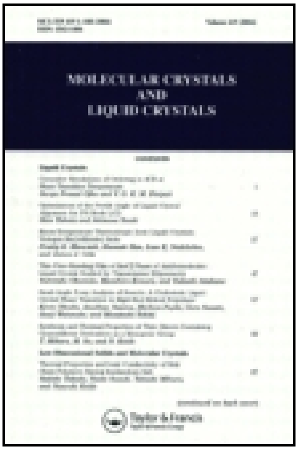

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REDUCTION OF THE SECOND STAGE $FeCl_4^-$ AND $FeCl_3$ GRAPHITE INTERCALATION COMPOUNDS

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Abstract $FeCl_4^-$ graphite intercalation compounds (GIC) were obtained by anodic oxidation of graphite in an aqueous solution and were subsequently submitted to galvanostatic reduction in a:

Li / $LiClO_4$ 1M in propylene carbonate / GIC cell.

The intensiostatic and structural data were compared to those obtained on partly reduced 2nd stage $FeCl_3$ GIC. Whereas a "one step reduction" is observed with the $FeCl_3$ GIC, the reduction of the 2nd stage $FeCl_4$ GIC takes place with at least four well defined plateaus. The beginning of the last step corresponds to a stable 6 th stage structure. Increasing the charge passed through the samples leads to the exfoliation of the graphitic lattice and to the formation of metallic iron, exhibited by important ferromagnetic susceptibility.

INTRODUCTION

Bidimensionnal metallic clusters in a lamellar matrix would be very important , either for magnetic or catalytic applications. As stated by some authors, the direct intercalation of transition metals into graphite seems to be energetically difficult if not impossible [1,2]. Therefore many attempts tried to produce graphite - transition metal intercalation compounds by a two steps process, including the intercalation of a metallic halide in the graphite lattice and its subsequent reduction[3].

In our work we were interested by the development of new graphite intercalation compounds (GIC) with iron. Traditionally, iron chloride GIC are prepared either by chemical [4, 5, 6] or electrochemical [7] methods. Recently we developed a new process allowing to obtain a second stage $C_{28}FeCl_4,2H_2O$ compound in an aqueous medium [8].

Since most of the experiments concerning the chemical or electrochemical reduction of $FeCl_3$ GIC are still discussed, we better preferred to use $FeCl_4^-$ GIC as starting materials. For a comparison, the 2nd stage graphite-$FeCl_3$ was also reduced. Some new data obtained by EXAFS on this material will be given in this paper.

EXPERIMENTAL

The 2nd stage $FeCl_3$ GIC was prepared by the two bulbs method by allowing HOPG platelets (Union Carbide 5x2x0,5mm^3) to react with $FeCl_3$ during 4 days at T_G = 300°C and T_{FeCl_3} =280°C. The ideal formula deduced from chemical analysis was $C_{12}FeCl_3$. The 2nd stage $C_{28}FeCl_4$, $2H_2O$ and 3rd stage $C_{42}FeCl_4$, $2H_2O$ compounds were prepared by electrochemical oxidation of graphite (HOPG: 5x2x0,5mm^3) accordingly to reference [8].

For the reduction, we used the following electrochemical cell: Li (-) / $LiClO_4$ 1M in propylene carbonate / GIC (+). For improved electrical contact, the GIC sample was tightly wrapped in a nickel gauze. The building of the cell together with the reduction were realized under argon atmosphere (oxygen < 0.1 ppm) in a glove box. A constant courant intensity was imposed during the reduction : 5 $\mu A.mg^{-1}$. After partial or complete reduction, the samples were washed with dimethoxyethane in the glove box, and protected with a polyethylene film. For the X-ray diffraction characterizations we used a reflection set up working at 1.5405 Å (Siemens D 500 goniometer).

The thickness of the samples used for the X-ray absorption measurements was selected to obtain the most important variation at the iron absorption edge. After partial or complete reduction and rinsing with propylene carbonate in a glove box, the specimens were introduced in an air-tighted container, equiped with mylar windows. The X-Ray absorption measurements were realized using the DCI synchrotron radiation at LURE in Orsay

RESULTS AND DISCUSSION

Reproducible reduction curves were obtained for the 2nd stage $FeCl_3$ and $FeCl_4^-$ GIC in the intensiostatic mode (figure 1):

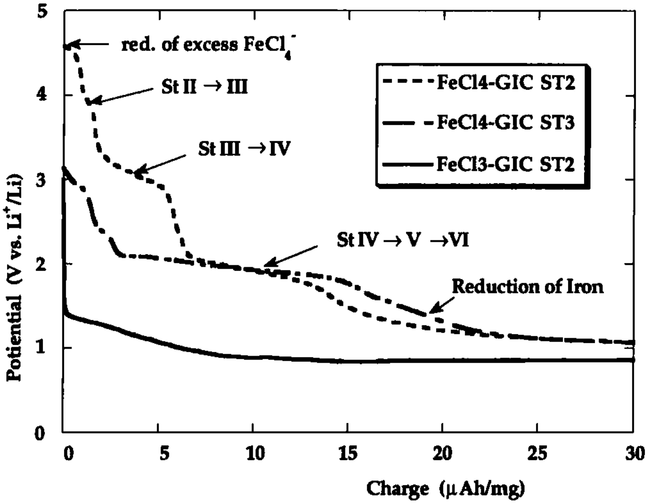

FIGURE 1. Intensiostatic reduction of the $FeCl_3$ and $FeCl_4^-$ GIC (1 M $LiClO_4$ in propylene carbonate ; i = 5µA/mg)

