Sciences

Chemical Intercalation of Potassium into Natural Graphite

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Abstract

The potassium binary graphite intercalation compound [GIC (K)] was prepared using classical double bulb chemical method and compared with different types of natural vein graphite from Sri Lanka and natural flake graphite of Madagascar. The first stage GIC (K) was always obtained for natural vein and flake graphite. These result indicated that the potassium intercalation does not depend on the graphite's physical texture or their morphology.

Keywords: natural graphite, intercalation compounds, rechargeable batteries

Introduction

Graphite shares in the ability to form intercalation compounds and there are at least two features of these compounds that are unique to the graphite parent. The first is that graphite can form compounds with both electron acceptors and donors. The second is that several distinct compounds can be prepared with the same intercalating species. Usually the most highly intercalated compounds are formed with relatively large alkali metals such as K, Rb or Cs but the compounds with Li and Na are not so easy to form. The chemical compositions for the compounds of M (K, Rb and Cs) are successively MC_6, MC_{24}, MC_{36}....for the stage 1, 2, 3.......

Potassium-graphite intercalation compounds, GIC (K) have been known since the pioneering work of Fredenhagen (Fredenhagen *et. al.*, 1926 and 1929). Since, some of these GIC (with Li in particular) present an interest to modern rechargeable batteries.

Chemical intercalation of graphite (natural and synthetic) with potassium metal has been studied by many authors (Hérold, 1955, Ubbelohde, 1966, Fisher,1970, Nixon, *et. al.*, 1998, Dresselhaus *et. al.*, 2002, Liu, et. al., 2010) but intercalations of different morphologies of natural vein graphite, with alkali metals are not reported elsewhere. The purpose of this study is to understand the chemical insertion of potassium into different types of natural vein graphite (Balasooriya *et. al.*, 2006) and to compare with natural flake graphite of Madagascar. Those are characterized in the following table (Table I).

Table 1: Different types of natural graphite

Country & Location	Occurrence	Graphite morphology
Sri Lanka: Bogala mine (B) & Kahatagaha-Kolongaha mine (K)	Vein	Shiny, slippery, fibrous graphite (BSSI &KSSI) Coarse flakes of radial graphite (BCFR & KCFR) Platy, needle graphite (BNPG & KNPG)
Madagascar	Flake	Graphite powder (E1099)

Material and Methods

Material preparation: Natural Sri Lanka vein graphite samples were collected from graphite mines of Bogala and Kahatagaha-Kolongaha. The raw graphite samples were crushed by using an agate mortar for few minutes and separated using a mechanical sieve shaker to the particle size of maximum 63 microns. The Madagascar graphite (10 microns) was used as received. The potassium metal (Aldrich) was used to be intercalated. Generally potassium metal is stored in a mineral oil to protect it from oxygen and humidity which are very reactive with it. So to eliminate this oil, potassium lump was dipped in benzene or heptane to remove this mineral oil before beginning the experiments. Otherwise, oil vapor may be blocked the potassium vapor to move the other side of the glass tube.

Preparation of GIC**:** The reaction between potassium metal and graphite was achieved by the double-bulb method (Hérold, 1955) (Fig.1). The Pyrex glass tubes are sealed under vacuum and placed in an oven at temperature of 250°C for few days with a little temperature difference between the graphite and the potassium: [T_G (graphite)> T_I (intercalant)].

The compound was transferred from the vacuum-sealed Pyrex glass tube into the X-ray cell by the means of a glove box, filled with argon. The X-ray cell was covered with an aluminum sheet using vacuum grease to protect it from atmosphere. X-Ray diffraction (XRD) studied were carried out within a Philips X-ray generator (using Cu K_α radiation with wavelength λ=1.5406 A°) to verify the structure characteristics of GIC(K).
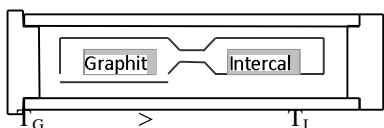

Figure1: Scheme illustrating the "Double-bulb" method

Results and Discussion

General characteristics of the GIC(K):

The blue color, second stage GIC(K) was quickly obtained at the beginning of the reaction. The first stage GIC (K) has a golden yellow color and can be observed after few days.

