Preparation of Expandable Graphite

(Observation of stacking disorder in the formation of graphite hydrogen sulfate)

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With more Frequent use of expandable Graphite for insulator and paint etc., our interest has been recently concentrated on it. Electric oxidation in sulfuric acid or hydrochloric acid or intercalation of acid. In the presence of an oxydizing agent with graphite is called Lamellar compounds. After the Lamellar compounds is treated, it is heated with high temperature (about 1000°C). Then the graphite expends several ten times and it is called expandable graphite. This paper aims at interesting the process of the formation of graphite hydrogen sulfate by closely looking in the structure of Lamellar compounds from 2 stage to 1 stage and the characteristics in each stage. Only phases with integer stage numbers have been observed in electrochemical oxidation of graphite in comcentrated sulfuricacid [1,2]. However, the degree of oxidation in a given stage can cover a certain span, e. g. from C_{28} to C_{21} for a stage 1 compound [2].

We have oxidized natural graphite flakes (0.1 - 0.2 mm) with a solution of $(NH_4)_2 S_2 O_8$ in 98% $H_2 SO_4$ (147 g/l). Whilst persulfate ions were intercalated, too, below 7°C, no evidence for intercalation of a peroxo compound was found at 22°C. The reaction was interrupted after various times by filtering and washing with concentrated $H_2 SO_4$ X-ray diffraction showed that the 2nd stage compound had already been formed after 2 minutes. We could only follow further oxidation the blue stage 1 compound which was completed after 35 minutes.

The reflexes of the 1st stage compound were predominant already after 10 minutes (Fig. 1); additional reflexes near the positions expected for a 2nd stage were shifted in an irregular manner. Such non-integral reflexes are typical for stacking disorder [3,4]. The positions do not agree with those calculated [4] for completely random distribution of the $HSO_4 /H_2 SO_4$ layers. After oxidation for 15 and 20 minutes, the diffraction patterns for a 1st stage showed weak satellites of the (002) and (004) reflexes.

The I spacings for the various oxidation times are listed in Table 1. It has been found in earlier work that the I values decrease form 798 pm to 788 pm with oxidation from $^C C$ 28 + to C 2; +[2]. This has been explained by the stronger Coulombic attraction with increased charge density on the layers. Our results are in contrast to this observation. Furthermore, a mixture of two stage 1 phases with different c-spacings was found after 24 minutes. Since

both phases were in electric contact during XRD, it seems impossible that they had different degrees of oxidation. We ascribe the differences in Ic to differences in ordering within the intercalated layers as has been suggested earlier [5].

The densities of the compounds and of the intercalated layers have been determined from buoyancy measurements [6]. The degree of oxidation was determined from the reflectance spectra, assuming a linear shift of the reflectance minimum with oxidation from the 2nd stage C_{48} + to the 1st stage C_{24} +. From these data, the ratio x of H_2SO_4 molecules to HSO_4 ions can be estimated. The resultes, summarized in Table 1, show clearly that the density of the compounds and the ratio x pass through a minimum after 15 minutes oxidation. This implies less ordering rin the intercalated layers.

We interpret our observations with the assumption that packages of 2nd and 1st order sequences are stacked in an irregular, but not completely random manner in the 10 minutes preparation which also contains pure 1st stage. After 15 and 20 minutes, the oxidation to the 1st stage is 80 to 90 % complete, and the remaining unfilled interstices give rise to the observed satellite reflexes. The disorder is due to the rapid intercalation process. In contrast, the electrochemical intercalation experiments which led to separate, well-ordered phases have been performed using very low current densities, i.e. on a much larger time scale.
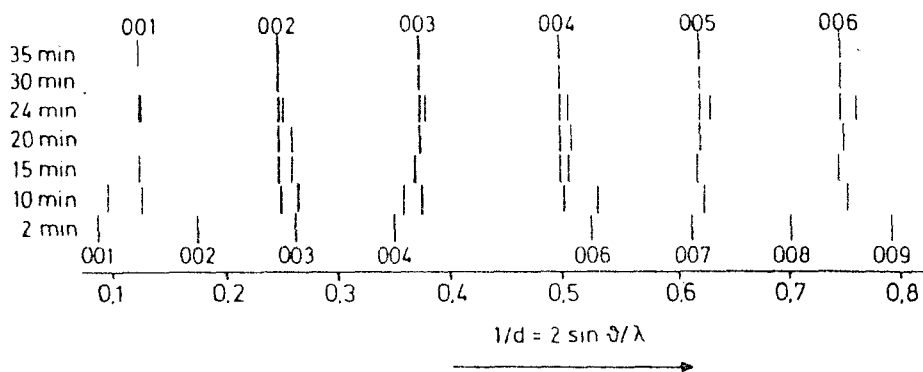

Fig. 1. (001) X-ray diffraction pattern as function of oxidation time. Relative intensities are indicated by the widths of the lines. Top indices: 1st stage, bottom indices: 2nd stage.

Table 1. I_c spacings, degree of oxidation and densities as function of oxidation time.

Oxidation time minutes	I_c pm	n in C_n^+	density g/cm^3	ratio x H_2SO_4/HSO_4^-
2	1136	49	2.104	2.424
10	797.3	31.4	2.058	2.372
15	803.6	28.5	2.033	2.369
20	801.1	26.5	2.036	2.389
24	801.1 +788.6	25.5	2.037	2.402
30	801.1	24.7	2.038	2.415
35	801.1	24	2.040	2.428

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