This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 18 February 2013, At: 13:25
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

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

New Data on Graphite Intercalation Compounds Containing $HClO_4$: Synthesis and Exfoliation

D. Petitjean [a], G. Furdin [a], A. Herold [a] & N. Dupont Pavlovsky [a b]

[a] Laboratoire de Chimie du Solide Minéral, U.R.A. 158, BP 239, 54506, Vandoeuvre les Nancy, FRANCE

[b] Laboratoire Maurice Letort, C.N.R.S., 54600, Villers-Les-Nancy, FRANCE

Version of record first published: 23 Oct 2006.

To cite this article: D. Petitjean , G. Furdin , A. Herold & N. Dupont Pavlovsky (1994): New Data on Graphite Intercalation Compounds Containing $HClO_4$: Synthesis and Exfoliation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 213-218

To link to this article: http://dx.doi.org/10.1080/10587259408051691

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever

caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:25 18 February 2013

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 213–218
Reprints available directly from the publisher
Photocopying permitted by license only
© 1994 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:25 18 February 2013

NEW DATA ON GRAPHITE INTERCALATION COMPOUNDS CONTAINING $HClO_4$: SYNTHESIS AND EXFOLIATION.

D.PETITJEAN, G.FURDIN, A.HEROLD AND N.DUPONT PAVLOVSKY*
Laboratoire de Chimie du Solide Minéral, U.R.A.158, BP 239, 54506 Vandoeuvre les Nancy, FRANCE.
*Laboratoire Maurice Letort, C.N.R.S., 54600 Villers-Les-Nancy, FRANCE.

Abstract: Second to fourth stage graphite intercalation compounds (G.I.C.) with 70% perchloric acid have been synthetized according to a purely thermal process, and characterized by chemical analysis and *00l* X-ray diffraction. Moreover, an exothermic transformation, evidenced by means of thermal analysis of these compounds, was assigned to the intercalate dissociation during the sample exfoliation. This specific property was utilized to carry out the exfoliation of natural and artificial graphites with particles of different diameters. Exfoliated materials were characterized by scanning electron microscopy (S.E.M.). The specific surface area and surface homogeneity of the samples were determined by means of krypton adsorption.

INTRODUCTION

The exfoliation of graphite intercalation compounds (G.I.C.) is generally produced by their abrupt heating over a critical temperature. This thermal shock causes the rapid vaporization and dissociation of the intercalate. The exfoliation appears to result from an endothermal process [1] whose limits can be estimated: in order to produce exfoliation, the heating rate (or thermal shock) has to be adapted to the particle diameter [2,3]. If its value is lower than that of a critical diameter (100 μm), the main part of gas or vapor can be blown out without graphite exfoliation.

A new procedure of exfoliation is thus proposed in this paper, which is based on the exothermal dissociation of the intercalate ($HClO_4$). This method should enable the exfoliation of all carbonaceous materials [4] which can be intercalated. The $HClO_4$ molecule is known to intercalate into graphite, forming a thermally unstable G.I.C. [5]. In this study, the explosive properties of the $HClO_4$-G.I.C have been controlled by dilution.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:25 18 February 2013

EXPERIMENTAL DETAILS AND RESULTS.

Synthesis and characterization of the graphite perchlorate.

Intercalation of commercial grade diluted perchloric acid (70% $HClO_4$) was carried out by a purely thermal process, without the usual chemical or electrochemical assistance. Samples of highly oriented pyrographite (H.O.P.G.) were heated during one hour in a large excess of this diluted solution. $HClO_4$ oxidizing power increases with temperature. Second, third and fourth stage G.I.C. were thus synthetized at 150°C, 130°C and 110°C respectively [4,6]. Increasing temperature over 150°C results in the sample exfoliation. Consequently the first stage has never been observed.

The compounds were characterized using *(00l)* X-ray diffraction (MoKα radiation). Figure 1 presents X-ray diagrams of the second and fourth stage G.I.C.. The identity periods of the second, third and fourth stage, deduced from the *(00l)* diagrams were estimated to be 1.104±0.007, 1.443±0.006, 1.769±0.003 nm respectively. The interplanar distance calculated with these latter values is in agreement with previous works [7,8].

