Intercalation of PerfluoroalkyIsulfonic Acids in Graphite

by

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Introduction

Electrochemical intercalation of sulfuric acid into graphite has been described repeatedly $^{1-4}$. Potential vs. time curves in galvanostatic oxidation show two-phase ranges with constant potential, corresponding to two stages in equilibrium, and steps of increasing potential correspon-ding to a single phase (stage) 3,4 . The slope of the ascending portions of the curves indicates that the charge of the layers is variable to some extent in a given stage 3 . A peculiarity is the appearance of a ministep in the region of pure stage 2 2,4 which also appears as a separate peak in linear-sweep voltammetry 4. A decrease of the interlayer spacing I_C during charging in the single-phase regions has been explained by the increased Coulombic attraction 3,4. We have now done similar intercalation experiments with CF, SO, H, $C_4F_9SO_3H$, and $C_6F_{13}SO_3H$.

Experimental

Flakes of Madagascar graphite with a diameter of > 1.6 mm and a thickness of 150 - 200 μ m were mostly used. A few experriments were done with HOPG. CF, SO, H was obtained from Fluka, C₄F₉SO₃H and C₆F₁₃-SO, H were prepared from their potassium salts and 100 % H₂SO₄.

Galvanostatic oxidation gave wellresolved curves only with current densities $\leq 500 \ \mu$ A per cm² of prism faces. Cyclovoltammetry was performed with samples of 2 - 4 mg and a sweep rate of ca. 10 μ C/s. Graphite foil was used as a reference electrode. The reactions were interrupted at various points in the curves, and X-ray powder photographs were taken. The measurements were supplemented by dilatometry ⁵.

Results

The observations with CF_3SO_3H were very similar to those described for H_2SO_4 ⁴. The intercalation of $C_4F_9SO_3H$ was studied in more detail. Fig.1 presents typical curves

for galvanostatic oxidation and for cyclic voltammetry (oxidation cycle only shown). The charge on the graphene layers (C_n^{+}) is marked for various points (A - K) on the curves. The interlayer spacings are listed in Table 1. It was difficult to interpret the X-ray pattern in the A,B region. A pure stage 3 compound had formed at point C. In their further course, these curves show more details than the corresponding curves for H_2SO_4 . In the stage 2 region, from D to G, two sub-steps (E and F) are observed, and there is also a step (I) in the stage 1 region, which does not appear in H_2SO_4 intercalation. Well-resolved peaks in the voltammograms show that current is taken up at these points, that is that the charge on the layers increases.

The sharp knee at point G when the first stage begins to form appeared at a current uptake corresponding to C_{46}^+ to C_{50}^+ . The value cited in Fig.1, C_{48}^+ , as well as the other values are the averages of 6 - 7 runs. At H, the blue color of stage 1 appeared.

The inserts in the voltammogram in Fig.1 show that the ratio of the areas of peaks E and F was not constant with rising temperature. The sum of the areas was constant, however.

The I_C spacing was 8.04 Å for the first stage CF,SO,H compound and 26.25 Å for the compound with $C_6F_{13}SO_3H$. Otherwise the results with the latter acid were comparable with the observations with $C_4F_9SO_3H$.

Discussion

The results show clearly that the anion density in a given stage is variable to a considerable extent. Within stages 2 and 1, separate phases can be recognized which differ in I_c spacing by ca. 3.2 Å. The I_c spacings were observed to expand as well as to contract during passing of the singlephase regions. The changes were confirmed by dilatometry. The contractions can be explained by the increasing electrostatic at-





Fig.1. (a) Potential curve in galvanostatic oxidation of Madagascar graphite in $C_4F_9SO_3H$, (b) corresponding linear sweep voltammogram at room temperature, insets at the temperatures indicated.

traction; expansions must be caused by changes in the molecular packing of the intercalate which seems to be influenced by the charge density. Effects of order - disorder phenomena on the I_C value have also been observed with graphite hydrogen sulfate 6.

It is known from studies of clay minerals with intercalated n-alkylammonium ions (plus free base) that the alkyl chains are in all-trans conformation, and that they are arranged at an angle to the layer planes which depends on the charge density on the layers 7. Similar results were found with TiS, with intercalated n-alkyl amines⁸. Our results indicate that the C_nF_{2n+1} chains



Fig.2. Model of the structure of the intercalated $C_4F_9SO_3^-/C_4F_9SO_3H$ layers.

Table 1. Observed I_C spacings at the various points marked in Fig.1.

Point	I _c in Å	stage
с	27.64 [±] 0.17	3
C - D	27.7 + 21	3 + 2
D	20.86 + 0.10	2
E	21.14 [±] 0.08	2
E - F, near E	21.05 ± 0.13	2
F	20.48 [±] 0.17	2
G	24.34 [±] 0.09	2
G - H, near G +	24.17 ± 0.23 17.61 ± 0.14	2 + 1
Н	17.55 - 0.12	1
I	17.73 [±] 0.07	1
ĸ	20.99 - 0.04	1
over K	20.86 [±] 0.11	1
chem.oxidn. w. K ₂ Cr ₂ O ₇	21.01 [±] 0.08	1

are packed analogously. PTFE has a helical structure, however. With the short C_4F_9 chains the bulky CF, end groups seem to prevent such a packing. The observed widths indicate that the intercalated layers must consist of double layers of $C_nF_{2n+1}SO_3^-$ anions and free acid molecules (Fig.2). It is estimated that they form an angle (S to F of CF₃) of ca. 63° with the layer planes in the 21 A phase, and of ca. 46° in the 17.6 A phase.

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