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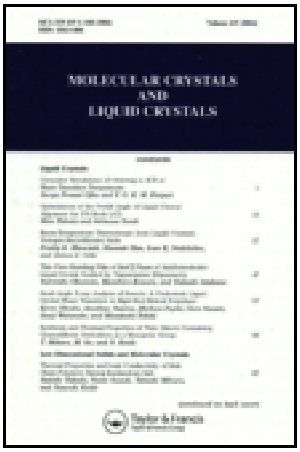

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Electrochemical Exfoliation of HOPG in Formic - Sulfuric Acid Mixtures

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Version of record first published: 04 Oct 2006

To cite this article: E. Bourelle, B. Claude-montigny & A. Metrot (1998): Electrochemical Exfoliation of HOPG in Formic - Sulfuric Acid Mixtures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 321-326

To link to this article: http://dx.doi.org/10.1080/10587259808045356

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Mol. Cryst. Liq. Cryst., 1998, Vol. 310, pp. 321-326
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Electrochemical Exfoliation of HOPG in Formic - Sulfuric Acid Mixtures

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Abstract It is shown that HOPG electrochemically intercalated by mixtures of sulfuric and formic acids exfoliates at room temperature, leading to "pneumatic" expanded products, in which CO bubbles are trapped between graphene layers sewn at their edges by oxygen bonds.

Keywords: graphite intercalation compound, expanded graphite, exfoliation, electrochemical exfoliation.

INTRODUCTION

Graphite exfoliation has found for decades an application in the preparation of graphite foils[1] and more recently a potential use as absorbent for water or air de-pollution[2]. Exfoliation is usually performed under gaseous environment by thermal decomposition of a GIC ([3] and ref. therein) but in the last few years new chemical [4] and electrochemical[5,6] methods have been reported allowing liquid media and room temperature processing i.e. a soft route. D.D.L. Chung[3] proposes a classification of the experimental modes of exfoliation including for instance external heating and internal Joule heating. A. Hérold et al[7] distinguish from a thermodynamic point of view two exfoliation types : an endothermic one, which generally results from brutal heating or from adiabatic decompression of a GIC, and an exothermic one based on the dissociation of an unstable intercalate, for example $HClO_4$.

The electrochemical way for such a process is particular because it includes two distinct steps : initial electrochemical intercalation, and afterwards gaseous evolution from intercalated species. The first process is generally endothermic, but the second one may be either endothermic or exothermic. When using CF_3COOH[5], the Kolbe's decomposition of the intercalated acid into C_2F_6 and CO_2 is for example endothermic. On the contrary, in the electrochemical process we shall describe here, the decomposition of HCOOH in the presence of intercalated H_2SO_4 appears exothermic. Noteworthy, the obtained products present novel textures, compared to classical ones.

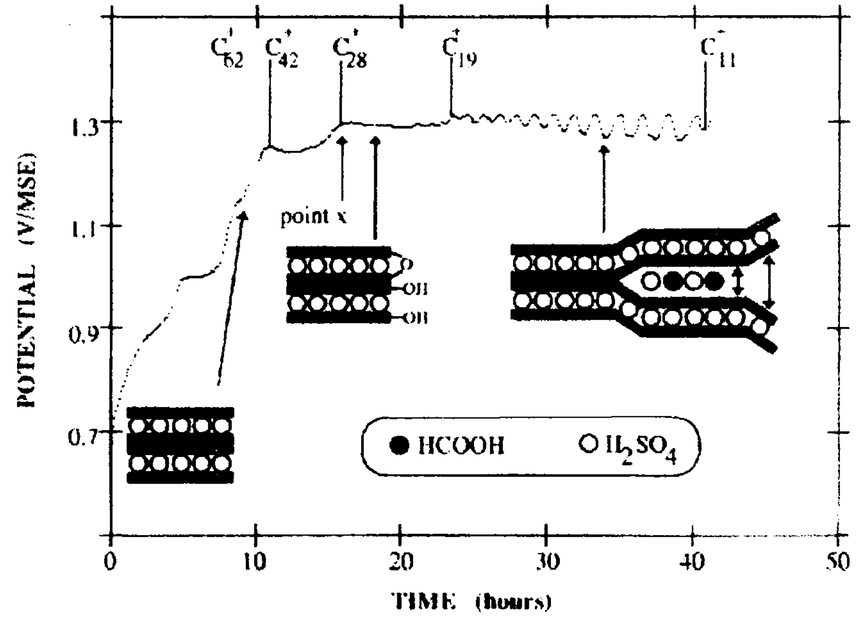

FIGURE 1 Potential-time curve obtained during galvanostatic exfoliation of HOPG in a 5M H_2SO_4 / HCOOH solution (i = 10 mA/g of C).

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THE ELECTROCHEMICAL METHOD

Electrochemical intercalation is performed in a 5M solution of H_2SO_4 in HCOOH, using a classical three electrode set with a computer driven galvanostat "MacPile". Fig. 1 shows a typical experimental curve E = f(time) For the first ten hours no visual exfoliation is observed while *in situ* X-ray diffraction points out the *00l* diagrams of pure H_2SO_4 GICs. So this curve is interpreted as the classical pure H_2SO_4 intercalation one, without HCOOH.

