

DISCUSSION ON THE MECHANISM OF THE INTERCALATION INTO CARBON MATERIALS FROM ORGANIC SOLUTIONS

*O. Tanaike and M. Inagaki**

Graduate School of Engineering, Hokkaido University, Kita-ku, Sapporo 060-8628, Japan

Introduction

In our previous papers[1-6], it was shown that alkali metals and iron chloride were taken up as guest intercalates from their organic solutions into poorly graphitized host carbons to form intercalation compounds. We studied the criteria for host carbon materials by following not only the intercalation reaction into host carbons with different textures and crystallinity but also the degradation behavior of host carbon particles during intercalation reactions. In the present paper, the mechanism for the intercalation reactions of alkali metals and iron chloride in their organic solutions were discussed by considering the governing factors for the formation of ternary and/or binary intercalation compounds.

Crystallinity of Host Carbons

From our results on the intercalation of alkali metals, Li, Na and K, from their solutions of different ethers, it was found that even if ether molecules were coordinated to these alkali metals during intercalation, the lower limit of host on its crystallinity available to be intercalated did not change in most cases, and the disturbance to intercalation of complexes of alkali metals coordinated by organic molecules into poorly graphitized hosts occurred only for a few cases, such as intercalation of lithium in THF as reported in our previous paper[1]. Since the donor alkali metals are easy to transfer their electrons to poorly crystallized carbon hosts having positive holes as carriers, it is reasonable that all carbon hosts, even those with low crystallinity, were intercalated by alkali metals.

It was shown that the limit of host crystallinity for intercalation of FeCl_3 with nitromethane (NM) was at $d_{002} = 0.341 \text{ nm}$, the same criterion of host crystallinity available to be intercalated by FeCl_3 itself from its vapor [7]. Since poorly crystallized hosts do not have carrier electrons which transfer from host carbons to metal chlorides during intercalation, it is reasonable that acceptor metal chlorides could not intercalate into such a poorly crystallized host, in

* Present address: Aichi Institute of Technology, Dept. Appl. Chem., Yakusa, Toyota 470-0392, Japan

contrast to donor alkali metals which could react with almost all carbon hosts. For the intercalation of sulfuric acid, which is the same acceptor, a similar discussion on the criteria of host was performed[8].

Orientation in Host Carbons

The discussion based on the mechanism of charge transfer mentioned above seems to be worth while for all intercalation reactions. However, some hindrances of intercalation were observed for carbon hosts in the critical range for the intercalation both of alkali metals and iron chloride. One of the factors, which have to be taken into consideration, is the orientation of crystallites in host carbon particles.

Pyrolytic carbons had rather high degree of orientation of crystallites, 2D texture, irrespective of graphitization degree and always allowed the intercalation of large complexes of alkali metals and ether molecules, such as Li-THF complexes. On the other hand, the cokes having 3D texture could not be intercalated by large complexes even though they have the same crystallinity measured by X-ray diffraction as pyrolytic carbons. Also for the intercalation of FeCl_3 in NM, pyrolytic carbons showed an advantage for intercalation; they allowed to be intercalated with weak oxidizing conditions, although graphitized cokes with a similar crystallinity did not react.

From these experimental facts, a hindrance from easy expansion of layer spacing in the particles of host carbons was concluded to be very important factor. In pyrolytic carbons, the resistance to expansion is not so strong because of their planar orientation that they can accept even large complexes with weak coordination between main intercalates and solvent molecules. Into cokes, on the other hand, intercalation was hindered because of the difficulty for expansion of particles due to their 3D orientation. This hindrance by coke was mainly limited in poorly crystallized one.

Coordination of Solvent Molecules

Since solvent ethers coordinate to alkali metal cations and to

make them soluble, it can be considered that the voluminous complexes of alkali metals and ether molecules need more force to expand the carbon layers during intercalation. Hence the possible effect of ether molecules on the criterion of host for alkali metals intercalation is mainly related to a steric hindrance, in other words, the resistance to expand in order to accept intercalates. Since the coke with the lower crystallinity is the more difficult to expand, it is very reasonable that voluminous Li-THF complex is prevented from intercalation into poorly crystallized cokes, such as 1500°C-treated ones, even though Li-THF bonding is the most strong.

