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ELECTROCHEMICAL SYNTHESIS OF IRON SUPPORTED ON EXFOLIATED GRAPHITE

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Abstract—A graphite intercalation compound (GIC) of acceptor type with complexed transition metal (iron) has been selected as a catalyst precursor. Supported iron particles were prepared using an all-electrochemical method which overcomes most of the disadvantages of the other processes based on GIC precursors. In the first step, the 2nd stage C_nFeCl_4, 1.5 H_2O, 0.5 HCl compound was prepared by anodic oxidation of graphite in a concentrated solution of $FeCl_3$ in 12 M HCl, where the main species present in the solution are $FeCl_4^-$ anions. The $FeCl_4^-$–GIC was then submitted to cathodic reduction in the presence of $LiClO_4$ in aprotic medium (mixture of ethylene carbonate and diethylcarbonate). When reduction proceeded, the graphite exfoliated, and at the end of the process, the solid phase was a mixture of graphite, 6th stage GIC, LiCl and Fe°. The co-intercalated solvent molecules are responsible both for the exfoliation and for the partial reduction in metallic iron. The method allows to obtain highly dispersed iron on exfoliated graphite at room temperature. Such a nanocomposite may have applications in catalytic reactions for which supported metals are required.

Keywords: A. metals, A. inorganic compounds, B. X-ray diffraction, D. electrochemical properties.

1. INTRODUCTION

The preparation of supported metallic catalysts for industrial applications has seen intense development during the last 10 years. Among the supports, graphite is very interesting for its chemical inertness and also for its ability to modify the performance of the catalyst by metal-support interaction. Recently, new methods have been developed which lead to metal/graphite nanocomposites, using the chemical or electrochemical transformation of graphite intercalation compounds (GIC).

The chemical reduction of G–MCl_n derivatives by metallic potassium at 300°C [1, 2] leads to well dispersed metallic M° clusters occluded in the graphite matrix. Therefore, they are not accessible for any reagent, even oxygen from the atmosphere. Moreover, the KCl by-product is also occluded and is only partly eliminated by washing with outgassed water. Owing to the low accessibility of M and the poisoning effect of KCl, the catalytic activity of these materials is very poor. This method was improved by reducing the G–MCl_n derivatives with potassium–naphthalene complex in THF solution at room temperature [3]. The metal M° is still occluded, but together with potassium and THF, i.e. in a residual graphite–potassium–THF ternary compound. Therefore, it can be rendered accessible by rapid heating of the graphite phase at about 500°C. Owing to the presence of intercalated THF, the pressure increase induced by heat treatment leads to important exfoliation of the graphite matrix. In this way, the metal M° and KCl become accessible, and KCl can easily be removed by washing with water. Unfortunately, water washing leads at least to partial oxidation of M, and additional reduction would be necessary before catalytic use. The main disadvantage of this process is the coalescence of the metallic particles provoked by the relatively high temperature which is necessary to obtain exfoliation.

The chemical reduction of MCl_n salts by KC_8 in THF medium [2, 4], produced M° and KCl clusters located on the edge planes of graphite, indicating that the redox process occurred at the defects present on the edge carbon atoms. Consequently, KCl can easily be eliminated by rinsing with water, but the metal is oxidized and the samples cannot be handled in air. Due to the low surface developed by the edge planes, the clusters are highly aggregated, which is a big disadvantage for catalytic activity. Metallocenes were used in a similar process [5], instead of a MCl_n salt. The C_5H_5K by-product is soluble in the solvent used for the reaction and can, therefore, be eliminated without any further treatment. These products are directly usable, but as for the previous case, cluster aggregation is a hindrance to activity.

Electrochemical reduction of G–MCl_n derivatives with a lithium anode is another way to produce metallic clusters [6]. As for the reduction by metallic potassium, the metal M° and LiCl are occluded in the graphite matrix, however, since this reaction occurs at room temperature, it can produce smaller particles than potassium reduction.

The main disadvantage of most of these processes is that they can give rise either to occluded catalysts with a low activity, or to catalysts contaminated by side-products which can act as inhibitors. Therefore, we were interested in developing the synthesis of a $FeCl_4^-$-GIC precursor in water medium. Its subsequent electrochemical reduction can lead to the formation of iron supported on exfoliated graphite under certain conditions [7]. Due to the particular interest of this process especially capable of generating *in situ* the metal at room temperature in a non-polluting way, the parameters influencing the formation and the reduction of this precursor will be more carefully considered.

