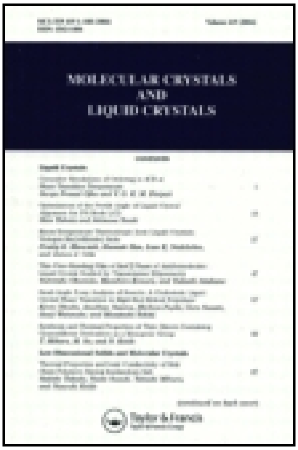

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Graphite Intercalation with Perfluoroalkylsulfonates, and Perfluoroalkylsulfonyl Imides and Methide

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The graphite intercalation compounds $C_xC_8F_{17}SO_3\cdot yF$ and $C_xN(CF_3SO_2)_2$ are prepared in 48 % hydrofluoric acid, using the oxidant K_2MnF_6 under ambient conditions. Analyses of PXRD peak position and periodic oscillation of the peakwidth indicate that the stable product $C_xC_8F_{17}SO_3\cdot 4F$ is comprised of a random solid solution of stage 2 and 3. The addition of conc. HNO_3 or fuming H_2SO_4 to 48% aqu. HF produces a stage 2 GIC. Structure refinement indicates a helical conformation of the anion. Stage 2 $C_xN(CF_3SO_2)_2$ (x = 37) is obtained within 15 minutes under ambient condition in 48% aqu. HF. The anion orientations for these GICs are evaluated by structural refinement. Larger anions containing $-C_nF_{2n+1}SO_2$ substitutents can also be intercalated.

Keywords: graphite; intercalation; perfluoroanions; GICs

INTRODUCTION

Boehm et al first described the electrochemical preparation of GICs with perfluoroalkylsulfonate anions. [1] Our group also reported electrochemical synthesis of $C_xC_8F_{17}SO_3$ in CH_3NO_2 / $LiC_8F_{17}SO_3$ electrolyte. [2] We are here to report a simple bench top chemical synthesis of GICs with $C_8F_{17}SO_3^-$, $N(SO_2CF_3)_2^-$ and other larger anions containing $-SO_2C_nF_{2n+1}$ substituents.

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EXPERIMENTAL

Hydrofluoric acid (Mallinckrodt AR, 48 % (w / o)), fuming H_2SO_4 (Baker, fuming 30 – 33 oleum %), and conc. HNO_3 (Mallinckrodt, 69.2 %) were used as received. K_2MnF_6 [3] and $KC_8F_{17}SO_3$ [4] salts were synthesized according to literature methods. Two types of graphite reagent were used; SP-1 powder (Union Carbide, 100 um avg. particle diameter) and natural graphite flakes (Aldrich, 1 - 2 um). Other intercalant anion sources were the $LiN(CF_3SO_2)_2$ (3M), $LiC(CF_3SO_2)_3$ (Covalent Assoc., 99 %), $LiN(CF_3CF_2SO_2)_2$, (3M), $LiN(CF_3SO_2)(CF_3(CF_2)_3SO_2)$ (Central Glass Co., Japan).

$C_xC_8F_{17}SO_3$, $C_xN(CF_3SO_2)_2$, and GICs of the larger anions containing $-C_nF_{2n+1}SO_2$ substituents are prepared in 48% aqu. HF or mixed acids as reported previously. [4] PXRD data were collected on a Siemens D5000 powder diffractometer, using CuKα radiation. Thermal analyses of powdered samples were carried out at 5 °C / min under flowing N_2 using a Shimadzu TGA-50.

Energy-minimized structural models for anions were calculated using Gaussian 94 [7] and full geometry optimizations were carried out with the B3LYP6-31G(d) basis set.

RESULTS

Preparation / Characterization of $C_xSO_3C_8F_{17}$

When graphite is added to the solution of K_2MnF_6 and $KC_8F_{17}SO_3$ in hydrofluoric acid, the structure evolves rapidly through a series of stages or mixtures of stages of a GIC containing $C_8F_{17}SO_3^-$ (C_xPFOS). A relatively constant pattern is obtained after 15 – 24 h (Fig. 1), although a broad peak at 40 ° appears at long reaction times due to the precipitation of an amorphous Mn-containing phase. Some PXRD show additional broad reflections at 5.8 and 5.5 Å, which are ascribed to graphite fluorides. A faster reaction was observed when graphite was oxidized in a solution containing conc. HNO_3 with 48% aqu. HF and a stage 2 GIC was obtained.

For the PXRD patterns obtained in 48% aqu. HF, a good fit of (00*l*) peak positions is not obtained using a single cell parameter, a weighted average of I_c from stage 2 and 3 provides an improved fit. Resolvable peaks, with maxima separated 1 – 2 °, should occur at 5 – 15 ° 2θ for a physical mixture of stages. In each pattern obtained, however, only single peak is seen, indicating that the products are solid solutions.

Two factors contribute to peak broadening in these GICs. One is the strain – domain size broadening, which shows a linear relation between FWHM and tanθ [5]. The other effect is due to the disordered presence of the two component sequences (in this case, stage 2 and stage 3), which results in an oscillating peakwidth as 2θ increases. Fig. 2 displays a Williamson-Hall plot for the solid solution C_xPFOS product of 79:21 of 2nd:3rd staging content. (Fig 2a) and stage 2 GIC from mixed acid solution (Fig. 2b).

