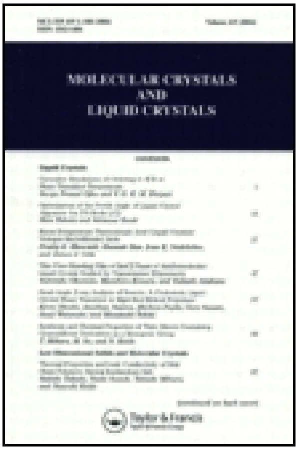

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Criteria for the Intercalation of Sulfuric Acid

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Version of record first published: 23 Oct 2006.

To cite this article: Michio Inagaki , Norio Iwashita & Yoshihiro Hishiyama (1994): Criteria for the Intercalation of Sulfuric Acid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 89-94

To link to this article: http://dx.doi.org/10.1080/10587259408050087

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 89–94
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Printed in the United States of America

CRITERIA FOR THE INTERCALATION OF SULFURIC ACID

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Abstract The criteria for the intercalation of sulfuric acid were studied. The intercalation reaction was found to be governed by the relation between the onset potential values for each stage structure and the upper limit of the saturated potential. It was also shown clearly that the intercalation of sulfuric acid was possible on the hosts with the crystallite thickness along the c-axis above 20 nm and also with positive magnetoresistance at room temperature.

INTRODUCTION

The intercalation of sulfuric acid into graphite either by electrochemical or chemical oxidation has been studied by various authors. So far, a two-capacitor model for the electrochemical intercalation process was proposed by Metrot[1]. The effects of dilution of sulfuric acid were discussed[2,3]. The effect of defects of host graphites during chemical oxidation on the intercalation reaction of sulfuric acid was studied[4]. We have shown that the reaction process of sulfuric acid intercalation by chemical oxidation is fundamentally the same as that by electrochemical oxidation. The intercalation of H_2SO_4 caused by chemical oxidation was followed by measuring the potential change on the host carbons[5-7], and was found to consist of sequential repetition of charging and intercalation steps, the former showing an abrupt increase of potential and the latter a plateau. The intercalation process of H_2SO_4 can be characterized by diferent potential values; onset potentials for each stage structure, saturated potential and threshold potential[5-7].

In the present work, we selected the intercalation reaction of sulfuric acid through the chemical oxidation in order to discuss the criteria on reaction conditions and host carbon materials.

EXPERIMENTAL

Since we selected sulfuric acid as the intercalate and chemical oxidation by nitric acid as one of synthetic conditions a priori, it was carried out to clarify the criteria on the concentration of sulfuric acid and on the amount of oxidant. Three concentrations of sulfuric acid, 18, 14 and 10 mol/dm^3, were used, and the amount of oxidant was defined by the molar ratios to host carbon, HNO_3/C. The host carbon materials were selected in a wide range of structure (degree of graphitization) and texture (plane and axial orientations). On these carbon materials, the relations between structural parameters were discussed and the details of the materials were reported in the previous paper[8].

The intercalation reaction was performed in a sulfuric acid solution, which contained an oxidant and was kept at 0^oC, by holding these host carbons in between two plastic plates. The potential change on the host carbon was measured by referring to $Hg/HgSO_4$ electrode. The details of the cell assembly and procedure for potential measurement have to be referred to our previous paper[5].

RESULTS AND DISCUSSION

Amount of Oxidants

In Fig. 1, the potential changes with time are shown as a function of the amount of oxidants on the natural graphite with an average flake size of 400 μm in a sulfuric acid of 18 mol/dm^3. In the figure, the stage numbers are also indicated on the intercalation compounds formed after reaching the saturated potential.

The saturated potential is governed by the amount of oxidant HNO_3. A small amount of the oxidant (HNO_3/C=0.17) can not make the potential of host graphite high and, since the potential saturated is a little above 0.6 V which is the onset potential for the stage-3 structure, the intercalation compound obtained has the stage-3. With the increase in the amount of HNO_3 the saturated potential increases and consequently the stage number of the compound finally obtained decreases. The addition of HNO_3 above 3.3 gives the saturated potential of 1.1 V and the stage-1 compound. This means that there is an upper limit of saturated potential for the oxidation by HNO_3.