Crystallography structure of GIC(K) along graphite C-axis:

The several stages of GIC(K) : stage 1 (KC_8), stage 2 (KC_{24}), stage 3 (KC_{36}) and stage 4 (KC_{48}) were identified by Rudörff (Rudörff *et. al.,* 1954). The Rudörff crystallography model of C_8K was concerned the sequence of AαAβAγAδ leading to the formation of hexagonal sites with neighbor distance of 4.92 Å between each potassium atom (Fig.2a). The potassium ions stay systematically in contact with twelve carbon atoms in the intercalated layer, leading to the formation of octal structure according to the Wolten model (Wolten, 1960, Carton, 1972) (Fig.2b & 2c), which is a single geometric model for arrangement of atoms in the first stage of GIC(K) (Setton ,1965) or a rigid spheres model (Guérard *et. al.*, 1984, using the π orbital of carbon (Fig.2d). The result of these work leads to the model of the Fig.2c (Lagrange, 1978): an orthorhombic cell, a = 4.92 Å, b = 8.52 Å consisting in four different layers of potassium atoms with c = 4*Ic =4*5.35 = 21.40 Å .
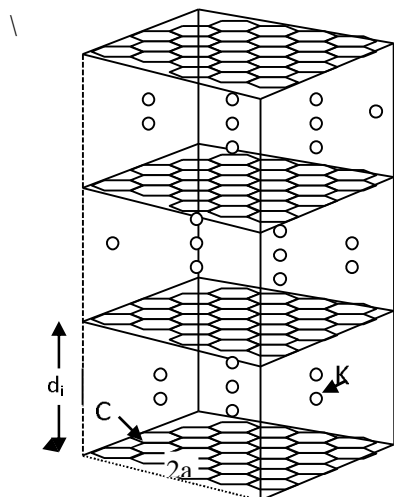
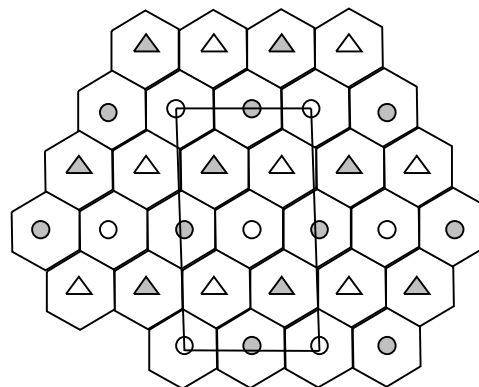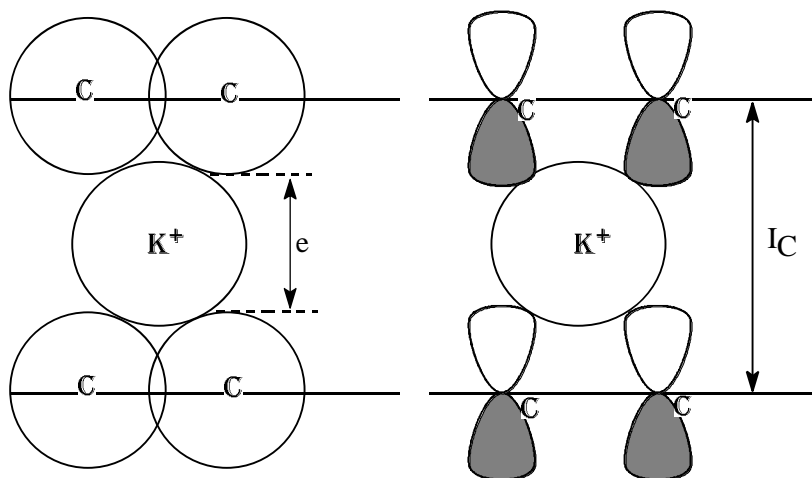**Figure 2a**: Rudörff model of KC_8(d_i=5.41 Å)
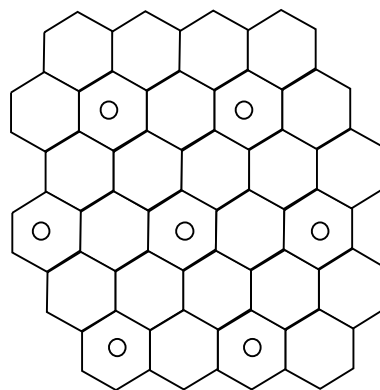
Figure 2b: Arrangement of KC_8 along the c-crystallography axis

2b

2c

Figure 2c: Wolten octahedral model of KC_8 (a=4.92Å, b=8.52 Å and c=21.40 Å)

Figure 2d: Atomic arrangement of GIC(K); I_c-repeat distance along the c-axis and e-thickness of the intercalate layer.