The first plateau on the curve of the 2nd stage G- $FeCl_4^-$ is attributed to the reduction of excess iron chloride adsorbed at the surface of the sample. The following plateau corresponds to the transition from stage 2 to stage 3. After this transformation the two curves of stage 2 and stage 3 $FeCl_4^-$ GIC are quite similar, indicating comparable phenomena.

The most important difference, observed for the potential variation between the two curves of the 2nd stage $FeCl_3$ and $FeCl_4^-$ derivatives in figure 1, is a continuous decrease for G-$FeCl_3$, whereas G-$FeCl_4$ is reduced through several steps. In the two cases, the end of the process is represented by an almost horizontal plateau, located not far from the value corresponding to the decomposition of propylene carbonate (0.8 Volt vs Li^+/Li). All the intermediate X-ray Diffraction spectra recorded in the course of G-$FeCl_3$ reduction showed the coexistence of graphite and starting 2nd stage G-$FeCl_3$, indicating a continuous process, as revealed by the intensiostatic curve (figure 1). On the other hand, starting from the 2nd stage G-$FeCl_4$, the plateaus on the reduction curve (figure 1) are the signature of stage changes. At the beginning of the last plateau (figure 2) we

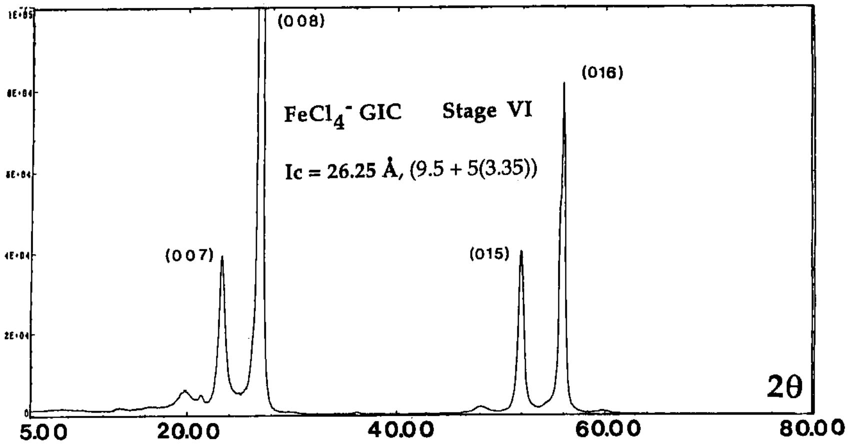

FIGURE 2. X-Ray Diffraction at the beginning of the last plateau on the reduction curve of G-FeCl$_4^-$. All the lines are attributable to the 6th stage compound. (λ = 1.5405 Å)

detected a stable 6th stage phase. After reaching the last plateau, exfoliation can occur by increasing the charge passed through the sample, whatever the starting GIC . After compressing the exfoliated specimens, X-ray diffraction (figure 3) revealed only the 002 line of graphite when starting from G-FeCl$_3$, whereas an additional line corresponding to the 6nd stage phase remained for G-FeCl$_4^-$. We were however never able to detect lines corresponding to a Fe-GIC or to metallic iron. The presence of the latter is suggested by the important ferromagnetism observed for the totally reduced samples. It must be pointed out that, in the 001 reflection mode, X-ray diffraction could not detect metallic particules in the oriented graphite matrix [9].

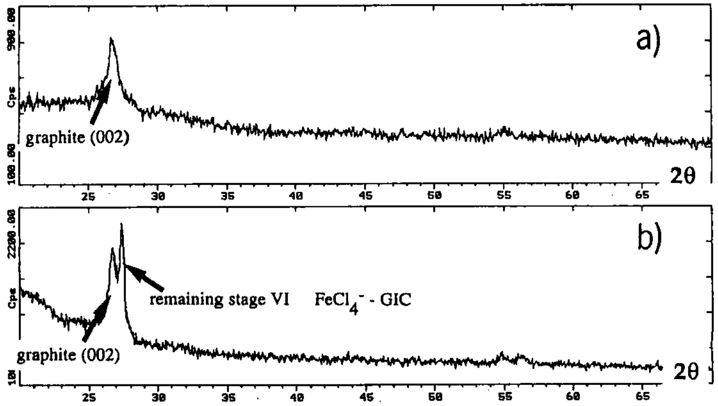

FIGURE 3. X-Ray Diffraction on almost completely reduced FeCl$_3$ -GIC (a) and FeCl$_4^-$-GIC (b) (λ = 1.5405 Å)

