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Comparison of the Intercalation into Graphite of Phosphorus-Potassium and Mercury-Potassium Binaries

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Potassium-phosphorus binaries are able to intercalate into graphite as potassium-oxygen or potassium-sulphur binaries, so that phosphorus behave as a classical electronegative element. But, it is able, on the other hand, to behave as a metal such as mercury, so that potassium-phosphorus and potassium-mercury binaries intercalate into graphite by very close synthesis routes. Phosphorus appears thus as a linking element between strongly and fairly electronegative species.

Keywords: graphite; mercury; phosphorus; potassium; ternary GICs; electrical resistivity

INTRODUCTION

In spite of very large differencies in their chemical behaviour, mercury, that is a metallic element, and phosphorus, that is, on the contrary, a metalloïd, exhibit nevertheless relatively close electronegativities (1.9 for mercury and 2.1 for phosphorus in the Pauling's scale).

Associated with potassium, mercury is able to give amalgams (or metallic alloys). It is well established that, in solid state, several intermetallic binary compounds are known [1] : KHg and KHg_2, which exhibit melting points of 180°C and 280°C respectively, and KHg_3, KHg_4 and KHg_8, which exhibit, on the contrary, a decomposition below their respective melting point. In the liquid state, mercury and potassium are miscible for all compositions.

In the case of phosphorus, it is possible, in the solid state, to synthesize several potassium ionic salts [2] : K_3P, KP, K_2P_3 and K_3P_7 (potassium phosphides). But, in the liquid state, the miscibility of phosphorus and potassium seems not to be well known.

We report here a comparison between the respective intercalation into graphite of potassium-mercury and potassium-phosporus binaries.

INTERCALATION INTO GRAPHITE OF K-Hg BINARIES

This intercalation [3] is carried out, at 200°C, between an HOPG platelet and a liquid KHg amalgam, according to the classical route, that is used for the metallic alloys. The reactor is a sealed under vacuum glass tube. The first stage ternary compound, that is obtained, is pink, its chemical formula is $KHgC_4$, and its repeat distance reaches 1016 pm.

If we use as reagent the liquid KHg_2 amalgam, at 300°C, the reaction leads to a blue second stage ternary compound, whose chemical formula is $KHgC_8$ and the repeat distance 1351 pm. The decrease of the intercalated amalgam amount is essentially due to the decrease of the activity of the alkali metal, which is more diluted, and that appears always as the mover element of the intercalation reaction.

In both ternary compounds, the intercalated metallic sheets are three-layered, according to the K-Hg-K c-axis stacking. The 2D unit cell of the intercalated sheet is hexagonal and commensurate with regard to the graphitic one [4].

The graphite-potassium-mercury ternary compounds are more stable in the air than the corresponding KC_8 or KC_{24} binary compounds. But, they are nevertheless largely oxidizable, and it is not possible to handle such samples in the ambient atmosphere.

INTERCALATION INTO GRAPHITE OF K-P BINARIES

If we wish from now on to intercalate into graphite both phosphorus and potassium, we have to carry out the reaction using the route, which allows to intercalate potassium associated with an anti-metallic element such as oxygen, sulphur or selenium [5, 6]. The HOPG platelet reacts, in a stainless steel reactor and under argon atmosphere, at 390°C, with liquid potassium, that contains only 1 at. % of red phosphorus. The reaction product is a blue first stage ternary compound, whose chemical formula is $KP_{0.3}C_{3.2}$ and the repeat distance 886 pm [7]. As previously, the intercalated sheets are three-layered, according to the c-axis K-P-K stacking. In Fig. 1, is drawn the c-axis electronic density profile, which is calculated, by Fourier transform, from the experimental *00l* structure factors of the compound.

The 2D structure of the intercalated sheet is complex. Two different bidimensional unit cells indeed have to be considered in order to describe the arrangement of the intercalated species.

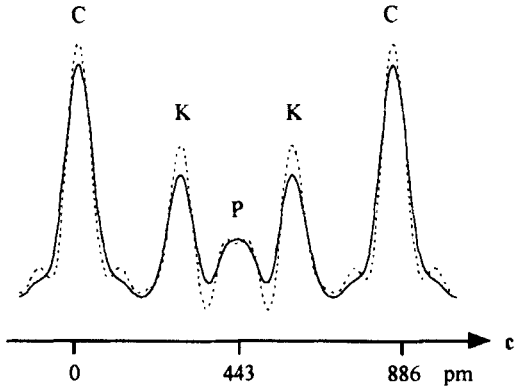

Figure1 : 1D electronic density profiles of the first stage $KP_{0.3}C_{3.2}$ compound (solid line : experiment ; dotted line : model)

We have seen previously that mercury and phosphorus exhibit very close electronegativities in the Pauling's scale, so that it was inviting to consider phosphorus as a « metallic element ». For this reason, it is interesting to try the intercalation into graphite of a potassium-phosphorus binary, using the route usually reserved for the metallic alloys.

This reaction is carried out, at 380-390°C, between an HOPG platelet and a liquid phase, that contains 33 at. % of red phosphorus and 67 at. % of potassium (K_2P composition). By this method, it is possible to synthesize a first stage ternary compound again, that exhibits a repeat distance of 900 pm and still possesses three-layered K-P-K intercalated sheets. In spite of a very large dilution of the potassium in the reagent, the intercalated phosphorus amount remains close to the previous value (P/K = 0.3) and the stage remains unchanged.

