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A short Overview on the Binary and some New Ternary Sodium GICs

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A short overview on the binary and some new ternary sodium GICs

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In a first part a thermodynamic explanation of the differences between the binary sodium GICs and those of the other alkali metals (low stages lack, octal structures at the high stages) is proposed. The second part mainly concerns the cointercalation of sodium and its halides leading to ternary GICs. Their composition and structure are connected to the reaction temperature and to the structure and lattice energy of the free halides.

BINARY COMPOUNDS

It is well known that the binary sodium GICs differ from those of the other alkali metals by the lack of the low stages. Moreover, the in-plane structure of the sodium intercalated sheets is "octal", leading to the formula NaC_{8s} (s = stage), whereas on and above the second stage, the formula of the heavy alkali metal GICs is MC_{12s}. What are the reasons of these more or less mysterious singularities ?

Lack of sodium GICs rich in metal : a kinetic or a thermodynamic cause ?

Udod et al. [1] have proposed for the alkali metals an original intercalation mechanism called "splitting chain model" founded on the ability of the

diatomic alkali metal molecules to occupy two neighbour crystallographic sites of the graphene sheets. Taking into account the M-M atomic distances in these molecules, lithium and heavy alkali metals should be able to move in the graphite galleries, but not sodium. Unfortunately the diatomic molecules of the alkali metals exist at a very small concentration in their vapour, do not exist in the solid state, nor in the graphite galleries which contain the metal in form of M^+ ions.

Now, let us consider the experimental data : a NaC_{64} compound of stage 8 has been synthesized by Asher and Wilson [2] [3]. Moreover, Metrot et al. have isolated GICs of stages 8, 7, and 6 by action of the sodium saturating vapour on pyrographite samples at 400, 235 and 175°C respectively [4]. The formation of definite stages clearly shows that sodium is mobile in the graphite galleries, although its mobility does not agree with the "splitting chain model". On the other hand, the decrease in stage with temperature cannot be explained by a kinetic model. It is a consequence of the exothermic character of sodium intercalation, in agreement with the principle of Le Chatelier. However the energy of formation is small so that only high stage compounds may be synthesized. This conclusion is confirmed by the easy and massive intercalation of sodium in the soft carbons [5]. In these materials, the graphene sheets contain chemical defects (H, O, N, S atoms) and crystallographic defects (interstitial carbon atoms, sp^3 bonds...) which play the role of electron acceptors, leading to a decrease of the Fermi level, and therefore promote the sodium intercalation with respect to the pure graphite [6]. The number of these defects decreases with the highest treatment temperature (HTT), so that 1rst, 3rd and 5th stage compounds have been obtained for HTT = 650°C, 1250°C, and 1600°C respectively [5].

So the experimental data allow concluding that the cause of the lack of low stages GICs is their thermodynamic instability.

A minimum of stability of the sodium compounds among the alkali metal GICs. How may we explain this irregular evolution in the series ? It is now generally admitted that the intercalated alkali metal atoms are completely ionized. Thus the formation energy of an alkali metal GIC may be

calculated using the following Born-Haber cycle :

- increase in the interplanar distance from 335 pm to the d_i value required by the intercalate thickness :   "spacing work" $E_1 > 0$
- sublimation of the alkali metal $E_2 > 0$
- ionization of the alkali metal $E_3 > 0$
- capture of the electrons by the graphene sheets $E_4 < 0$
- intercalation of the M^+ ions : Coulomb's energy $E_5 < 0$

The formation energy of a GIC is the algebric sum of the positive energies, unfavourable to intercalation and the favourable negative ones. [7]

Now, by passing from Li to Cs, the increase in the radii of the M^+ ions leads to :

- an unfavourable evolution by increasing E_1 and decreasing the absolute value of E_5
- a favourable evolution by increasing the absolute value of E_4 as a consequence of the decrease in the repulsion between the electrons carried by the graphene sheets.
- a favourable evolution by decreasing E_2 and E_3.

Finally the minimum of stability observed for the sodium GICs is a consequence of the variations in parallel and in opposite directions of several positive and negative energies as different and not linear functions of the atomic and ionic radii of the alkali metals.

MC_{8s} formula for the sodium GICs, MC_{12s} for those of the heavy alkali metals on and above the 2nd stage. What is the reason of this difference ?

Intercalation only occurs if the spacing work is balanced by the bonding energy between the graphene sheets and a convenient number of intercalated atoms. In the first stage GICs of the heavy alkali metals the required in-plane concentration of the M^+ ions corresponds to an octal structure (M/C = 1/8). However, the experimental data show that the stability of the GICs increases with stage, thus the bonding energy per metal atom increases too. So, on and above the 2nd stage, the less dense dodecal structure promoted by the in-plane repulsion of the M^+ ions becomes stable. In the case of sodium, the

small bonding energy per metal atom even at the high stage compounds always requires the dense octal structure.

An other factor which affects the in-plane density, thus the formula of the alkali metal GICs is the screening of the Coulomb's repulsion between the M^+ ions by the π orbitals of the graphene sheets. This screening, which promotes the dense in-plane structures of the intercalate goes on increasing from Cs to Li, and is almost complete in the lithium GICs.

Conclusion : the cause of the sodium GICs singularities with respect to those of the other alkali metals is of a thermodynamic nature.