Conductivity of GICs:

The best conductivity at room temperature in GIC intercalated with strong acids, such as SbF_5, AsF_5 is higher than copper (58 x 10^6 Ω^{-1} m^{-1}) (Vogel,1977, Dresselhaus *et. al*., 2002, Eleni Ziambaras *et. al*., 2007). However, Sri Lankan natural graphite posses sufficient electrical conductivity of $0.7 - 1$ x 10^2 Ω^{-1} m^{-1} at room temperature (Amaraweera *et. al*., 2013) . A comparison of principal conductivities for GICs is given in table 3 that shows that in some cases, maximum conductivity is found for second or third stage compounds. The highest conductivities at the room temperature were found for acceptor type GICs but the reason for their higher conductivity is not completely given (Spain, 1981).

The increase in the donor GICs, such as K-GIC can be understood by considering the increase in the density of carriers. For (low intercalation) $C_{36}K$ (third stage) each intercalated metal atom may be considered to donate one electron to the conduction band of graphite. When raise the Fermi energy, the density of holes is reduced until only electrons are present (Fig.3). For (high intercalation) K-GICs (K C_8 and KC_{24}), the Fermi level is believed to be raised above the bottom of the metallic density-of-state curve. In this case of less than one electron per potassium atom is transferred into the graphite conduction band (Spain, 1981). For stronger compounds such as first and second stage GIC(K), the Fermi level is believed to be raised above the bottom of the metallic density-of-state curve. In this case less than one electron per potassium atom, the electron is transferred into the graphite conduction band (Spain, 1981).

Characterization of the GIC(K) using XRD:

The potassium that is an electron donor element, intercalates very easily into graphite leading to the KC_8 binary intercalation compound. The compound with composition KC_{24} is a second stage compound, since two graphite layers exist between each layer of the intercalant (Fig. 4). When intercalation takes place in a perfect crystal of graphite, all atoms are located between layer planes and formed the lamellar compound. When the graphite is imperfect, some intercalant is located sites associated with defects, and is much more strongly bonded. When the compound is heated to remove the intercalant, the remaining compound is called residue compound.

Table 2: Comparison of principal conductivities of graphite and some of GICs (Fisher, 1970)

GIC	σ_a (10^6 Ω^{-1} m^{-1})		σ_a/σ_c
	4-Point	Contact-less technique	
HOPG	2.5	2.6	2.3×10^3
C_8Rb	10	9.1	120
C_8K	10	12	30
$C_{16}Br$ stage IV	22	20	7×10^4
C_6HNO_3 stage I	25	13	2×10^5
$C_{12}HNO_3$ stage II	25	40	....
C_8AsF_5 stage I	25	47	$>10^6$
$C_{16}AsF_5$ stage II	22	58	$>10^6$

D(ε)
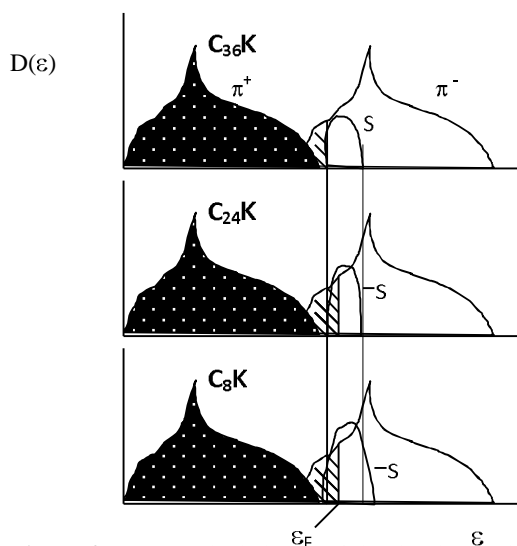
Figure 3: Hypothetical sketch of the density of first, second and third intercalate stages of GIC(K); D(ε), ε, ε_F and S indicate the density of carriers, energy, Fermi level, and density –of-state curve (Spain, 1981).