When the dilution of the potassium increases again (the liquid phase that reacts with the HOPG platelet contains the same amounts of potassium and phosphorus - corresponding to the KP phosphide -), it is very strange to observe that still occurs the intercalation reaction. The intercalated sheets are still three-layered, according to the same K-P-K sequence. Meanwhile, in this

case, the ternary compound, that is blue-grey, belongs to the second stage. Its repeat distance reaches 1206 pm, and its chemical formula is $KP_{0.05}C_6$. The c-axis electronic density profile of this compound is submitted in Fig. 2. It appears that the decrease of the alkali metal activity becomes enough high in order to induce the change from the first to the second stage. This phenomenon is very frequently observed in the intercalation reactions into graphite of metallic alloys.

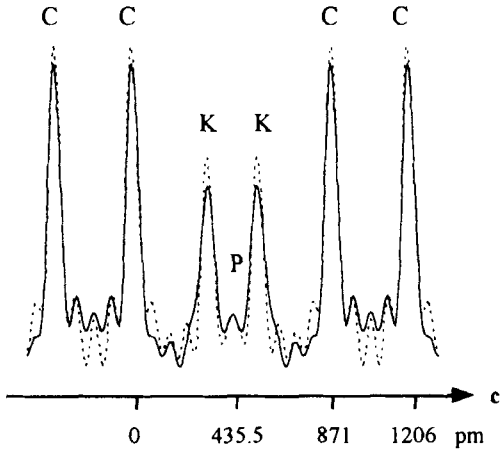

Figure 2 : 1D electronic density profiles of the second stage $KP_{0.05}C_6$ compound (solid line : experiment ; dotted line : model)

In these latter experiments, the phosphorus element, which is clearly a metalloïd, behaves as a metallic species. Indeed, the classical intercalation route used for the metallic alloys is also usable for the phosphides.

All these graphite-phosphorus ternary compounds are remarkably stable in the ambient atmosphere, so that they can be easily handled in the air.

Electrical resistivity measurements were carried out along the c-axis between 300K and 4.2K on both first stage and second stage graphite-potassium-phosphorus compounds, using four points methods.

The first stage compound exhibits a metallic behaviour (Fig. 3a), like numerous ternary graphite-potassium-third element compounds, in which this

element could be mercury or a more electronegative element as a chalcogen. Indeed, the electrical behaviour along the c-axis of the first stage $KP_{0.3}C_{3.2}$ compound is very similar to that of $KHgC_4$ compound as well as that of $KS_{0.25}C_3$ compound. For the second stage graphite-potassium-phosphorus compound, the electrical resistivity shows a maximum around 270K (Fig. 3b). This is typically due to a competition between two conduction mechanisms. The less metallic temperature coefficient for compounds belonging to higher stage than one is well known for ternary GICs and especially for the second stage $KHgC_8$ compound [8].

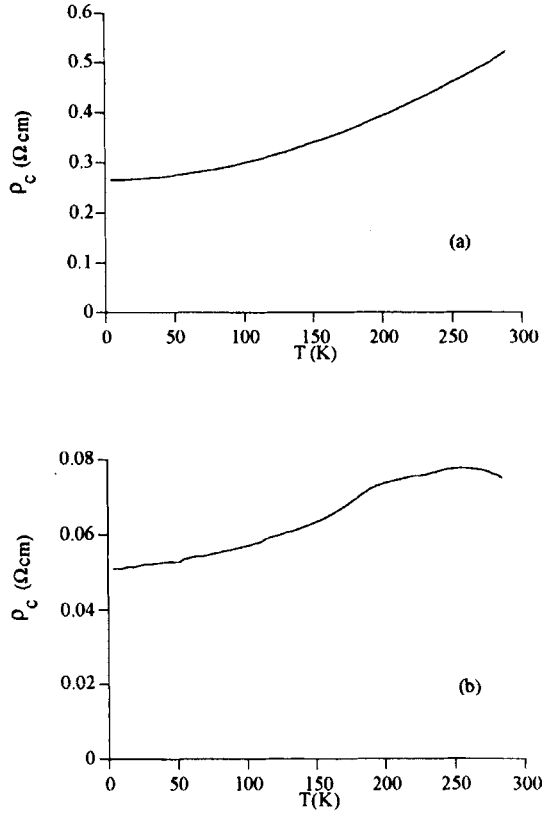

Figure 3 : Electrical resistivity along the c-axis
(a) first stage $KP_{0.3}C_{3.2}$ compound (b) second stage $KP_{0.05}C_6$ compound

CONCLUSION

Concerning its intercalation into graphite assisted by potassium, phosphorus is able to behave as all the largely electronegative elements. A very low phosphorus concentration in the liquid potassium allows indeed to synthesize a first stage ternary compound, whose intercalated sheets are three-layered.

On the other hand, it is also able to behave as mercury. Indeed, the liquid KHg and KHg_2 amalgams lead respectively to first and second stage ternary compounds. In the same manner, the K_2P and KP liquids lead to synthesize also first and second stage ternary compounds. In both cases, the intercalated sheets of these compounds are three-layered, and the more electronegative element (mercury and phosphorus) is sandwiched between two potassium cations planes.

This double behaviour, that exhibits phosphorus, shows clearly that this metalloïd is a linking element between strongly and fairly electronegative elements of the periodic table. The phosphorus metalloïd is thus situated between the mercury metal and the oxygen anti-metal.

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