At the end of the "overcharging" domain of stage two an over-oxidation process begins with a potential jump (point x). We note that this jump dissapears when anodization is started again after some rest. It may be explained as the formation of covalent C-OH bonds at the edges of graphene layers due to water originating from the external dehydration of HCOOH in presence of H_2SO_4 :

$$HCOOH \xrightarrow{H_2SO_4} H_2O + CO_{(g)} \qquad (1)$$

Such an over-oxidation is classically observed in H_2SO_4-H_2O mixtures[8,9]. Then the hydrophilic character of the newly formed graphite oxide should favor the co-intercalation of HCOOH with H_2SO_4, leading to an unstable first stage compound which exfoliates because of the interlayer gas evolution due to reaction (1). Alternatively the formation of H_2O favors the over-oxidation itself, initiating an oscillating behavior. Meanwhile this slow exfoliation pursues linearly during hours and, for a cumulated charge of 8000 C/g, an expansion of approximately 400 with regard to the initial thickness is observed.

CHARACTERISATION OF THE EXPANDED PRODUCTS

Electrochemical Impedance Spectroscopy measurements have been performed at rest potential in the mother solution. Comparing the sample capacity determined by this method with a typical double layer capacity of 10 $\mu F.cm^{-2}$, we get developed areas around 130 $m^2.g^{-1}$. Consequently, taking into account the value of 2600 $m^2.g^{-1}$ for an isolated graphene layer, the exfoliation corresponds to 20 layers packets. This result suits to a thorough exfoliation.

S.E.M observations of the expanded graphite samples have been made after drying under vacuum at room temperature.

The "accordion-like" or "worm-like" structures of thermally exfoliated graphite bisulfates are well known[10,11]. Quite similar but more aired structure are noticed (fig. 2, type A), when graphite is electrochemically intercalated by H_2SO_4 up to stage two and then anodized in pure HCOOH. In this medium we observe that any further exfoliation is blocked when the current has been stopped for some time.

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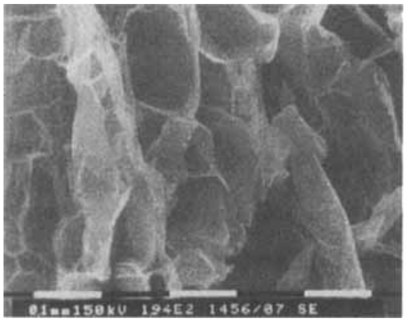

FIGURE 2 Stage 2 H_2SO_4-GIC exfoliated in pure HCOOH (type A)

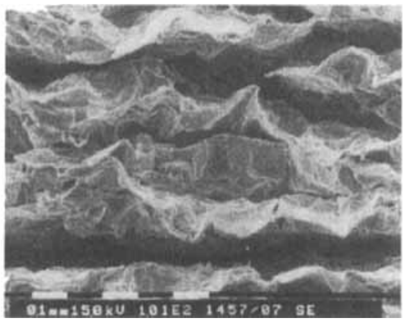

FIGURE 3 Graphite exfoliated in H_2SO_4/HCOOH mixture (type B)

On the other hand, when anodization is directly performed into a 5M H_2SO_4/HCOOH solution, a quite different "smocking-like" texture appears (Fig. 3, type B) in which larger vacancies separate packets of crinkled layers. Furthermore, when these products are dried at 100°C under vacuum, the structure changes even more : dispersed "balloons-like" packets coexist with vacancies (fig. 4, type C).

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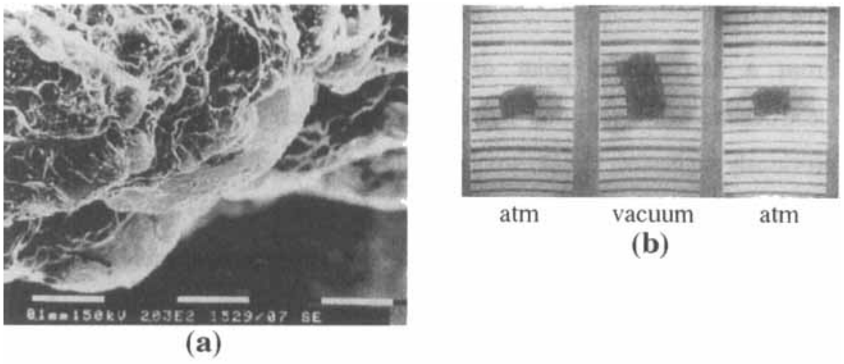

FIGURE 4 (a) : Exfoliated graphite vacuum dried at 100°C (type C)
(b) : Reversible swelling of exfoliated graphite (type B)

DISCUSSION

The "smocking-like" and "balloons-like" aspects of the expanded products (types B and C) may be explained by accumulation of CO gas between graphene layers sewn at their edges through oxygen bonds. Two experimental observations agree with this interpretation :

- the sample expands reversibly under vacuum showing the presence of confined gas (Fig. 4 b).
- the presence of presumed "sewing" bonds is confirmed by IR-ATR analysis on samples either vacuum dried or not. On the spectra absorption peaks reveal the presence of ether, epoxy and carbonyl bonds which may prevent CO expulsion.

In fact, we think that the "seam" is essentially due to ether bonds because C-O-C interlayer bonds seem easier to form than C-C ones. Furthermore such a "seam" process may explain the observed blocking of any intercalation or exfoliation when the anodization in pure HCOOH has been stopped for a while, as noticed above.

CONCLUSION

From a fundamental point of view advances in the knowledge of electrochemical intercalation mechanism have been obtained. Practically, as previously suggested, the electrochemical route for exfoliation may be efficient to obtain expanded graphite dispersions in liquid media. Noteworthy the products got in HCOOH-H_2SO_4 mixtures seem to present specific properties, i. e. trapped gas bubbles confer a "pneumatic" elasticity to these products, explained by the "seam" of graphene layer edges.

Acknowledgments

We thank Dr A. W. Moore (Union Carbide Corp.-Parma, OH) for having kindly supplied us with HOPG samples, Dr F. Montigny (University of Tours) for the IR measurements and C. Collet.(DESS-ATS, Reims) for her contribution to a part of this work.

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