TERNARY COMPOUNDS

Introduction
The ternary sodium GICs are much richer in metal than the binary ones, and many of those belong to the first stage. This is a consequence of two factors :
- the elements or molecules associated with the sodium atoms often play the role of "spacers" [8] : they separate the Na^+ ions from each others and screen the repulsive Coulomb force between these cations.
- the chemical bonds between the two species stabilize the intercalated sheets.

During the last ten years, several GICs in which sodium is associated with the hydroxide [9] [10], peroxide [11] [12] and halide [13] ions have been synthesized in Nancy.

The sodium-graphite-halogen ternaries : principle of the synthesis
Graphite single crystals or pyrographite platelets (PGCCL from Le Carbone Lorraine) are heated in a large excess of liquid sodium in the presence of a halide in the solid (sometimes liquid) state. The reaction is carried out in stainless steel tubes sealed under an argon atmosphere, at temperatures between 450°C and 850°C. The reaction time depends on the temperature and on the nature of the halide, and varies from several hours to about ten days [13].

After reaction the samples are separated from sodium and halide excess by a short washing with cold water : contrary to the binary sodium GICs, the

ternary ones are rather stable in air and cold water. In former, each Na^+ ion repulses the other , and is able to move rapidly to the sides of the sample and reacts with air or water. On the contrary, in the latter, the intercalated atoms of opposite charges are strongly bonded and their mobility is extremely small. Nevertheless, the study of the washed samples by S.E.M. indicates an attack at the side and the surface defects. Therefore the formulae obtained by chemical analysis slightly differ from the crystallographic ones.

The sodium GICs containing chlorine and bromine

Both kinds of compounds are very similar. Below about 500°C, 4th stage ternaries may be obtained ; 3rd stage ternaries between 500°C and the melting points of the halides (801°C and 747°C respectively) ; 2nd stage phases above the melting points. At 850°C in the presence of molten chloride, the reaction time is about one day. Under these conditions, the graphite matrix partly dissolves in the liquid sodium in form of $C-C^{2-}$ ions. The loss of carbon may reach 70% for a pyrographite sample. Moreover, the ternary GICs contain a high number of chloride inclusions visible by S.E.M. and characterized by X-ray diffraction.

The structure of the ternaries containing chlorine and bromine mainly differ by their interplanar distances which are 756 and 771 pm respectively. The intercalated sheets are tri-layered, made of a median plane of halogen atoms surrounded by two planes of sodium atoms distant of 240 pm and 300 pm.

The in-plane lattice of the intercalated sheets is hexagonal, commensurate with that of the graphene sheets and rotated of $\pm$ 30° with respect to its axes. The unit cell, with a parameter $a_i = a_G \sqrt{3}$ contains 2 sodium atoms and 1 halogen atom, and covers 6 carbon atoms. The crystallographic formula of the ternaries is hence $NaC_{3s}X_{0.5}$ in which X = Cl or Br, and s is the stage. The chemical analyses have given for the Na/C ratio values between 85 and 90% of the crystallographic one, and values of 88 to 100% for the Cl/Na and Br/Na ratios. The structure of the intercalated sheets may be connected to the cubic face centered structure of the free halides. If a is the parameter, the distance between two neighbour sodium (111) planes is

a√3/3, 325 pm for NaCl and 345 pm for NaBr. Hence, after intercalation, the pristine distances between the sodium (111) planes are reduced of 26 and 13% respectively. Parallely, the Na-Na distances in the (111) planes of NaCl and NaBr, which are a√2/2, thus 398 and 423 pm in these free halides change into the unique value of 426 pm a_G √3. Intercalation promotes an increase of about 7 and 1% of the in-plane Na-Na distances respectively.

The sodium-graphite-iodine ternaries

Between 450 and 800°C, after a sufficient reaction time, 2nd stage compounds are always obtained. But they differ in their composition and structure. By increasing temperature, the C/Na ratio increases from 5 to 7 approximately, the I/Na from 0.3 to 0.66, the interplanar distance from 768 to 795 pm. Often the intercalated sheets are made of a mixture of two or more phases. At low temperature a pure phase with d_i = 768 pm and an in-plane commensurate lattice of parameter a_i = 3 a_G = 740.5 pm has been often characterized. Its ideal formula is $NaC_6I_{0.33}$. Many phases containing intercalated sheets with hexagonal incommensurate structures of large parameters have been characterized, especially in the compounds synthesized at higher temperatures.

Thermodynamics

The stage decrease by increasing synthesis temperature of the sodium-graphite-chlorine intercalation compounds is a thermodynamic effect : indeed, after heating near 500°C in liquid sodium in the presence of NaCl, sodium-chlorine GICs of stage 2, phases of stage 3 or 4 could be characterized. One can conclude that the cointercalation of sodium and NaCl is an endothermic reaction : as far as we know the first endothermic one in the graphite intercalation chemistry.

The transformation of the tridimensional unit cell of the free halides into an intercalated bidimensional one requires the breaking of a part of the cation-anion bonds, thus absorbs a part of the lattice energy of the pristine crystals, which decreases in absolute value from NaF to NaI (Table I). The intercalation of NaI is probably weakly endothermic : the highest content in iodine has been obtained above the melting point. Those of NaBr and NaCl are largely

TABLE I Lattice energy of the sodium halides (kJ/mole)

NaF	NaCl	NaBr	NaI
- 934	- 775	- 730	- 674

endothermic. That of NaF should be very endothermic : at 1000°C (NaF melts at 988°C), only binary sodium GICs of 7th or 8th stage containing a small amount of fluorine have been obtained. New experiments at temperatures above 1000°C are in progress.

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