

hibits a long plateau at higher charging. This and the X-ray diffraction data for the various products indicated the materials produced in the aqueous electrolyte were related to those formed in AHF.

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, $C_x^+F(HF)_y^-$ (3rd stage: $x = 24$, 2nd stage: $x = 16$; $1 \leq y \leq 4.7$). These salts (see Table 1) evolve HF and increase in stage (from second to third, or first to second stage) 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, $C_xF_{1-\delta}(HF)_\delta$ ($2 \leq x \leq 5$; $x/\delta \sim 12$) in which fluorine is bound to carbon in semi-ionic bonding. The graphite fluorides, on the other hand, remain first stage on dynamic evacuation. As x decreases from 5 to 2 in $C_xF(HF)_{1-\delta}$, the gallery height of the vacuum stable material increases from 5 Å to more than 6 Å. Simultaneously, as has been 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 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 a composition $\sim C_{5.5}F.yHF$ (y being small in evacuated samples). Both products are indistinguishable from those produced from the action of elemental fluorine and AHF on graphite.

At the oxidation limit in aqueous HF (50%) a mixture of first ($c_0 \sim 5.7 \text{ \AA}$) and second ($c_0 \sim 9.1 \text{ \AA}$) 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 equilibration in the electrolyte until the electrochemical potential of the graphite compound 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 ($<100 \mu A/cm^2$) galvanostatic reduction in either aqueous or anhydrous HF. X-ray diffraction 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 found to be appropriate for $C_{14}F$ (see Table 2). After removal of volatiles 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 2nd 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 AHF.

In the electrochemical syntheses, the working electrode (apparent surface area = 2 cm²) was formed by mixing 15-70 mg of SPI 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

* Oxygen analysis of the material depended on the extremely favorable 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 mole % of the intercalant present.

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

Cu rod and Cu or Pt wire served as the reference and counter electrodes respectively. The electrodes were sealed into 3/8" 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 evacuated before condensing in AHF (~ 5ml). In the aqueous system, 50% aqueous HF (Fischer Scientific) was used and the cells were left open to air.

Electrochemical techniques were performed with a PAR M273 potentiostat/galvanostat. X-ray powder diffraction data was obtained by the Debye-Scherrer method on a GE Precision camera of 45 cm circumference using Ni-filtered $\text{CuK}\alpha$ radiation.

Acknowledgment

The authors gratefully 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.

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, Syn. 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, Phil. Trans. R. Soc. Lond. A, 1985, 314, 179.
- 7 T. Mallouk, Ph.D. thesis, 1983, University of California, Berkeley, California.

Figure 1. Galvanostatic oxidation of graphite in 50% aqueous HF and AHF/1 M NaF. The curves are normalized to the same potential scale. Charge rate is approximately $-150 \mu\text{A}/\text{cm}^2$. Oxygen evolution is observed to be a competing oxidation process in the aqueous electrolyte at potentials above +1.6 v.

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

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

Galvanostatic Charging of Cx in HF

	<u>chemical fluorination</u>		<u>electrochemical fluorination in AHF</u>	
	in situ	evacuated	in situ	evacuated
stage c ₀ (Å) composition	2nd 9.61 C ₂₄ F(HF) _{2.5} *	3rd 12.98 C ₂₄ HF ₂		
stage c ₀ (Å) composition	1st 6.46 C ₁₆ F(HF) _{4.3}	2nd 9.76 C ₁₆ HF ₂	1st 6.40 C ₁₆ F(HF) _{4.7} [†]	2nd 9.47 C ₁₆ HF ₂
stage c ₀ (Å) composition	1st 7.55 C _{4.2} F(HF) _{1.5} [‡]	1st 5.55 C _{4.2} F(HF) _{0.4}	1st 7.46 C _{5.5} F(HF) _{1.8}	1st 5.51 C _{5.5} F(HF) _{0.6}
stage c ₀ (Å) composition	1st 6.70 C _{2.8} F(HF) _{0.4}	1st 6.17 C _{2.8} F(HF) _{0.2}		

* Calculated from gravimetric data. The evacuated hydrofluoride salts were vacuum stable and assumed to contain only bifluoride.

† Calculated from coulometric data and the known unit cell volume.

‡ Calculated from gravimetric data. The C:HF ratio was assumed to be 12:1 after 24 hrs evacuation.

Table 1

-Q applied [†] (coul/mmol C)	stoichiometry by discharge [‡]	OCV at 24hrs	X-ray data	
			in situ	after evac
1.42	C ₁₃₇ ⁺	+1.4v		
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

[†] 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 1.6v.

[‡] As determined coulometrically by galvanostatic discharge in aqueous or anhydrous HF after equilibration in the aqueous HF electrolyte.

Table 2

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720