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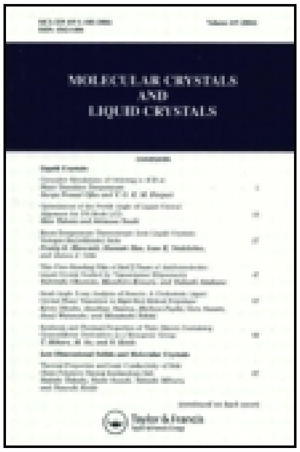

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Sodium - Oxygen Graphite Intercalation Compound: XPS, UPS and STM Study

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SODIUM - OXYGEN GRAPHITE INTERCALATION COMPOUND : XPS, UPS and STM STUDY

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XPS, UPS and STM are used to characterize a second stage NaO_xC_y compound. The charge distribution and the cleavage localization are discussed.

Keywords : XPS, UPS, STM, Graphite-Intercalation-Compound, Na-Oxide.

INTRODUCTION

The binary alkaline Metal-Graphite Intercalation Compounds (M-GICs) as well as the ternary H- or Hg-M-GICs have been thoroughly studied through numerous techniques including X- and UV-photoemission spectroscopy. In this paper, one of the relatively newcomers[1,2,3] in the great GIC family, the ternary compound NaO_xC_y will be compared with clean or slightly oxidized binary stage 2 M-GICs[4,5] called MC_{24}. The comparison will concern their charge distribution seen by XPS and UPS and the structure of their outermost atomic layer of an in situ cleaved surface seen by STM.

PREPARATION AND EXPERIMENTS

The slice of Na-peroxide intercalated in the second stage ternary compound NaO_xC_y here studied has been proved[1] to be composed of 5 atomic layers inserted between two graphene layers, i.e. successively Na, O, Na, O, Na, with a repeat distance of 7.45 Å.

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The conditions of preparation of such a ternary compound has been given elsewhere[1]. In present work, the homogeneity of the intercalation was only checked by the blue color of the surface, characteristic of a second stage.

The sample was first cleaved in air before its introduction in the analysis chamber of a photoemission spectrometer coupled to an UHV-STM. The pressure of the chamber was 6.10^{-11} Torr and remained constant after introduction. The following cleavages of the cooled sample were performed in-situ with tape[3]. Contrarily to the binary M-GICs, the NaO_xC_y compound is not easily cleaved in that the remaining film on the tape, is not regularly thin and complete. In this sense, only two in-situ performed cleavages could be considered as almost satisfactory.

EXPERIMENTAL RESULTS

XPS Core Level Spectra

The total energy XP-spectrum (Mg source (hν = 1253.6 eV) only shows the core level peaks of C, Na and O.

The **carbon 1s peak** is almost identical in position (E_B = 285.00 eV) and in its dissymetrical shape to the C1s peak in MC_{24} [4] (figure 1). From those similitudes between binary and ternary stage 2 GICs, we conclude that:

1/ the graphene Π and/or interlayer functions bear the same charge, transferred from the guest compound (deduced from the E_B) and that this charge participates to the conduction (deduced from the asymmetrical shape).

2/ when fitting the line, as in MC_{24}, a small component, about +1 eV from the main one, must be assumed, which may, as well, be attributed both to carbon atoms located in regions crumpled during intercalation and to an intraband plasmon. 3/ The interband plasmon lies respectively at 6.8 and 5.1 eV in MC_{24} and NaO_xC_y.

Each of the **Na core level** spectra in NaO_xC_y may be fitted with only one broad, symmetrical essentially gaussian shaped peak. Their binding energies are given in Table 1 compared to those of oxide and free metal found in the literature.

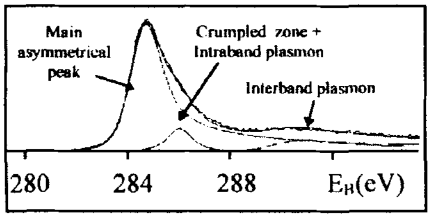

Fig.1 NaO_xC_y XPS C1s spectrum. (See Color Plate II).

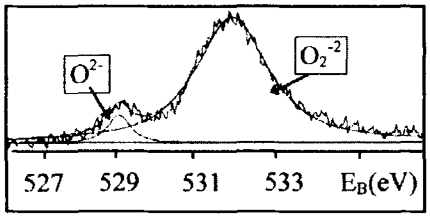

Fig.2 In situ cleaved NaO_xC_y XPS O1s spectrum. (See Color Plate III).