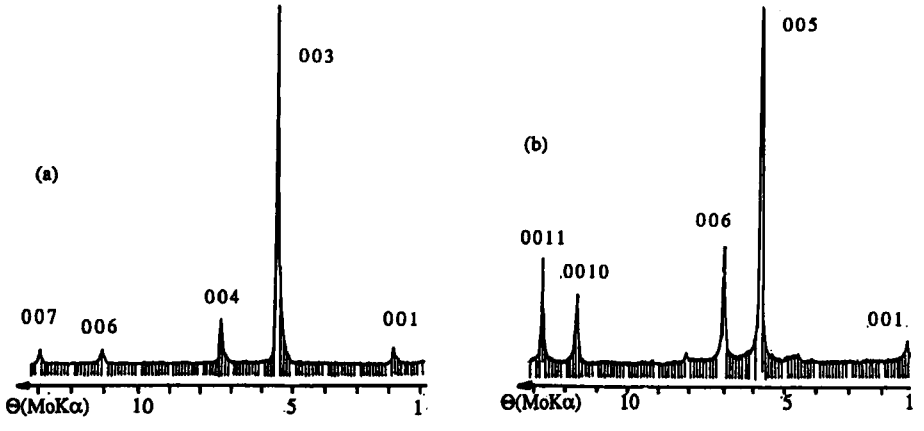

FIGURE 1 *(00l)* X-ray diagram of second (a) and fourth (b) stage graphite perchlorate.

(10l) X-ray analysis yields information on c axis stacking of the graphene layers. This analysis was performed for the 3rd stage sample. The successive layers along c axis were shown to have the sequence ABA/BAB/ABA...; c parameter is thus equal to $2 \times I_c$ =2.886±0.012 nm.

The C/Cl ratio of the second stage compound is estimated to be 29.3

from chemical analysis. Assuming that the intercalate composition is the same as that of the azeotrope (72.4% $HClO_4$), the formula of this compound can thus be written: $C_{29.3}$ $HClO_4$ $(H_2O)_{2.3}$. The following location of ClO_4^- and H_2O species between the graphene layers can then be proposed, taking into account the *(00l)* reflections relative intensities: the ClO_4^- tetrahedral groups and oxygen atoms of H_2O occupy two symmetric planes. This structure with the interatomic distances is shown on figure 2. The reliability factor between theoretical and experimental relative intensities is 8.6% for the second and 15% for the third stage (when taking only into account C/Cl changes).

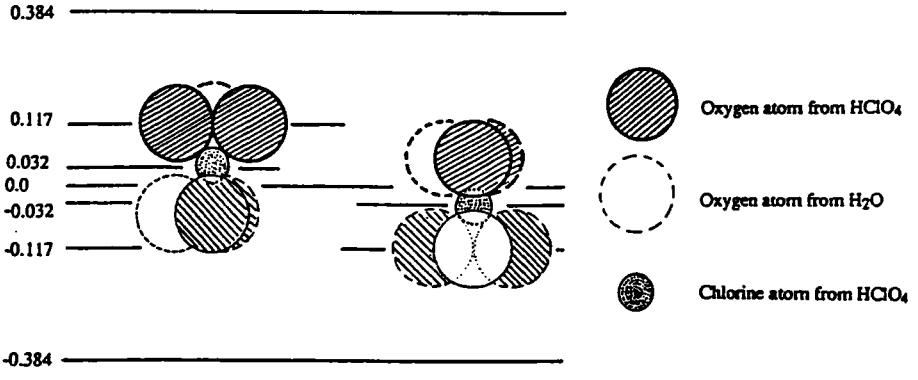

Figure 2 Disposition of the ClO_4^- tetrahedral groups and oxygen atoms of H_2O molecules between the graphene layers (in nm).

Exfoliation of the graphite perchlorate compounds.