2. EXPERIMENTAL

Electrochemical synthesis of the $FeCl_4^-$-GIC was performed by galvanostatic oxidation of HOPG (Highly Oriented Pyrolytic Carbon from Union Carbide) under a current density of 6 mA/g. The electrolytic bath consisted of dissolved $FeCl_3$ (50.4 g) in 18 ml of 12 M HCl. The reduction of the prepared $FeCl_4^-$-GIC was carried out in a Li(−)/GIC(+) cell with aprotic solvent at a constant current density of 10 mA/g. The methods are described in detail elsewhere [7]. The GIC samples before and after reduction were analysed by X-ray diffraction at 1.5418 Å (Siemens D500). The texture of exfoliated graphite and the dispersion of iron particles on the graphite matrix was investigated using scanning electron microscopy (SEM) (Cambridge Instruments).

3. RESULTS AND DISCUSSION

All the methods described above present some disadvantages. Therefore, our target was to develop a process which could allow exfoliation together with *in situ* generation of highly dispersed metal at room temperature (in order to avoid coalescence).

Electrochemical reduction is interesting, because it can occur at room temperature. To produce exfoliation, co-intercalated solvent molecules are necessary. Here, we will show that the cathodic reduction of the C_nFeCl_4, $1.5\,H_2O$, $0.5\,HCl$ derivative leads, at room temperature, to simultaneous formation of M° and exfoliation of the graphite matrix, owing to the rapid evolution of the solvent molecules which initially solvated the $FeCl_4^-$ anions. We consider this process as the best for controlling the synthesis of this kind of catalyst. Since solvent has a great importance, we will compare the reduction of the "as prepared" and dried $FeCl_4^-$-GIC. Therefore, we will first determine the stability of the C_nFeCl_4, $1.5\,H_2O$, $0.5\,HCl$ derivative either in air atmosphere or under vacuum.

3.1. *Stability of the* C_nFeCl_4, $1.5\,H_2O$, $0.5\,HCl$ *compound*

The 2nd stage $FeCl_4^-$-GIC synthesized by anodic oxidation of graphite in the chlorocomplex bath started to form at about 1.1 V vs SCE. We noted an increase of the charge passed for preparing the 2nd stage with aging of the bath: this is attributed to side-reactions, as for instance, oxidation of Fe(II) species appearing in the bath with time. In our experiments, the formula of the 2nd stage derivative, deduced from the charge passed, varied from $C_{36}FeCl_4$, for the fresh bath, to $C_{20}FeCl_4$ after 7 days working.

After preparation, a sample was pumped under vacuum at 120°C, and the evolving vapour was condensed in a trap cooled with liquid nitrogen. For the identification of the gases, we used transmission IR spectroscopy showing both the vibration bands of water and HCl [7]. The quantitative determination of these two compounds was realized by thermogravimetric analysis (TGA) showing a two-step weight loss in the range from 60 to 140°C. The amount of HCl was determined more successfully by dissolving the vapour in water and by titrating HCl with a standard NaOH solution. From all these data, we could establish the following formula for the 2nd stage compound: C_nFeCl_4, $1.5\,H_2O$, $0.5\,HCl$ with $n = 20$–36. From this formula, it can be noticed that the proportions of HCl and H_2O are almost the same as in the 37% HCl solution used for the electrochemical intercalation, i.e. $HCl/H_2O = 0.29$.

The X-ray diffractogram of the compound showed very well defined $00l$ lines, even at high indices, suggesting high crystallinity. The identity period along the c-axis is 12.78 Å, which gives in the hypothesis of a 2nd stage phase an interplanar distance $d_i = 9.43$ Å close to the value observed for the $FeCl_3$-GIC (9.4 Å). Considering the general formula C_nFeCl_4, $1.5\,H_2O$, $0.5\,HCl$, one can calculate the volume V_i of the intercalated species:

$$V_i = 2.62 \times n/2 \times (I_c - 2 \times 3.35),$$

where 2.62 $Å^2$ represents the surface of one graphitic carbon atom and n the number of carbon atoms in the hypothetic cell.