The effect of ether coordination to alkali metal ions which causes steric hindrance for their intercalation was thought to be enhanced for sodium compared with lithium and potassium. As a consequence, a steric hindrance to prevent from co-intercalation of ether molecules with sodium was considered to occur with a wide range of carbon hosts and many ethers. Detailed relation between the hindrance and the coordination style of ether to sodium has been discussed in our paper [4].

For the intercalation of FeCl_3 in NM, no size effect of NM molecules on the intercalation was anticipated because nitromethane itself had a smaller size than that of FeCl_3 . One possible role of NM during intercalation of FeCl_3 was to modify the mechanism of electron transfer from host carbon to intercalates since NM had a role not only to coordinate to FeCl_3 but also to create an oxidative atmosphere in the solution of FeCl_3 .

Discussion on the Mechanism

In Fig. 1, a schematic mechanism of intercalation into poorly crystallized carbon hosts is illustrated. This model was mainly based on the present results of alkali metals intercalation in ether solutions, but believed as a useful guide for many other intercalation.

Intercalate consisted of complex of more than two species has a possibility to deform their morphology in carbon gallery during intercalation. Strong coordination results in the formation of ternary intercalation compounds with large interlayer spacing, but weak and/or voluminous one is governed by its steric hindrance and results in either deformation of the complex or prevention from intercalation. 2D texture of host carbons can accept the complexes with relatively small steric hindrance, but 3D texture causes hindrance due to the difficulty for the expansion.

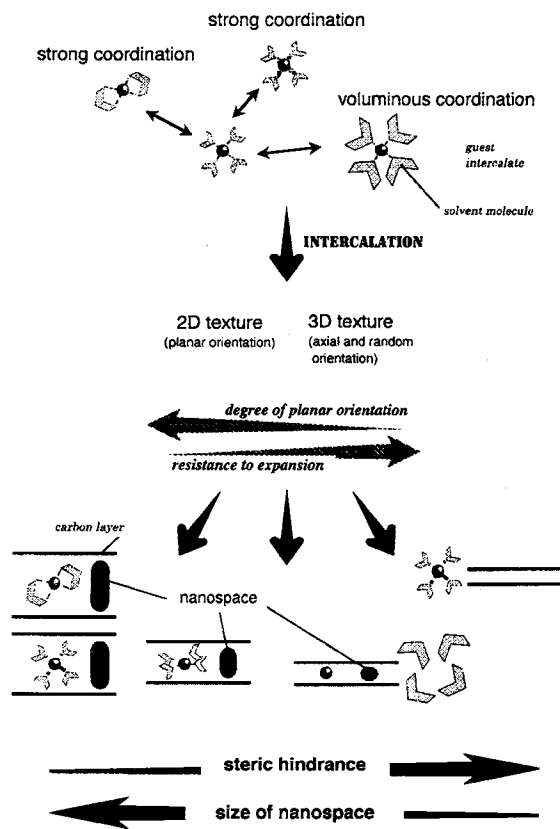


Fig. 1 Scheme of the mechanism for the intercalation in organic solutions

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References

- [1] Inagaki M, Tanaike O. J Phys. Chem Solids 1996; 57: 795-798.
- [2] Tanaike O, Inagaki M. Carbon 1997; 35: 831-836.
- [3] Tanaike O, Inagaki M. Synth Met 1997; 90: 69-72.
- [4] Tanaike O, Inagaki M. Synth Met 1998; 96: 109-116.
- [5] Tanaike O, Hoshino Y, Inagaki M. Synth Met (in press).
- [6] Tanaike O, Inagaki M. Carbon (in press).
- [7] Sugiura T, Sato M. 18th annual Meeting of Carbon Society of Japan, 1991.
- [8] Inagaki M, Tanaike O, Iwashita N. Synth Met 1995; 73: 83-85.