The first stage GIC(K), which contains a mono-layered intercalated sheet in each graphitic interval, was observed in x-ray diffractogram for different types of natural vein graphite and compared with Madagascar graphite (Fig. 5a, b & c). The reflections of the first stage compound were predominant with an average d_i= 5.35 Å but additional reflections of second stage GIC, near the position of graphite (002) were also observed. Table 3 shows that the variation of interplanar distances of the GIC(K) comparing with some reference values (Madagascar and HOPG).
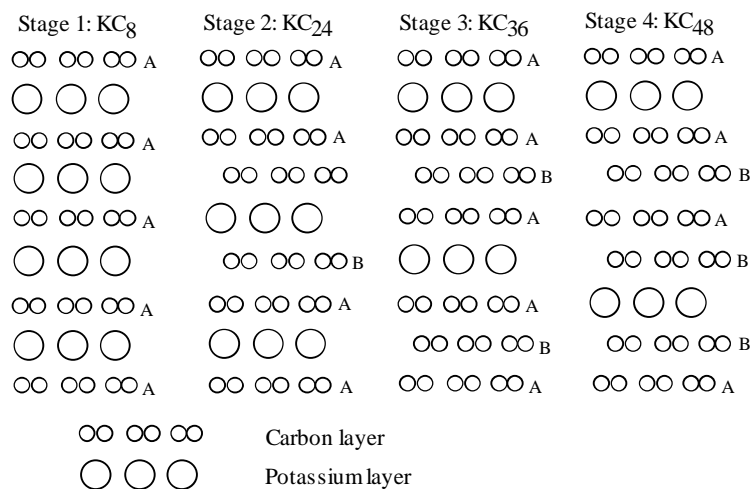

Figure 4, Illustration of the concept of stage for GIC(K)

Table 3: Variation of interplanar distance (d_i) of the GIC(K); The distances, d_i have been calculated using (001) reflection.

Graphite morphology	Particle size	Repeat distance along the c-axis for 1st stage GIC(K), Ic (Å)	d_i (Å)			Ref.
			Stage I	**Stage II**	**Stage III**	
BSSI BCFR BNPG	63µm	5.348 5.372 5.349	5.348 5.372 5.349			

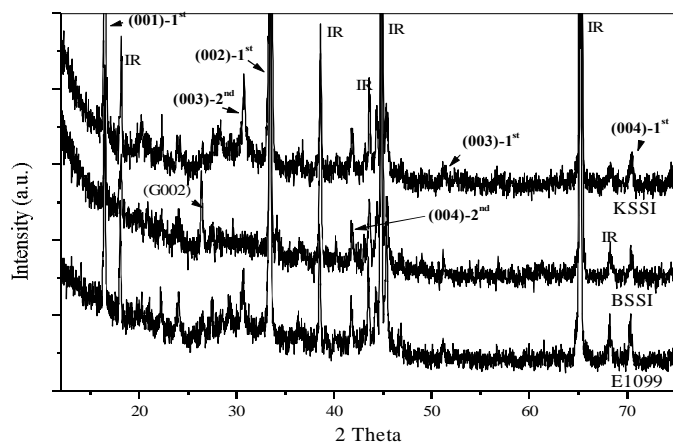|						
KSSI	63µm	5.349	5.349			
KCFR		5.347	5.347			
KNPG		5.353	5.353			
E1099	40µm	5.352	5.352			
HOPG			5.35	8.72	12.10	Parry, 1969
HOPG			5.41	8.77	12.12	Rudörff,1959

Figure 5a: Comparison of the X-ray diffractometry for shiny slippery fibrous graphite (SSI) and Madagascar graphite- E1099 (***IR*** indicates the internal reference of aluminum).
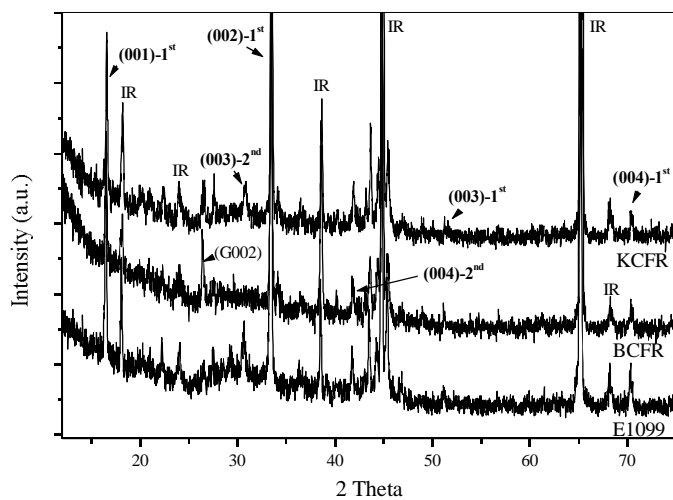