To obtain more information about iron, samples taken at various steps of the reduction were examined by X-ray absorption at the K edge of iron. From the EXAFS oscillations on an almost completely reduced G-$FeCl_3$ sample (fig. 4a), we detected three phases : the starting 2nd stage G-$FeCl_3$ (~ 40%), metallic iron Fe$^{\circ}$ and Fe_2O_3. This result is an other confirmation that the reduction of G-$FeCl_3$ is a continuous process which leads to an amount of metallic iron increasing with the charge passed through the sample. The only origin of Fe_2O_3 is the partial oxidation of highly reactive surface iron particles which react with the oxygen impurities present either in the glove box or in the container for X-ray absorption measurements.

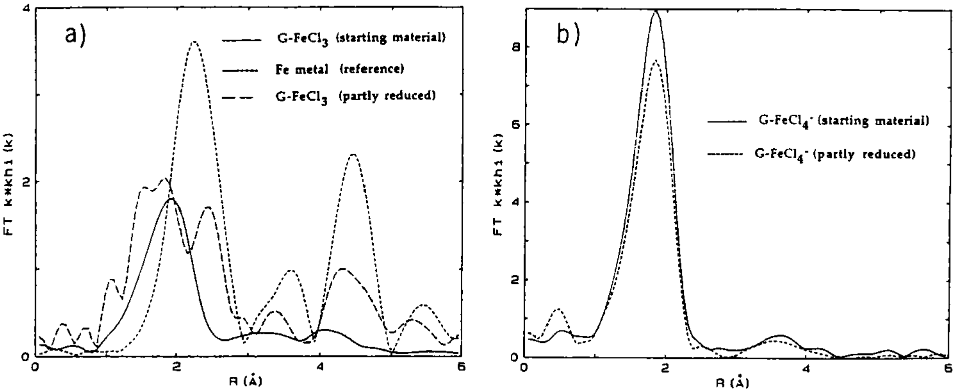

FIGURE 4 EXAFS on starting and partly reduced: a) $FeCl_3$ GIC and b) $FeCl_4^-$ GIC

The EXAFS analysis at various steps in the course of the reduction of G-$FeCl_4$ did not show any modification in the radial pseudo distribution (figure 4b). In all cases the unique peak at 2.20 Å corresponds to the Fe-Cl distance with iron in a spherical symmetry. This distance is quite comparable to that deduced from crystallographic data on $As(C_6H_5)_4$ [$FeCl_4$] [10]. The spectra in figure 4b were obtained respectively on the starting 2nd stage $FeCl_4^-$ GIC and on the 6th stage sample formed at the beginning of the last plateau on the reduction curve. Therefore we conclude that the first steps in the reduction of the G-$FeCl_4^-$ derivatives are only due to the deintercalation of $FeCl_4^-$ leading to a stage increase. A further reduction leads to the decomposition of the 6nd stage compound together with the exfoliation of the specimen, giving graphite and metallic iron.

CONCLUSION

The reduction mechanism of the graphite-iron chloride derivatives is strongly depending on the charge of the intercalated species. In the case of the G-$FeCl_3$ derivative, our observations are compatible with a two steps process, identical to that already proposed by Armand [11]:

1- Intercalation of the electrolyte leading to the formation of a solid solution:

$$C_nFeCl_3 + y\,Li^+ + ye^- \quad <===> \quad < C_nLi_yFeCl_3 >$$

2- Decomposition of the product:

$$< C_nLi_yFeCl_3 > \quad \longrightarrow \quad n\,C + Fe^\circ + y\,LiCl$$

Due to the ionicity of $FeCl_4^-$, the charge transfer is more important in G-$FeCl_4^-$ than in G-$FeCl_3$. Therefore, the first step in the reduction of G-$FeCl_4$ is the deintercalation of an important part of $FeCl_4^-$ leading finally to the very stable 6th stage derivative :

$$C_n^+FeCl_4^- + x\,e^- \quad <===> \quad C_n^{+(1-x)}(FeCl_4^-)_{1-x} + x\,FeCl_4^-$$

Increasing the charge passed through the cell, metallic iron can be formed, accordingly to the mechanism suggested before :

$$C_n^{+(1-x)}\,(FeCl_4^-)_{(1-x)} + y\,Li^+ + y\,e^- \quad <===> \quad < C_nLi_y(FeCl_4)_{(1-x)} >$$

$$< C_nLi_y(FeCl_4)_{(1-x)} > \quad \longrightarrow \quad n\,C + (1-x)\,Fe^\circ + y\,LiCl$$

As suggested by Metrot et al [12], the apparent stability of the 6th stage compound could be due to a kinetical limitation in the diffusion of lithium. Another explanation could be a larger stability of the intercalated $FeCl_4^-$ compared to $FeCl_3$, and the role of the co-intercalated species. The exfoliation of the sample, is probably due to the decomposition of intercalated electrolyte.

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