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TABLE 1 Na Core level binding energies in NaO_xC_y

Core level ↓	NaO_xC_y	Oxide[6]	Metal[7,8]
Na2p	31.8	31.1	30.5
Na2s	64.71	64.0	63.4 63.7
Na1s	1073.3	1072.5	1071.7 1070.8

They are all high binding energy shifted and this shift may be interpretated using the classical electrostatic rule : the electronic charge decreases in following order : metal > oxide > NaO_xC_y . This means that no residual charge remains on the Na atom contrarily to the M-GICs in which the alkali metal bears part of the charge contributing to conduction. This conclusion is in complete agreement with the Na symmetrical line shapes, whereas in the M-GICs, all the alkaline lines are asymmetrical due to electron-hole pairs creation

The **oxygen 1s core level** spectrum of in situ cleaved NaO_xC_y is given on (fig.2). Only two peaks are present at E_B = 532.4 and 528.7 eV (≈10% of the total intensity), attributed, as on oxidized surfaces[5], respectively to the O_2^{2-} peroxo- and O^{2-} oxo- species. In grazing detection, the ratio between both species does not change : the distribution of both species does not depend on the probed depth and the whole intercalated layer is mainly of sodium peroxide.

The **stoichiometry** has been determined by integrating XPS peak area and taking account of the core level cross sections. For both in situ cleavages, we obtain $NaO_{0.31}C_{6.3}$ and $NaO_{0.21}C_{5.6}$ Compared to the mean chemical formula[1] $NaO_{0.44\pm0.06}C_{5.84\pm0.06}$, the results are in fairly good agreement with a weak detected deficiency in oxygen due to a slight oxide overlayer sublimation.

UPS results

From the UPS spectra (fig. 3) obtained after in situ cleavages, we deduce :

1/ at the Fermi level, a small but noticeable peak indicates the donor nature of the compound with a noticeable density of states;

2/ the energy edge of the emission gives the work function of the surface if it is homogeneous or the lowest W value when it is inhomogeneous : W = 4.2 eV (in graphite W = 4.4 eV and in binary M-GICs W ≈ 2 eV or 3.4 eV after strong oxidation);

3/ the strong and narrow peak at 15 eV from E_F has been yet identified with the image of the Π^* unoccupied level. Following [9,10] this level may be considered as invariant by intercalation relatively to the vacuo level. If this is also true in NaO_xC_y , we may say that the Fermi energy is shifted by + 1.5 eV relatively to the graphite one (1.7 eV in stage 1 M-GICS and 1.2 eV in stage 2 and 3);

4/ the smoother features located between E_F and the Π^* image, are due to the O2p levels at binding energies 3.5, 5.6 and 10.6 eV from E_F. The presence

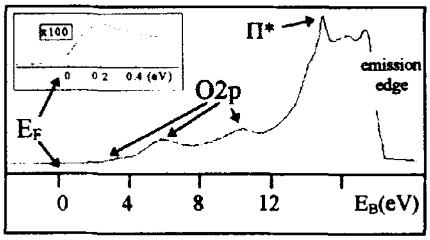

Fig 3 In situ cleaved NaO$_x$C$_y$ UPS spectrum. (See Color Plate IV).

of only 3 peaks could mean that the oxygen species is mainly the O_2^{2-} peroxo-one as concluded from the C1s spectra. However, the energy distances between the O2p peaks are relatively different from the ones measured in the alkali peroxide[5] : obviously, the oxygen in the intercalate is not quite identical to oxygen in classical peroxide in spite of the equal O-O distance (1.52 A), maybe due to the isolated character of the oxygen anion pairs or to the reduced distance between O- and Na atoms[1].

STM imaging.

N.B.: The choice of images in near field microscopy is always arbitrary. For definitive and reliable conclusions, statistical imaging would be necessary!

The NaO$_x$C$_y$ surface has been observed by STM after the XPS and UPS measurements, in an UHV chamber coupled to the X and UV-photoemission spectrometer. Its surface is relatively flat but with many 6 Å high terraces (in green on fig. 4; 0.5 x 0.5 μm^2), contrarily to HOPG or to binary M-GICs, even after oxidation[12]. The terrace surfaces are structured by a regular atomic

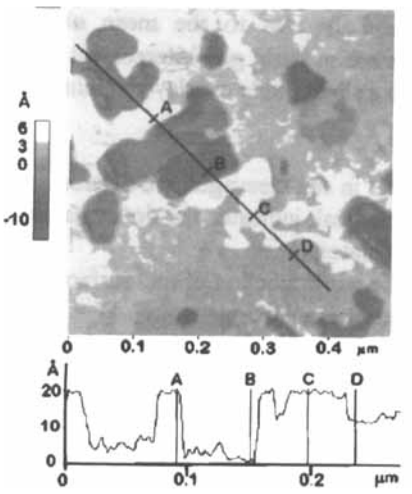

Fig. 4 (0.5x0.5)μm^2 in situ cleaved NaO$_x$C$_y$ STM image with a line profile. (See Color Plate V).

