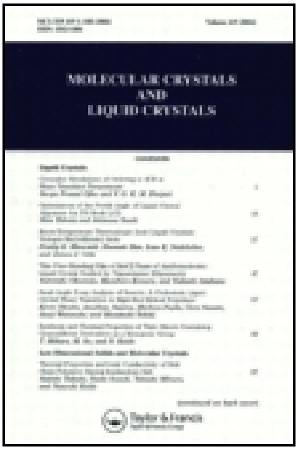

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Percolation Process of the Intercalation of Alkali Metal Atoms and Halogen Molecules into "Carbolite"

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Percolation Process of the Intercalation of Alkali Metal Atoms and Halogen Molecules into "Carbolite"

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The time dependent resistivity associated with the intercalation of alkali metal atoms and iodine molecules into "carbolite", the quasi one dimensional carbon crystal, was measured at a constant temperature. After maintaining a value suitable for semiconducting behavior during a long time of intercalation, the resistivity suddenly decreased by several orders of magnitude, corresponding to a metallic conduction. Alkali atoms or halogen molecules randomly attacked the triangular lattice of the carbon chains and become located at the inter-chain sites. The intercalants of the nearest neighbor sites formed local clusters. As the intercalation proceeded, clusters aggregated to make larger clusters. When aggregation reached such an extent that the cluster sizes were comparable to the sample size, conducting paths throughout the sample opened up. This means that the resistance changes from semiconductive to metallic. This change occurs like an electronic phase transition as the nature of a percolation process.

Keywords: percolation; intercalation; carbolite

CRYSTAL STRUCTURE OF "CARBOLITE"

Carbolite was synthesized in 1995 by the author and A.Palnichenko [1] by condensing carbon atoms onto a copper substrate in a carbon arc in an inert gas, argon or a mixture of hydro-

gen and argon. The carbon film thus obtained with a thickness of a few microns seemed semi-transparent, having a color of pale orange. The crystal structures determined by X-ray analyses are shown in Fig.1 (a) and (b). They show (a) a hexagonal lattice which was obtained in an atmosphere of argon and (b) a rhombohedral lattice in a mixture of hydrogen and argon. (The former is used in this work.) As is seen in the figure, carbon atoms make chains of which a unit length consists of 4 atoms and each chain is made up in a zig-zag way, as the figure shows to provide a quasi one dimensional structure. These zig-zag chains make a triangular lattice in which the inter-chain spacing of 0.344 nm is near the inter-layer spacing

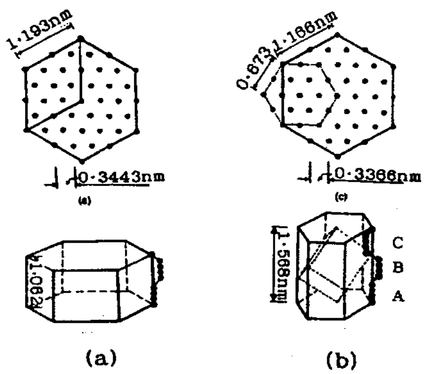
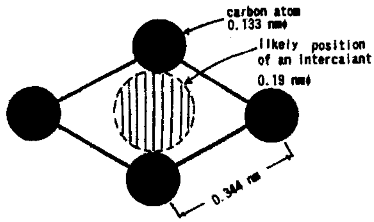


FIGURE 1 Crystal structures of (a) carbolite I and (b) carbolite II.

of 0.335 nm in graphite, suggesting that the inter-chain bonding is π-bonding. The intra-chain atomic spacing is estimated as 0.132 nm on average, which is near the intra-layer atomic spacing of graphite, 0.142 nm, suggesting that the intra-chain bonding is σ-bonding. The specific weight was calculated as 1.46 g/cm^3 and this value was confirmed experimentally. As this value was the smallest among those of the carbon allotropes, the name "carbolite" was given to this material. (Carbolite I and II designate the hexagonal and rhombohedral crystals, respectively.)

INTERCALATION OF ALKALI METAL ATOMS AND IODINE MOLECULES INTO CARBOLITE

The most likely position for the intercalated species is the inter-chain space which is smaller than the diameters of the ions of Na^+, K^+, Cs^+ and I_2^- as shown in Fig. 2. Nevertheless, we expect that the intercalation takes place because the inter-chain force is thought to be of the Van der Waals type for π-electrons and the length of the bonds may stretch in order to accommodate intercalants. Actually the alkali metal atoms and iodine molecules were intercalated and checked by the changes of resistance they produced.[2]



Intercalant ion	diameter of ion
Na^+	0.204 nmφ
K^+	0.276 nmφ
Cs^+	0.340 nmφ
I_2^-	(0.440 nmφ)

FIGURE 2 Comparison of the extent of a hole of the likely position of intercalant species and the diameter of intercalantion.

Carbolite samples for intecalation were prepared on sapphire plates which were used as thermally conducting and electrically insulating substrates with dimensions of 1 cm in length, 1 cm in width and 1 mm in thickness. Four thin gold wires were attached to the corners of the substrate plate by using conducting paste as the lead wires, and the sample assembly and a small amount of intercalant material were sealed in a vacuum in a pyrex tube with vacuum sealed outlets of lead wires as illustrated in Fig.3.

