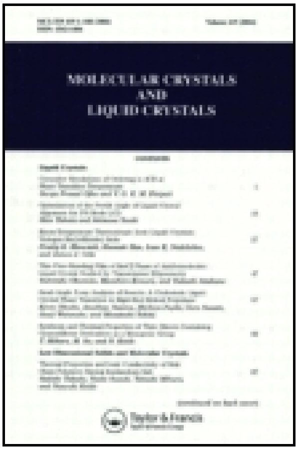

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Graphite and Fullerite Host Structures for Intercalation-Oxido/Reduction Reactions

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Graphite and fullerite C_{60} exhibit low dimensionality crystal structures, which allow to observe numerous intercalation reactions. These latter are always accompanied with an electron transfer. When the graphene sheet or the fullerene molecule have been reduced, we obtain generally strongly reactive anionic species. However, their reducing character can disappear in several cases.

Keywords: graphite; fullerite; oxidizing host structures; potassium; chemical reactivity; reducing anionic species

INTRODUCTION

Graphite is a strongly anisotropic material. It appears indeed as the stacking of graphene planes along its crystallographic c-axis. In these hexagonal graphene planes, each carbon atom, which is sp^2 hybridized, is strongly bound with three other carbon atoms by covalent bonds. These carbon planes are stacked by the means of London's forces, which are rather weak. The interplanar intervals are, for this reason, considered as Van der Waals's gaps, where it is possible to intercalate easily various chemical species. This phenomenon needs that the graphene layers largely spread apart in order to allow the setting up of the foreign atoms or molecules. Because of its amphoteric character, graphite allows the intercalation of electron donor as well as electron acceptor chemical species[1].

Fullerite C_{60} exhibits a three-dimensional stacking of quasi-spherical fullerene molecules. As previously, each carbon atom, which is $sp^{2.3}$

hybridized, is strongly bound with three other carbon atoms by covalent bonds. But, in this case, the graphitic plane is incurvated by the presence of pentagons, which regularly replace some hexagons, and it closes up in quasi-spherical manner. These quasi-spheres are stacked, as in graphite material, by the means of London's forces. As the dense metals, the fullerite material adopts the classical compact face-centered cubic (FCC) structure. For these reasons, the Van der Waals's gaps consist, in this material, of the octahedral and tetrahedral sites of the FCC structure. The large size of these interstitial sites (their diameters reach respectively 416 and 226 pm) allows the intercalation of alkali metal atoms, for instance, without very perceptible increasing of the crystal parameter[2].

Thus, both graphite and fullerite materials exhibit low dimensionality structures. Their dimensionalities are respectively 2 for graphite and 0 for fullerite. Indeed, for graphite, the Van der Waals's gaps are infinite planes, distributed between the graphene layers, whereas, for fullerite, they appear as the interstitial sites of the FCC structure, which are distributed in all directions of the 3D space.

GRAPHITE AND FULLERITE C_{60} AS OXIDIZING HOST STRUCTURES

When the chemical species to intercalate is reducing (electron donor), an electron transfer necessarily occurs from this electron donor to the elemental carbon structure (graphene sheet or fullerene molecule, according to the cases), which appears consequently as a chemical oxidizing species[3].

These reactions are very complex and appear as the result of numerous energetical processes. For instance, the classical intercalation reaction of an alkali metal, as potassium, into graphite or fullerite needs the following energetical operations[4] :

1) the increasing of the crystal parameter, which is very large in the case of graphite and especially weak in the case of fullerite,
2) the sublimation of the alkali metal,
3) the ionization of this same metal,
4) the capture of the electrons by the carbon structure (graphene sheet or fullerene molecule),
5) the setting up of the potassium cations into the anionic host structure (Coulomb's electrostatic energy).

In the aggregate, these intercalation reactions must be considered by the chemist as oxido/reduction reactions. In order to give two examples, we have chosen both synthesis reactions of KC_8 (first stage potassium graphitide) and KC_{60}

(FCC potassium fulleride, for which the potassium cations are intercalated in the octahedral sites) :

$$K + 8\,C_{(graphite)} \rightarrow K^+, C_8^- \quad (KC_8)$$
$$K + C_{60} \rightarrow K^+, C_{60}^- \quad (KC_{60})$$

Due to the electronic transfer, these reactions lead to the formation of C_8^- macroanions and C_{60}^- anions.

The difference of dimensionality between graphite and fullerite (and consequently, their difference of geometry) leads these carbon host structures to exhibit strongly different behaviours concerning their respective way of carrying out intercalation reactions. Indeed, in a first approximation, we can consider the graphene planes as unlimited parallelepipedic blocks and the fullerene molecules as ideal spheres.

The stacking of the blocks is quite contiguous, without empty space, since the π orbitals of two adjacent planes are tangential : the compactness reaches 100 %. For this reason, the intercalation of any chemical species needs systematically the increasing of the interplanar distance. This operation leads to a large expenditure of energy. It is partly, but necessarily, compensated by the Coulomb's electrostatic energy, that exchange anions and cations, so that the charge transfer (that is to say the oxido-reduction phenomenon) appears as strictly indispensable.

On the other hand, the stacking of the molecular spheres is of course imperfect : the compactness reaches only 74 %. Because of the presence of large empty spaces, the intercalation reaction does not produce automatically any increasing of the crystal parameter. However, as previously, the charge transfer occurs again, in spite of a much lower necessity.