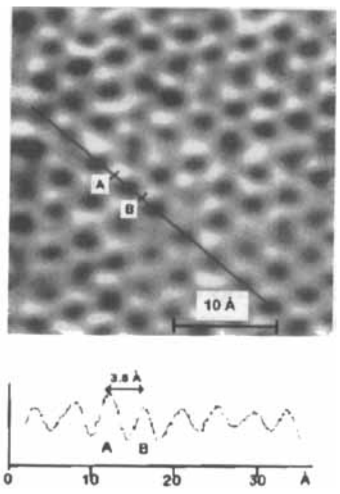

Fig.5 3.8 Å h.c.p. atomic lattice observed on green flat parts of fig.5 with a line profile. (See Color Plate VI).

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lattice (h.c.p., interatomic distance ≈ 3.8 Å, fig.5). Their height close to the oxide sandwich (Na-O-Na-O-Na) thickness and their lattice parameters close to the oxide in plane one[1] allows their attribution to superficial oxide (the lower terraces, colored in grey, about 3 Å high, could be due to half an oxide sandwich). Thus, the blue level is a graphene layer as expected : the cleavage mechanism does not break the carbon planes but always occurs between them.

In the case of oxide-GIC, the oxide sandwich has certainly a strong in-plane cohesion and its partition during the cleavage will occur at domain frontiers. Thus, the image shown on figure 4, may be a first image of a Daumas-Herold pleating, the tortuous contours of the oxide being due to a diffusion front during intercalation (and eventually to the front of oxide sublimation under vacuo). Previous evidence by STM[11] of such frontier has been yet proposed but more indirectly and at a much smaller scale.

Tortuous flat bottomed holes (red) are also seen on fig. 4. Their deepness, about 10 Å, greater than a repeat distance, means that they cut out at least two carbon planes. They may be the prints of pristine HOPG cristallites (Φ ≈ 2000 Å), loosened during intercalation and taken away by the cleavage. It is perhaps the first time, those cristallites are revealed with their jigsaw shape which usually insures the macroscopic cohesion of the pristine HOPG and of the corresponding GICs when the intercalation has not destroyed it. Such holes have never been observed neither on HOPG nor on other GICs but this observation may be related to what occurs in high pressure intercalated M-GICs. In these compounds, the HOPG microcristallites, after intercalation, have lost their interconnections and the sample its macroscopic lamellar and cleavable character. This cohesion loss (evidenced by the powder in which the sample is converted by hydrolysis) is of course limited in the case of NaO_xC_y which remains lamellar but with a bad tape cleavability.

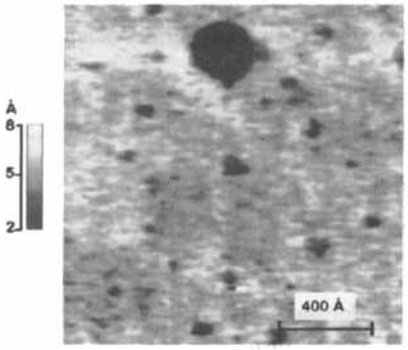

Fig.6 (160x160) nm^2 STM image after some days under vacuo. (See Color Plate VII).

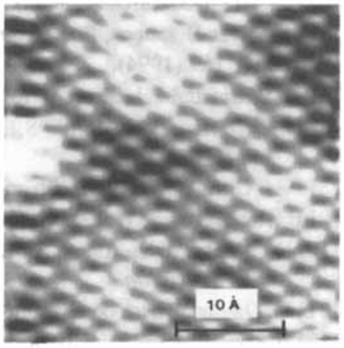

Fig.7 2D modulated 2.5 Å h.c.p. atomic lattice imaged on the surface observed in fig. 6. (See Color Plate VIII).

After some days in vacuo, the surface has evoluted and no more oxide structure were obtained, neither at atomic scale nor at larger one. The mean surface is relatively plane (fig. 6), with flat bottomed holes ($\Phi \approx 200$ Å, depth 5 Å). A small atomic lattice (h.c.p. interatomic distance ≈ 2.5 Å) similar to the usual graphite one is observed, very smoothly modulated (depth < 1Å, 2D period ≈ 20 Å). Several types of modulation of the outermost carbon layer have been yet observed by STM on GIC surfaces, both 1D and 2D, but their origin is not yet well understood[3,12-14].

CONCLUSION

Our surface experimental studies of Na-O-GIC need further confirmations, specially concerning the stability of the outermost atomic layer. However, our first XPS and UPS results show that 1/ the intercalated Na-oxide plays the role of a donor : the graphene lattice bears almost the same charge as in MC_{24} and the Fermi level is similarly shifted by about 1.5 eV; 2/ the oxygen is in a state similar to a peroxide with only slight differences; 3/ the sodium has completely lost its charge towards the oxygen and the graphene host lattice. Preliminar STM images give interesting informations on the structure of the outermost layer and on the specific alkali-oxide intercalation mechanism in HOPG.

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