Thermal analysis of the third stage compound obtained with H.O.P.G. was carried out. On the diagram shown in figure 3, two peaks are observed:

- the first, spread between 420 and 470K, is of endothermic type, and is assigned to partial desorption of the intercalate.
- the second peak, intense and narrow, is of exothermic type and exhibits a maximum at 484 K. It corresponds to the decomposition of the intercalate with exfoliation of the compound.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:25 18 February 2013

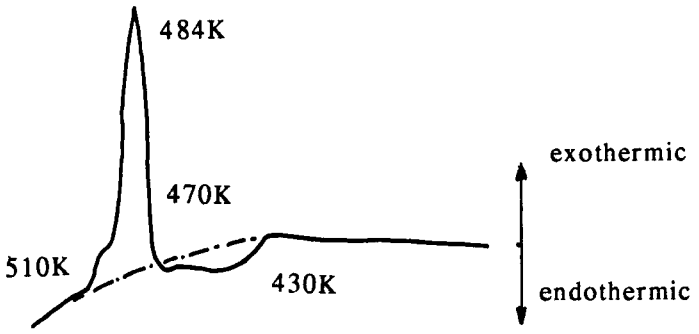

FIGURE 3 Thermogram of third stage graphite perchlorate obtained with H.O.P.G.(rate of the heating: 8K/min).

The specific properties of $HClO_4$ intercalation compounds obtained with H.O.P.G. were applied to the exfoliation of pulverulent graphites and cokes by using the same intercalate. The origin and characteristics of the samples are reported in Table 2. After intercalation performed as described above, the liquid acid in excess was separated by filtration, and exfoliation was carried out by throwing the wet product into a silica tube heated at 600°C.

TABLE 2 Characteristics and specific surface area of the pristine and exfoliated carbonaceous materials.

Samples	Natural graphites		Cokes	
	Madagascar	brazilian	graphitized 2600°C	heated at 1000°C
Particle size (μm)	500<ϕ<1000	ϕ<50	ϕ<112	ϕ<112
Specific area of the pristine carbons (m^2/g)	0.3	2.84	1.0	0.5
Specific area of the exfoliated compound (m^2/g)	153	74	26	25.3

Exfoliated materials were characterized by S.E.M.. Their specific surface area and surface homogeneity were determined by means of krypton adsorption at 77.3K.

S.E.M. observation (Figure 4a) of the sample obtained with pulverulent brazilian graphite shows the vermicular aspect characteristic of exfoliated compounds. Concerning exfoliated cokes (Figure 4b), it seems that the particle is expanded without any preferential direction, in

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:25 18 February 2013

agreement with the microtexture of the pristine material.

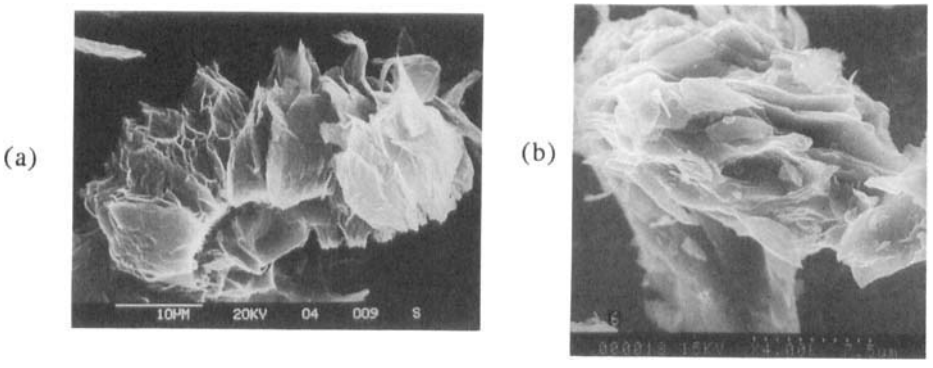

FIGURE 4 S.E.M. observations of exfoliated samples obtained with micronic brazilian graphite (a) and green coke (b) (H.T.T.1000°C).

From the results reported in table 2, the exfoliation is shown to cause an important increase of the specific surface area. The specific area of the exfoliated natural graphite is four times higher than that of the parent industrial product obtained by rapid heating of a graphite sulfate. The krypton adsorption isotherm at 77.3K on Madagascar flakes, exfoliated according to our method, is compared to the isotherm measured on the commercial exfoliated graphite prepared by "Carbone Lorraine" (Figure 5a). The surface of exfoliated Madagascar flakes is less homogeneous than that of the commercial sample, as shown by the slight slope of the step and the decrease of its linear part, which corresponds to krypton two dimensional condensation on the uniform part of the surface [9]. From the height ratio of the normalized isotherm linear parts, the extent of uniform surface was estimated to be 38% of the total surface area. When exfoliating brazilian graphite with the same procedure, we also obtain a sample with a large but not very homogeneous surface. The uniform part of the surface is, in this case, 47% of the total surface area.