The volume of $FeCl_4^-$ was deduced from the crystallographic data of $NaFeCl_4$ [8], and found to be 155 $Å^3$. The volumes of the HCl and H_2O molecules

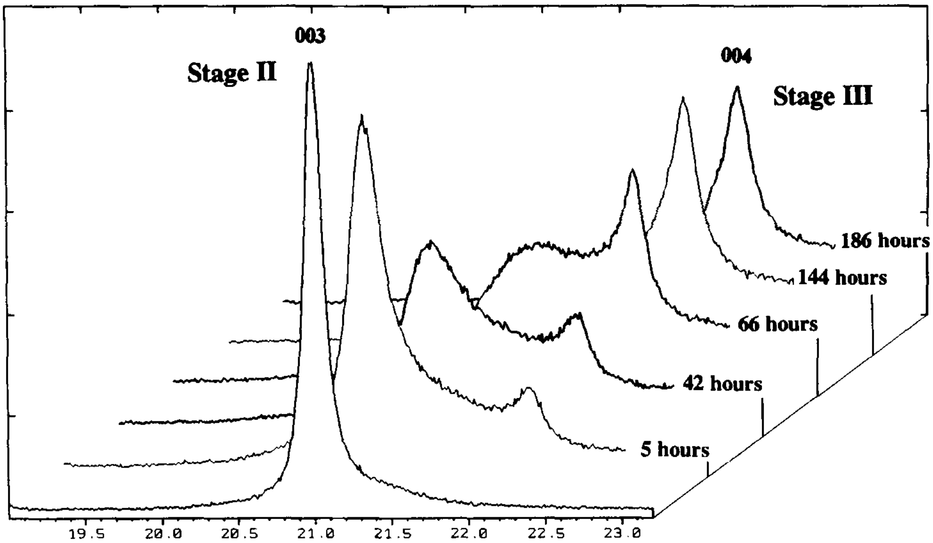

Fig. 1. Decomposition of the stage 2 $FeCl_4^-$-GIC on exposure to air. A part of the diffractogram showing the 003 line of stage 2 and the 004 line of stage 3 GIC.

are, respectively, 51 and 30 Å^3. The following equation can also be written:

$$V_i = 155 + (51 \times 0.5) + (30 \times 1.5) = 225.5\,\text{Å}^3.$$

By comparing the two formulae given for V_i, one can deduce $n = 28.4$. This value is in good agreement with the range determined from the charge passed, $n = 20$–36.

The 2nd stage $FeCl_4$ derivative was exposed to air atmosphere in order to determine its stability. X-ray 00l diffraction spectra were recorded as a function of air exposure (Fig. 1). After only 5 h, new 00l lines were observed, indicating the poor stability of this compound. With time, the intensity of the new lines increased, whereas the 2nd stage phase disappeared progressively. After 7 days, the spectra exhibited only one set of 00l lines, which are interpreted as due to a 3rd stage phase with $I_c = 16.16$ Å. Further air contact did not show any change in the spectra, indicating high stability of the 3rd stage compound. A similar effect, i.e. transformation to stage 3, was observed if the 2nd stage fresh sample was pumped under vacuum at a low heating rate up to 120°C. Taking into account indications given by TGA, all the water and HCl molecules are deintercalated at 120°C. Therefore, we can conclude that this 3rd stage derivative contains only intercalated $FeCl_4^-$ anions.

By analogy with the above calculations, if one assumes the C_nFeCl_4 formula for the 3rd stage phase formed, the space available for the $FeCl_4^-$ anions is:

$$V_i = 2.62 \times n/3 \times (I_c - 3 \times 3.35)$$
$$= 155\,\text{Å}^3, \text{ with } I_c = 16.16\,\text{Å}.$$

The computation then gives $n = 29$. This value is quite reasonable, since n is very close to its average value in the as prepared 2nd stage phase.

The transformation from stage 2 to 3 which occurs when the solvent molecules are deintercalated is easily interpreted according to the Daumas–Hérold [9] pleated layers model (Fig. 2). The surface occupation is 1/2 in the starting 2nd stage GIC and, when the HCl and H_2O molecules are evolving, it decreases and tends to 1/3 when all the solvent molecules are removed from the structure.

3.2. *Reduction of the* $FeCl_4^-$*-GIC*

Our target was to obtain supported Fe° particles by reducing the $FeCl_4^-$-GIC. Taking into account previous observations showing that this derivative can exist with or without solvent molecules, we decided to study the electrochemical reduction of the fresh samples and of the samples formed after pumping under vacuum.

The reduction was performed in an aprotic medium, due to the fact that the intercalation process was irreversible in water medium, in the range investigated (0.8–1.2 V vs SCE). Depending on the desired potential window, we used two kinds of solvents, either propylene carbonate (PC) or a 1 : 1 mixture of ethylene carbonate (EC) and diethylcarbonate (DEC).