Concentration of Sulfuric Acid

The value of the onset potential has been known to depend strongly on the concentration of H_2SO_4 by galvanostatic studies[9] and also by the chemical oxidation[5]. The upper limit of saturated potential was found to be governed by both the oxidant employed and its amount[6]. So, in Fig. 2, the values of onset potentials for the stage-1, -2 and -3, and the upper limits of saturated potential for the oxidant HNO_3 are plotted against the concentration of H_2SO_4.

In H_2SO_4 of 14 mol/dm^3, for example, we need the potential above 1.2 V in order to obtain the stage-1 structure, but the upper limit of saturated potential by HNO_3 is a little below 0.9 V, which means only the stage-3 structure is possible, no formation of the stage-1 and -2.

Fig. 2 shows clearly that the effect of dilution of sulfuric acid on stage number of the intercalation compounds formed is explained by the relation between the onset potential for each stage and the upper limit of saturated potential for the oxidant.

Crystallographic Structure of Hosts

In the plot of the crystallite size determined from the half width of 002 diffraction line, $L_c(002)$, vs. the degree of graphitization, P_1 (Fig. 3), the host carbon materials intercalated by sulfuric acid are differentiated from those not intercalated.

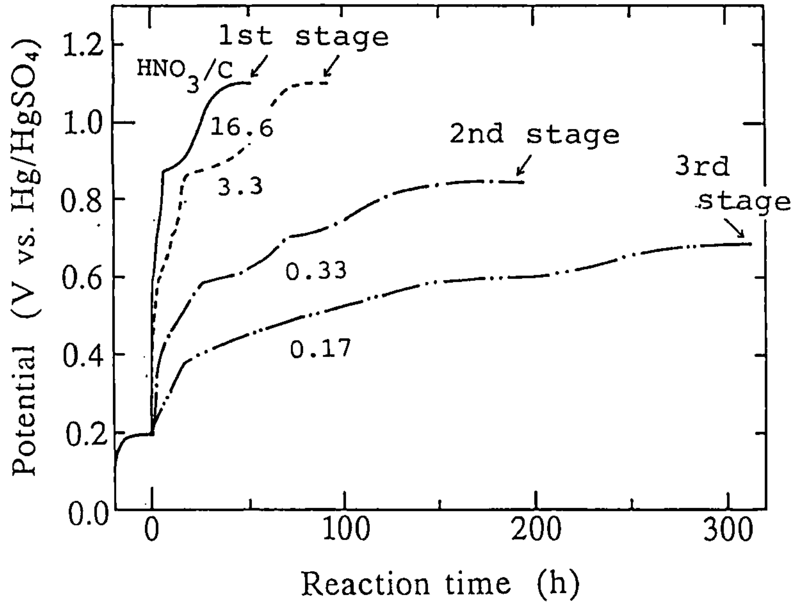

FIGURE 1 Changes of potential with time as a function of the amount of oxidant HNO_3 on the natural graphite with a flake size of 400 μm in a sulfuric acid of 18 mol/dm^3 at 0^{o}C.

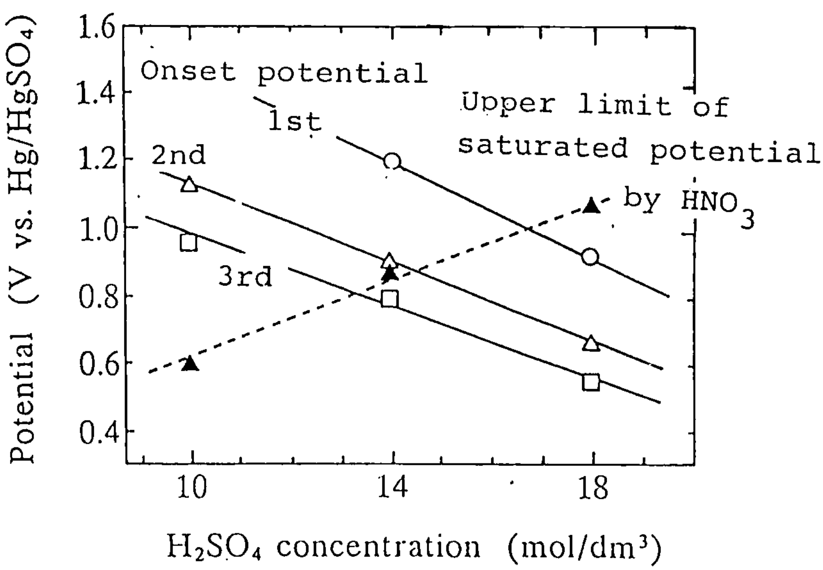

FIGURE 2 Onset potential values for the stage-1, -2 and -3, and upper limits of saturated potential for HNO_3 (HNO_3/C=3.3) at 0^{o}C as a function of the concentration of sulfuric acid.