Fig.4 (a),(b),(c) and (d) show the measured curves of the resistance versus the heat treatment time for the intercalations of Na, K, Cs and I_2, respectively. The measurements on Na, K and I_2 was already reported by A.V.Palnichenko and the author.[2]

The common feature of the measured curves, taking Figure 4(b) of K intercalation as an example, is the following. (I) The resistance of the non-intercalated carbolite is about 10 MΩ. (II) The resistance rapidly decreased to hundreds of kΩ by a heating for

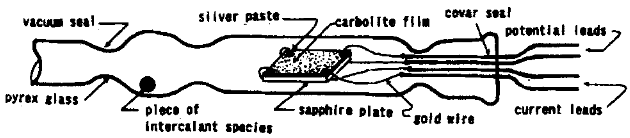


FIGURE 3 Sketch of the reaction tube containing a sapphire plate on which carbolite is deposited and a piece of intercalant material. Carbon chains are directed perpendicular to the sapphire plate.

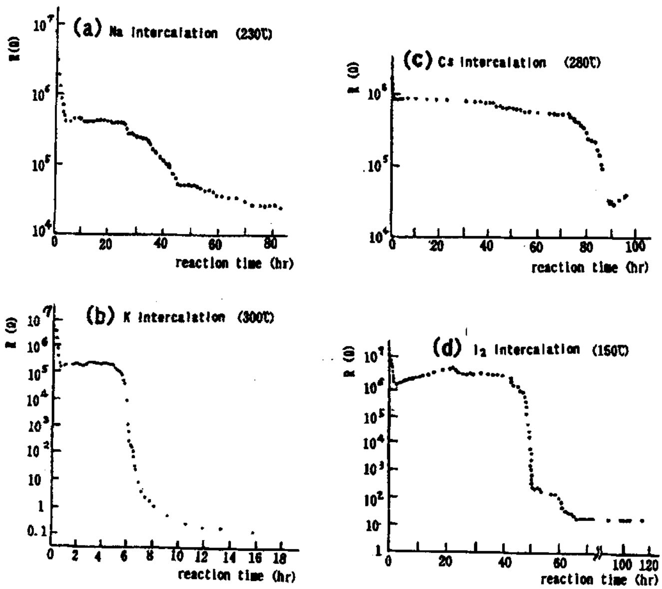


FIGURE 4 Resistance vs. heat treating time. Intercalations of (a)Na,(b)K,(c)Cs and (d)I_2.

the intercalation, and then roughy held its value making a plateau. (Ⅲ)After several hours, the resistance suddenly drops by five orders of magnitude and finally come to a plateau at 0.1 Ω

The resistance of the plateau of step (Ⅱ) is considered as the excitation process of carriers from the impurity level of every intercalant in the context of a semiconductor scheme.

The intercalant species randomly attack the surface of carbolite and make clusters of ions where a cluster means an assembly of intercalated ions occupying nearest neighbor sites with respect to each other. The cluster sizes increase by the progress of the intercalation but remain finite up to the step (Ⅲ). The conduction is limited inside each cluster.

Graphite has honeycomb layers made of σ-bonds. The carriers created by the charge transfer from the intercalated species to the graphite layers can move throughout the graphite layer and contribute to the conductivity of the specimen. Meanwhile, carbolite is made of a parallel assembly of quasi-one dimensional filaments being made of σ-bonds, so the conduction is only along the filament which lies perpendicular to the sample surface.

When the clusters grow through the progress of the intercalation and finally reach sizes comparable to that of the specimen, step (Ⅲ) occurs, i.e., the resistance decreases due to the electrical bridging between carbon filaments by the intercalated ions.

The theory of percolation predicts that the probability p_∞, that a cluster having infinite size appears, suddenly takes place when the percolation probability reaches 1/2 for the trigonal lattice as Fig. 5 shows. (The percolation probability p denotes the probability that an arbitrary site is occupied by an intercalant species.)

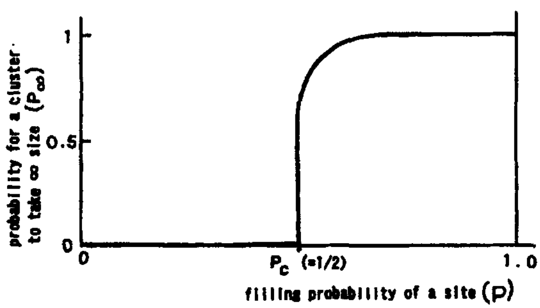


FIGURE 5 Formation of a quasi-infinite cluster for triangular lattice.[3]

Since the appearance of clusters having quasi-infinite size is so abrupt, the achievement of a percolation path is a kind of phase transition. The sudden decrease of resistance is a phase transition from semiconductor-like conduction to metallic conduction when the amount of intercalation results in a percolation probability of 1/2. The heat treating time for making the phase transition, which is directly related to amount of intercalation that has occurred, should be dependent on the kind of species as well as on the heat treatment temperature.

Acknowledgments

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