For experiments with PC, the reduction of the GIC was impossible below 0.9 V vs Li^+/Li due to the decomposition of PC on HOPG. With the mixture of EC and DEC, the reduction of the $FeCl_4^-$-GIC was carried out from the open circuit voltage (OCV) of about 4.7–4.3 to 0 V vs Li^+/Li.

Starting from the "as prepared" 2nd stage GIC, some plateaux were observed on the reduction curve which can be attributed to the transition to higher

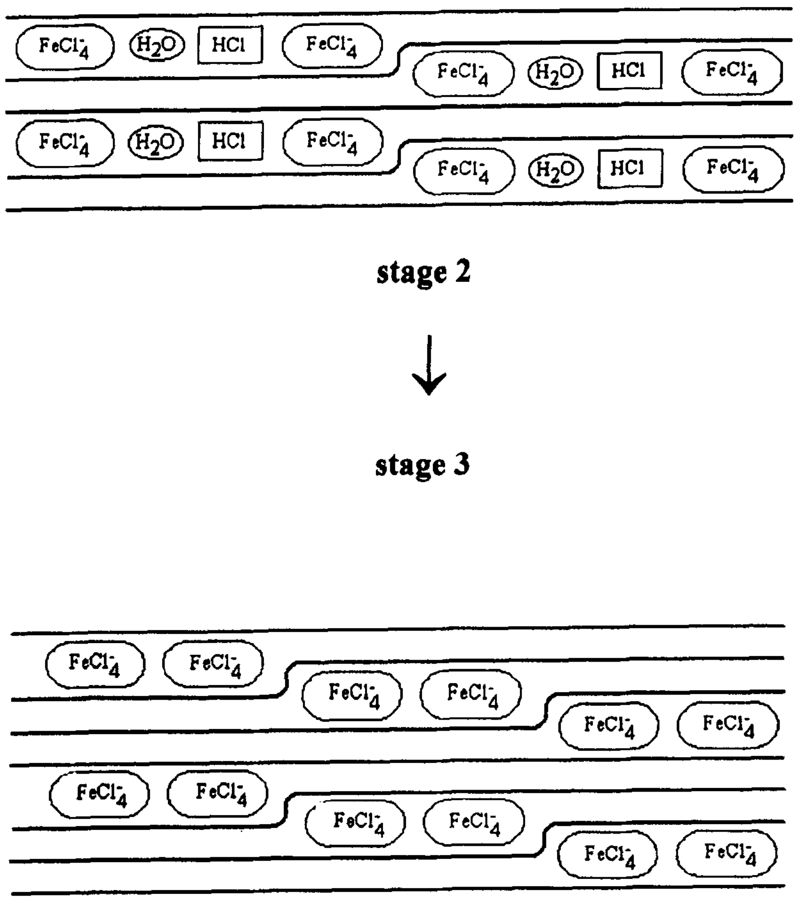

Fig. 2. Transformation of the stage 2 $FeCl_4^-$-GIC into a 3rd stage GIC according to the Daumas–Hérold pleated layer model.

stages (Fig. 3). During the reduction, remarkable exfoliation occurred as an accompanying phenomenon. After pressing the graphite material, XRD patterns confirmed the presence of a 6th stage GIC, LiCl, graphite and Fe° particles, whatever solvent was used. The presence of metallic iron was also confirmed by magnetic investigations. Scanning electron microscopy photographs (Fig. 4) demonstrate the important exfoliation of the graphite matrix. We could detect a number of minute Fe° particles, in the range of 200–300 nm, dispersed on the carbon layers (Fig. 5). This is an indication that the formation process of iron is not due to diffusion of $FeCl_4^-$ anions and subsequent reduction on the edge planes. This material contains small iron clusters on a high surface area matrix; this may allow high catalytic activity.

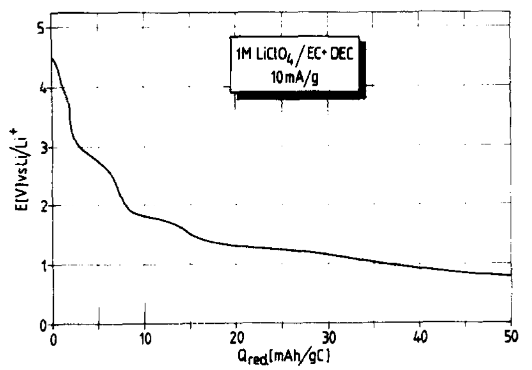

Fig. 3. Electrochemical reduction of the $C_n^+FeCl_4^-$, 1.5 H_2O, 0.5 HCl compound in a 1 M solution of $LiClO_4$ in EC + DEC.