The optimized geometry for the isolated PFOS anion shows a helical conformation of the C backbone with an average twist angle of 20°. Others have demonstrated that isolated molecules of perfluorododecanoic acid are

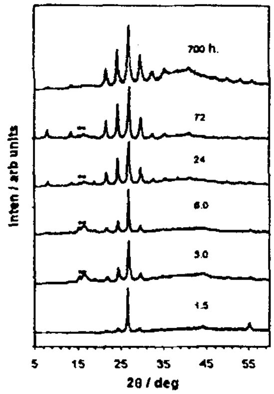

Figure 1. **PXRD obtained for C_xPFOS obtained in 48 % aqu. HF at 20 °C. The ** peaks are C_xF impurities.**

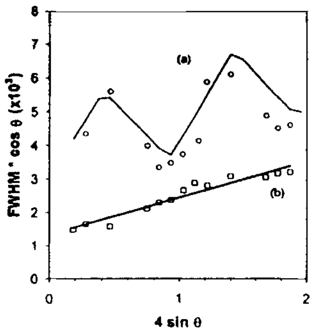

Figure 2. Williamson-Hall plot for C_xPFOS obtained from (a) 48% aqu. HF and (b) HF / HNO_3 (17:83 v / v). Circles in (a) are from PXRD data, triangles are calculated for a random solid solution.

helical, however, the molecules are linear when packed into a periodic structure. [8] The refined e-map incorporating a helical backbone provides an excellent match to the observed profile, as seen in Table 1.

Preparation / Characterization of $C_xN(CF_3SO_2)_2$

Rapid intercalation was observed for SP-1 graphite in a hydrofluoric acid solution of K_2MnF_6 and $LiN(CF_3SO_2)_2$. The graphite phase disappears after only 15 s., and a stage 2 GIC was formed within 15 min. (Fig. 3). The gallery height was determined to be 8.07(4) Å for all products. The products are best modeled as solid solutions of phases. By TGA analysis, the stage 2 has a final stoichiometry close to $x = 32$. Elemental analysis provides a slightly lower anion content.

The gallery height for $C_xN(CF_3SO_2)$ is only consistent with a single layer of intercalating anions aligned with the long dimension parallel to the graphene planes. We calculated the isolated $N(CF_3SO_2)_2^-$ anion geometry as similar to that reported previously [6], with the dihedral $<$ C-S-N-S = 91.2°. Transition state energies indicate dihedral angle rotation has a barrier of only 3.9 kJ/mol [6], thus the free anion has significant flexibility. The structure model for stage 2 $C_xN(SO_2CF_3)_2$, using the above anion geometry, places the

TABLE 1 Refined parameters and goodness of fit for the best-fit structural model of stage 2 C_xPFOS containing helical or linear anions.

	Helical model	Linear model
Chain take-off angle (deg)	60.0	58.8
Graphene plane to oxygen plane distance (Å)	2.95	3.05
Graphene plane to fluoride plane distance (Å)	3.8	3.9
Twist angle (deg)	16.4	0
R	0.062	0.168

anionic nitrogen (charge = -0.71) approximately 3 Å and O (charge = -0.54) approx. 2.9 Å from the graphene surface.

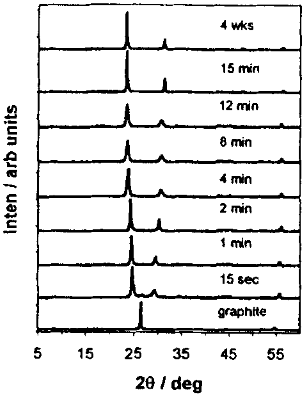

Figure 3 PXRD obtained for $C_xN(CF_3SO_2)_2$ obtained by reaction of graphite with a solution of $LiN(CF_3SO_2)_2$ and K_2MnF_6 in 48 % hydrofluoric acid at 20 °C.

Intercalation with Larger Anions:

When the chemical oxidation of graphite is carried out using $LiN(SO_2CF_2CF_3)_2$, $LiN(SO_2CF_3)(SO_2(CF_2)_3CF_3)$ and $LiC(SO_2CF_3)_3$ in 48% aqu. HF, GICs are formed dramatically slower (Table 2). Although the d_i values obtained are less accurate than for $C_xN(CF_3SO_2)_2$, it is clear that the larger imide anions must be oriented within the galleries in a manner similar to the $N(CF_3SO_2)_2^-$.

TABLE 2 Reaction rates and gallery heights for different fluoroanion intercalants in GICs.

Intercalant	20°C	70°C	d_i (Å)
$N(CF_3SO_2)_2^-$	15 minutes to stage 2	Seconds to stage 2	8.07(4)
$N(CF_3CF_2SO_2)_2^-$	1 month to a mixture of stage 3 and higher	2 days to stage 2-3 mix + graphite[a]	8.2(1)
$N(CF_3SO_2)(CF_3(CF_2)_3SO_2)^-$	1 month to high stage + graphite	6 days to a 3rd and 4th stage mixed + graphite[a]	8.2(1)
$C(CF_3SO_2)_3^-$	1 month to high stage + graphite	24 days to stage 4 + graphite[a]	10.6(3)

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