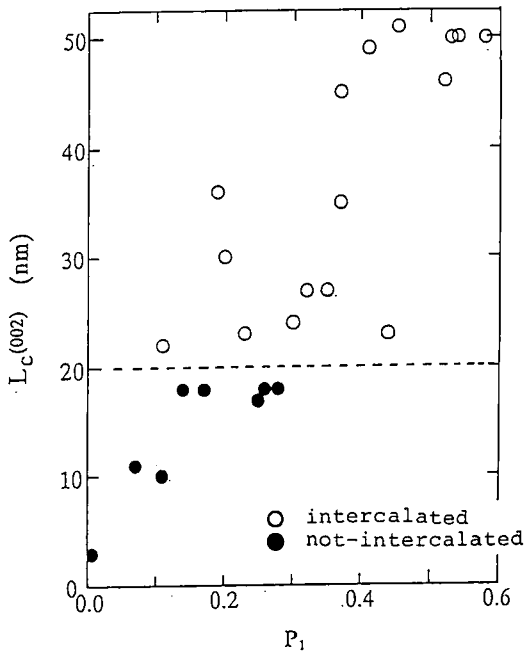

FIGURE 3 Plot of the crystallite thickness along the c-axis $L_c(002)$ against the degree of graphitization P_1 on the host carbon materials used.

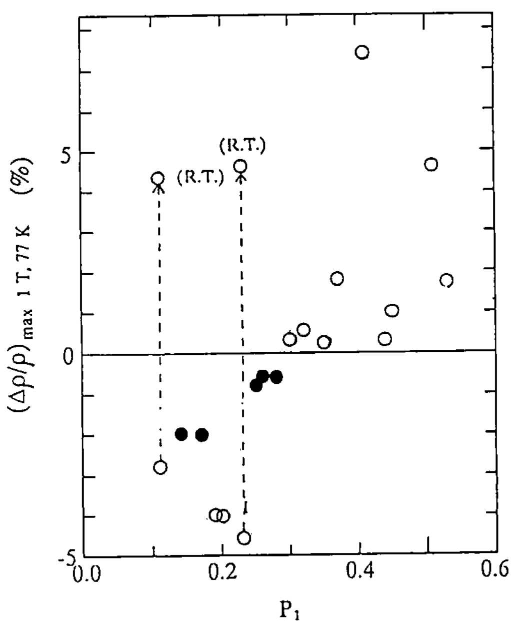

FIGURE 4 Plot of the magnetoresistance $(\Delta\rho/\rho)_{max}$ against the degree of graphitization P_1. Most of the $(\Delta\rho/\rho)_{max}$ values were measured at 77 K, but the ones indicated were measured at room temperature.

There is a clear criterion in $L_c(002)$ value above 20 nm for the intercalation of H_2SO_4, but no criterion in P_1. By taking account of the kind of carbon materials and the heat treatment temperatures for all experimental points, it was clearly shown that the intercalation reaction was governed by the crystallite thickness, neither by the carbon material, heat treatment temperature nor the degree of graphitization.

Electronic Structure of Hosts

In Fig. 4, the hosts intercalated by H_2SO_4 in the concentration of 18 mol/dm^3 at 0 ^oC are indicated on the relation between magnetoresistance $(\Delta\rho/\rho)_{max}$ at 77 K and the degree of graphitization P_1. All samples with positive $(\Delta\rho/\rho)_{max}$ at 77 K gave intercalation compounds. Some of the samples with negative $(\Delta\rho/\rho)_{max}$ at 77 K could be intercalated, but some could not. The formers were found to give positive $(\Delta\rho/\rho)_{max}$ at room temperature, as indicated by broken lines on two samples. On the latters, however, $(\Delta\rho/\rho)_{max}$-value was almost zero at room temperature.

From this experimental result, the criterion in electronic structure of hosts for the intercalation of H_2SO_4 must be the positive value of magnetoresistance $(\Delta\rho/\rho)_{max}$ at the temperature where the intercaration proceeds, suggesting that the presence of carrier electrons is essential for the intercalation of the acceptor H_2SO_4.

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