During the reduction process, the colour of the electrolyte turned to yellow-brown or brown, which is the evidence for the dissolution of an iron(III) salt, as demonstrated by atomic absorption spectrometry (AAS) analysis of the residual solution. This phenomenon could originate from the presence of the co-intercalated H_2O and HCl molecules which favor a partial dissolution of iron (III). Therefore, we decided to investigate the reduction of the 3rd stage C_nFeCl_4 derivative formed after pumping.

The "as prepared" 2nd stage $FeCl_4^-$-GIC was pumped under vacuum at 120°C, being pressed between two glass plates to avoid any exfoliation. During reduction in aprotic medium, the potential gradually changed from 4.5–4.3 (OCV) to 0 V, and

Fig. 4. Scanning electron microscopy after cathodic reduction of the 2nd stage $FeCl_4^-$–GIC in aprotic medium.

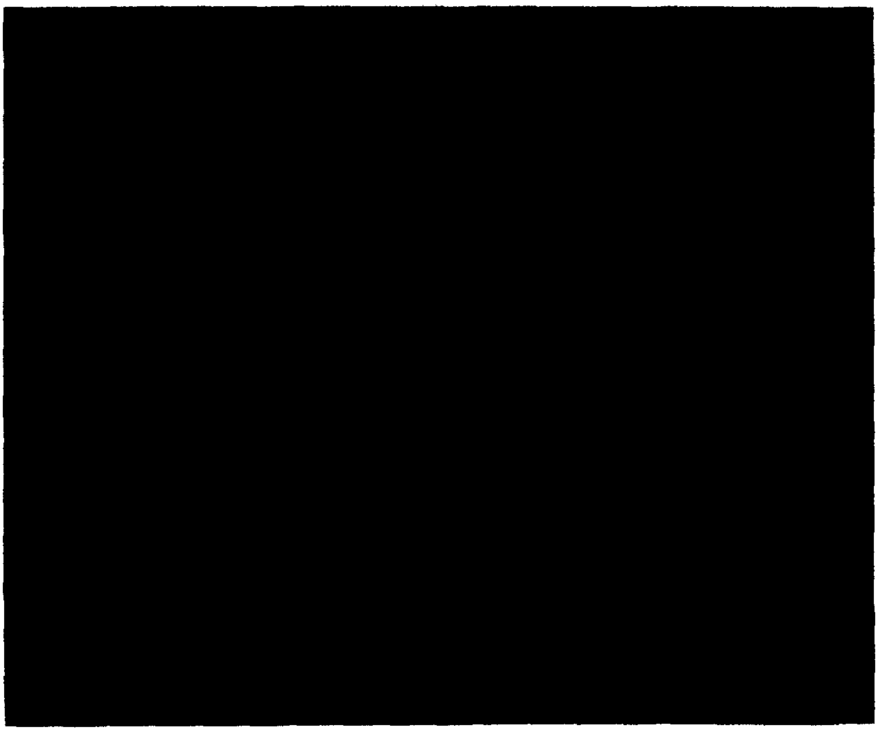

Fig. 5. Scanning electron microscopy on the sample of Fig. 4 showing the iron particles on the 00*l* surface of graphite after exfoliation.

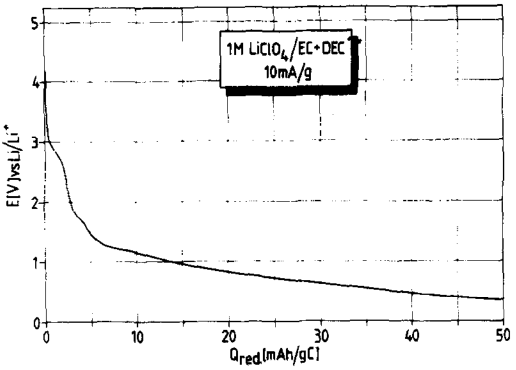

Fig. 6. Electrochemical reduction of the 3rd stage $FeCl_4^-$–GIC obtained after vacuum drying of the $C_n^+FeCl_4^-$, 1.5 H_2O, 0.5 HCl derivative at 120°C. $LiClO_4$ 1 M solution in EC + DEC.