REDUCING CHARACTER OF THE C_8^- MACROANIONS AND C_{60}^- ANIONS

Both anionic chemical species appear as strongly reducing ions. Indeed, they react very violently with water (or oxygen), in order to regenerate the neutral graphene layer or fullerene molecule, and consequently the graphite or fullerite material :

$$C_8^- + H_2O \rightarrow 8\,C_{(graphite)} + OH^- + 1/2\,H_2$$
$$C_{60}^- + H_2O \rightarrow C_{60} + OH^- + 1/2\,H_2$$

As usual, the K^+ associated cations do not react, since they appear as classical spectator ions. They remain in solution with the hydroxide anions, which have been produced by the reduction of the water, so that one obtains an aqueous solution of potassium hydroxide.

In both cases, the reduction reaction of the water is possible because the K^+ cations are able to leave the Van der Waals's gaps of the host carbon structure, in order to join the solution. In that manner, this transfer of the cations allows (and needs, in the same time) the discharge of the graphitide macroanions or the fulleride anions, which give up their excess of electrons to the oxidizing water molecules. These latter are reduced consequently in hydrogen gas form ; and this hydrogen is able to react immediately with the atmospheric oxygen, in order to produce water, by the means of a reaction, that appears as very explosive.

The strong reducing character of these anionic species leads the corresponding « ionic salts » to be extremely unstable in the ambient atmosphere. Indeed, they must be always transferred in an inert gas atmosphere (strictly pure argon, for instance).

HOW TO HIDE THE REDUCING CHARACTER OF THE C_8^- MACROANIONS ?

We know several examples of graphitides, for which the transfer of cations from the Van der Waals's gaps to the solution becomes impossible. In these compounds, the K^+ cations are indeed blocked in the host graphitic structure by the presence of a second intercalated element as oxygen or sulphur, for instance[5, 6], that is very more electronegative than the alkali metal.

The intercalated sheets of these ternary compounds always contain two superimposed potassium cations layers and the oxide (or sulphide) anions are sandwiched in the central plane. The presence of these anions in the heart of the intercalated sheets does not allow the K^+ cations to leave the graphitic intervals. Unable to leave the host structure, these K^+ cations prevent the discharge of the graphitide macroanions, so that these latter become unable to give up their excess of electrons to the water molecules.

Consequently, these compounds do not react with water (or oxygen) and appear as very stable in the ambient atmosphere. However, the reducing character of the graphitide macroanions has not disappeared ; it is hided only. This behaviour does not result of thermodynamical phenomena, but it is due to kinetic reasons.

HOW TO ELIMINATE THE REDUCING CHARACTER OF THE C_{60}^- ANIONS ?

In the case of fullerite host structure, we know an example for which the reducing character of the corresponding C_{60}^- anions entirely disappears. Indeed, the KC_{60} compound exhibits the rocksalt FCC structure, since each octahedral site of the pristine fullerite structure is occupied by a potassium cation[7]. But, it is thermodynamically metastable at ambient temperature, and this cubic binary compound, that consists of K^+ cations and C_{60}^- anions, has to turn, below 400 K, into an orthorhombic material, which consists of K^+ cations and $(C_{60})_n^{n-}$ polymeric fulleride chains, in order to become thermodynamically stable[8]. In this last structure, the C_{60}^- anions are polymerized owing to the formation of intermolecular C-C bonds, leading to [2 + 2] cycloadditions[9, 10, 11]. In these anionic chains, four carbon atoms of each C_{60} molecule are of course sp^3 hybridized. The positions of the K^+ cations in the material do not change, but the symmetry of the solid decreases, because the formation of the C_{60}-chains leads to the distorsion of the cubic unit cell, which corresponds to a dissymmetry of the three space directions. Indeed, the observed body centered orthorhombic structure of this material results of a squeezing of the FCC network along the diagonal line of one face of the elemental cube. In this direction, the inter-fullerene distance reaches only 911 pm, instead of 1010 pm, due to the previously mentioned cycloadditions. The weak Van der Waals's bonds, that lead to large intermolecular distances, are replaced, in this direction, by strong covalent bonds, that induce a large decreasing of these interfullerene distances.

On the other hand, this 1D macroanion appears as chemically very stable and does not exhibit reducing properties, so that the corresponding orthorhombic KC_{60} compound is also very stable, when the cubic one, on the contrary, is strongly reactive. We observe indeed that this orthorhombic KC_{60} compound can be easily transferred in ambient atmosphere without oxidation nor alteration. It appears thus that the C_{60}^- anions and the $(C_{60})_n^{n-}$ unidimensional macroanions possess very different chemical properties, concerning particularly their behaviour in the oxido/reduction reactions. We have to underline that the disappearing of the reducing character of this binary KC_{60} intercalation compound is due, in this hypothesis, to thermodynamical grounds.

In an other explanation, it is possible to consider that the K^+ cations become unable to leave the interstitial sites of the new structure, due to the intermolecular bondings, which destroy the mobility of these cations. As previously, these latter prevent the discharge of the $(C_{60})_n^{n-}$ polymeric fulleride chains, which remain unable to give up their excess of electrons to the water molecules.

CONCLUSIONS

As oxidizing host structures, graphite and fullerite C_{60} are able to be reduced by a very reducing chemical species as potassium. The macroanions or anions, that result of the corresponding electron transfer, are associated with K^+ cations, which are intercalated in the Van der Waals's gaps of the carbon host structures, in order to form binary salts, that one names potassium fulleride or potassium graphitide.

As a general rule, fulleride anions and grahitide macroanions appear themselves as strongly reducing species, so that they do not suffer the ambient atmosphere, which is indeed too oxidizing for these anions. They react also very easily with water, that appears likewise as an adequate oxidizing chemical species.

In order to obtain more stable intercalation compounds, it needs to use kinetic conditions, that hide the reducing character of the macroanions (case of graphite), or thermodynamical conditions, that destroy, by the means of an unidimensional polymerization ([2 + 2] cycloaddition), the reducing character of the fulleride anions.

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