With this procedure even green cokes and graphitized cokes can be exfoliated (Table 2). But the surface heterogeneity is increased by exfoliation as shown on Figure 5b, where normalized isotherms measured on pristine and expanded cokes are compared.

The enhanced surface heterogeneity probably originates from the intercalate explosion inside the graphite layers and from the basal planes oxidation.

Exfoliation of coke particles have been already performed by Inagaki

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:25 18 February 2013

and coll. [10]. Nevertheless, at our knowledge, no specific surface area measurement has been reported.

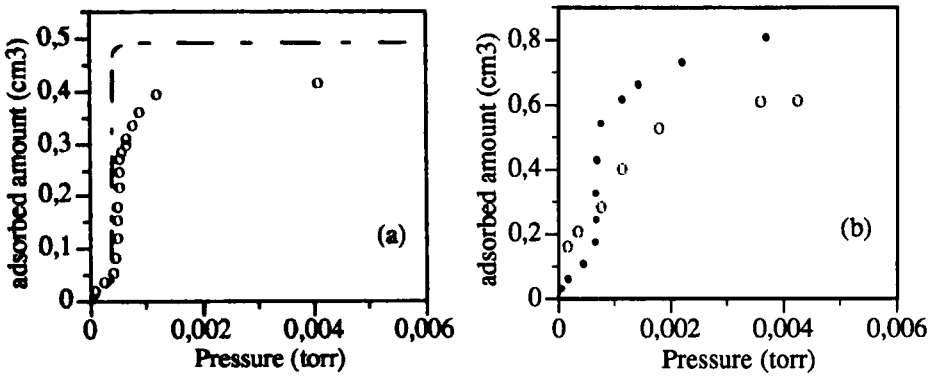

Figure 5a Normalized krypton adsorption isotherms at 77.3K on:

(a) exfoliated Madagascar flakes (o) (according to our method) and on commercial exfoliated graphite (- -).

(b) exfoliated coke (o) and on pristine coke H.T.T.2600°C (•).

In conclusion, all kinds of carbonaceous materials which intercalate dilute perchloric acid can be exfoliated by this procedure. The resulting exfoliated materials exhibit high specific surface areas (up to $100m^2/g$ for exfoliated natural graphite). Nevertheless, this exothermic exfoliation causes an important surface heterogeneity.

Acknowledgements: This work was partially supported by "Carbone Lorraine S.A.". The authors are indebted to Dr.A.W.Moore of Union Carbide Corp. for supplying the H.O.P.G..

REFERENCES

1. C.Mazières, G.Colin, J.Jegoudez and R.Setton, Carbon, 13, 289, (1975).
2. A.Thomy, J.C.Ousset, G.Furdin, J.M.Pelletier and A.B.Vannes, J.Physique C7, 115, (1981).
3. Y.Kuga, T.Oyama, T.Wabayashi, H.Chiyoda, K.Takeuchi, Carbon, 31, 1, 201,(1993).
4. D.Petitjean, Thesis, Nancy, (1992).
5. H.Fuzellier et A.Hérold, C.R. Acad. Sciences Paris C, 276,1287, (1973).
6. D.Petitjean, M.Lelaurain, E.Mc Rae, A.Hérold, G.Furdin, Solid State Comm. 86, 9, 535-540, (1993).
7. S.Aronson, S.Lemont and J.Weiner, Inorg. Chem. 10, 1296, (1971).
8. M.Klatt, Thesis, Nancy, (1985).
9. A.Thomy, X.Duval and J.Regnier, Surface Science Reports 1, 1-38, (1981).
10. M.Inagaki, K.Muramatsu, Y.Maeda and K.Maekawa, Synth.Metals, 8, 335, (1983).

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:25 18 February 2013