plateaux were also observed (Fig. 6). The GIC did not change the colour of the solution, confirming that in the previous experiment the presence of iron (III) was provoked by the co-intercalated solvents. The other effect of the absence of co-intercalated solvents is that there was not any exfoliation of the HOPG. At the end of the reduction, we observed the $00l$ lines of a 4th stage GIC. Since the starting derivative is a stage 3 phase, the formation of the 4th stage phase could be interpreted by the partial de-intercalation of $FeCl_4^-$ provoked by the cathodic polarization of the GIC. However, this interpretation is not very compatible with the absence of colour of the solution, which should turn brown or dark yellow if $FeCl_4^-$ was de-intercalated. Another effect, to explain the stage increase, could be that the intercalate concentrates on a smaller surface between the graphene layers.

Assuming that the formula of the 4th stage is the same as that found above for the 3rd stage, i.e. $C_{29}FeCl_4$, the available space for the intercalate would be:

$$V_i = 2.62 \times 29/4 \times (I_c - 4 \times 3.35),$$

$$\text{where } I_c = 19.5\,\text{Å}.$$

It gives $V_i = 116\,\text{Å}^3$, which is a little smaller than the value calculated for $FeCl_4^-$ in $NaFeCl_4$, 155 Å^3. Due to the method of calculation, the value of V_i is minimized. If we consider that the Cl atoms of $FeCl_4^-$ could be in the potential holes of the graphite honeycomb, a larger value should be found. Consequently, the formation of a dense 4th stage $FeCl_4^-$–GIC without any de-intercalation of $FeCl_4^-$ appears quite reasonable.

It is noticeable that the quantity of electricity transferred during the reduction of C_nFeCl_4, 1.5 H_2O, 0.5 HCl is definitely greater than during oxidation. The charge is consumed for some other reactions than the simple de-intercalation of $FeCl_4^-$. Theoretically, the formation of Fe(II) is possible at 3.35 V vs Li^+/Li, and Fe° could be formed at 2.19 V vs Li^+/Li. Therefore, partial reduction can only be expected, considering the plateaux of the reduction characteristics above 2 V (Fig. 3). Complete reduction of the intercalated $FeCl_4^-$ anions into Fe° would involve about four times greater a quantity of electricity (406 mAh/g) than the intercalation process.

However, any quantitative interpretation based on the charge passed during reduction is impossible for several reasons. At the end of the reduction, i.e. below 1.5 V vs Li^+/Li, lithium ions may be intercalated into the graphite matrix according to the following equation:

$$\text{GIC} + Li^+ + e^- \rightarrow \text{GIC–Li}.$$

Moreover, the intercalated lithium can react with the co-intercalated solvent molecules, causing the evolution of hydrogen which can contribute to the exfoliation of the graphite specimen. Finally, in the case of PC solutions, electricity can be consumed for its decomposition at low voltage.

4. CONCLUSION

Graphite intercalation compounds, donor or acceptor, are interesting precursors for obtaining supported metallic particles. All the processes are based on the decomposition of the GIC. In most cases, side-products are formed which must be eliminated by water dissolution, which generally induces oxidation of the supported metal.

An all-electrochemical method which overcomes most of the disadvantages has been found. An acceptor type $FeCl_4^-$–GIC has been prepared by anodic oxidation of graphite and then submitted to cathodic reduction in aprotic medium. The 2nd stage $FeCl_4^-$–GIC contains co-intercalated H_2O and HCl molecules, which can be eliminated either by exposing the compound to air or by pumping under vacuum at 120°C.

Different behavior was observed during the cathodic reduction of the $FeCl_4^-$–GIC, depending on the absence or on the presence of co-intercalated solvent. In the case of the dried specimens, reduction to Fe° does not occur, and the most likely reaction is probably intercalation of lithium. The "as prepared" $FeCl_4^-$–GIC strongly exfoliated during the reduction and highly dispersed Fe° particles were formed at room temperature. Such a solid phase may have applications in catalytic reactions for which supported metals are needed. The co-intercalated solvent molecules are responsible for the appearance of Fe(III) species in the solution. When the electrode potential decreases, the Fe(III) is reduced to Fe° at the surface of the exfoliated graphite. Taking into account all our observations, this process is considered better than reduction of iron in the interlamellar space of the graphitic material.

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