Figure 5b: Comparison of the X-ray diffractometry for coarse flakes of radial graphite (CFR) and Madagascar graphite- E1099 (***IR*** indicates the internal reference of aluminum).
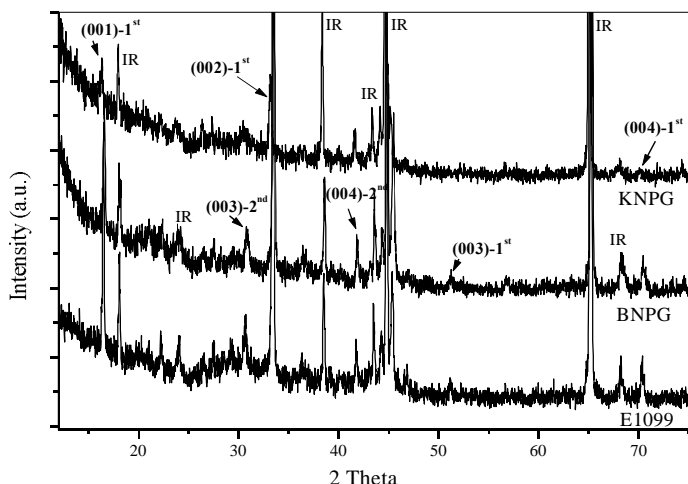
Figure 5c: Comparison of the X-ray diffractometry for needle platy graphite (NPG) and Madagascar graphite - E1099 (***IR*** indicates the internal reference of aluminum).

Pseudo-stage of GICs:

A pseudo-stage compound corresponds to a mixture of disordered stages compounds in the same crystallite. It is different of a mixture of different stages of the compounds. In order to calculate pseudo-stage (s), the strong peaks of both side in the zone of graphite (002) reflection (d_1 and d_2; $d_1<d_2$) were considered. The pseudo stage and thickness of the intercalate layers (e) were calculated for the first stage GIC(K), using the following equation (Buscarlet, *et. al.*, 1976).

For nth stage;

For e<3.35,
$$e = \left(1-\frac{3.35}{d2}\right) \Big/ \left(\frac{1}{d_1}-\frac{1}{d_2}\right) \qquad (d_1<d_2)$$

$$x = \left(\frac{e}{3.35}+n+1\right)\left[1-3.35\left(\frac{e}{3.35}+n\right)\right] \Big/ \left(\frac{1}{d_1}-\frac{1}{d_2}\right)$$

If $0<x<1$, Pseudo stage (s) = n + x

Table 4 shows, that the pseudo stage (about 1.00) and the thickness of intercalate layer (about 2.00) are constant for all vein and flake graphite (Balasooriya *et. al.*, 2013). We have noticed that the concept of pseudo-stage does not exist in the donor GIC contrarily to acceptor GIC (for example $FeCl_3$-GIC).

Table 4: Variation of pseudo-stage and thickness of the intercalate layer of GIC(K)

Graphite type	Particle size	s (Pseudo stage)	Thickness of the inter.layer,e (A^0)
BSSI	63μm	0.995	2.007
KSSI	63μm	0.992	1.998
BCFR	63μm	0.999	2.014
KCFR	63μm	1.000	1.999
BNPG	63μm	0.999	1.994
KNPG	63μm	0.999	1.999
E1099	40μm	1.002	2.004

Conclusion

The potassium binary graphite intercalation compound was prepared by classical double bulb chemical method using different types of natural vein graphite of Sri Lanka and natural flake graphite of Madagascar. The first stage GIC(K) was obtained for natural vein and flake graphite. The potassium intercalation was not depending on their physical texture or morphology. The content of impurities would have affected the intercalation of potassium but natural vein graphite having a high purity (the average carbon content exceeds 95%), no effect of impurities was observed. The ternary potassium GIC can be synthesized by chemical way using an organic solvent (ex: THF, PC…) (Solin *et. al.*, 1988, Dresselhaus *et. al.*, 2002). Generally these

compounds contain very large amount of potassium. The ternary potassium GIC constitutes a good model to understand the behavior of materials for recharging battery electrodes. Indeed, it would be very interesting to elaborate materials containing more and more alkali metal in order to improve their capacity.

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