

## Stage transformation characteristics of Li, K and Na-graphite intercalation compounds

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### Li, K과 Na-흑연 층간화합물의 stage 전이특성

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**Abstract** Stage transformation characteristics of Li, K and Na-graphite deintercalation compounds (GDICs) were studied under consideration of a deintercalation mechanism of the intercalants between carbon layers. Li-graphite intercalation compounds (GICs) synthesized by a controlling temperatures and pressures have been spontaneously decomposed in the atmosphere. By X-ray diffraction analysis the  $d_{001}$ -values of stage 1 and 2 were identified to be 3.71 and 7.06 Å, respectively. After 6 weeks, the deintercalation reaction of the Li-GICs ceased and only residual compounds could be observed. K-GICs were synthesized by the modified two-bulb method resulting in structural stabilities and stage transitions. By X-ray diffraction analysis the very stable K-graphite residue compounds were observed after 10 weeks. Na-GICs with stage 1 and 2 were synthesized using the high temperature and pressure technique. The temperature dependence of a deintercalation reaction and a thermal stability of Na-GICs were discussed. The structure changes of the Na-GDICs depending on heating rates were identified by X-ray diffraction. According to the deintercalation process, the stage transformations could be attributed to irregular deintercalations of the GDICs with disordered stages.

요 약 Li, K과 Na-흑연 층간화합물의 stage 전이 특성을 탄소층사이에 존재하는 intercalants의 deintercalation 메커니즘을 고려하여 제시하였다. 온도와 압력을 조절하여 합성된 Li-GICs(graphite intercalation compounds)를 분위기하에서 자발적으로 분해시켰다. 이들 화합물을 XRD 분석한 결과 1, 2 stage의  $d_{001}$ -값이 각각 3.71, 7.06 Å으로 나타났다. 분위기하에서 Li-GICs를 deintercalation 반응을 시킨 6주 후에 잔유화합물이 형성됨을 알 수 있었다. 또한, two-bulb 법으로 K-GICs를 합성하였으며, K-GDICs(graphite deintercalation compounds)의 구조적 안정성과 stage 전이에 대하여 조사하였다. X-선회절 결과로 부터 K-GDICs는 10주 동안 안정한 K-흑연 잔유 화합물을 형성하였다. 그리고 고온, 고압법을 이용하여 합성된 1, 2stage의 Na-GICs의 deintercalation 반응과 열적 안정성에 대한 온도 의존성에 대하여 논하였다. 열적 안정성과 관련하여 Na-GDICs의 구조변화를 XRD에 의하여 확인하였다. 이들 과정에 따르면 stage 전이는 무질서한 stage를 가진 GDICs의 불규칙적인 deintercalation에 의하여 형성됨을 제시할 수 있었다.

## 1. Introduction

A great deal of attention has been given to the preparation of the graphite intercalation compounds (GICs) formed by the insertion of atomic or molecular layers of guest chemical species, called the intercalate, between layers of a host material. The stability of the GICs is a crucial factor in the practical industrial and space or aircraft application of these materials [1-4].

Recently in putting the lithium secondary battery with high density and high output to the practical use the reversibility between the charge and discharge of lithium intercalation compounds which are used as an anode is on the rise as an important factor for battery mechanism [5]. The graphite has a layer structure, and the distance between the two layers is about 3.36 Å ( $d_{002}$ ), it means that the basal spacing is wide enough for lithium ion to be intercalated between the layers and to be used as an

anode for the lithium battery. In case of such Li-graphite intercalation compounds which are used as an anode for the lithium battery the intercalation and deintercalation process has to be performed easily. By the intercalation reaction Li-graphite intercalation compounds in form of  $\text{Li}_x\text{C}_6$  could be obtained and by the deintercalation process those in the form of  $\text{Li}_{(x-y)}\text{C}_6$ , where the values of  $x$  and  $y$  act as factors which determine the quantities of lithium obtained during the intercalation and deintercalation process.

The synthesized K-GICs are very unstable under temperature, pressure, humidity ( $\text{OH}^-$  and  $\text{O}_2$  in atmosphere) and other factors, and thus they can be readily decomposed upon exposure to the air or in contact with water. Daumas et al. [6] extensively investigated the chemical properties of K-GICs for various gas atmospheres. Therefore, many authors [7-8] have tried to study on the stability of GICs to solve

this problem.

Asher [9] reported the lamellar compound of sodium and graphite having an ideal formula  $C_{64}Na$  in which sodium was intercalated in every eighth interplanar gap appeared to be analogous to the K-, Rb- and Cs-graphite lamellar compounds. Belash et al. [10] synthesized the GICs with sodium  $C_2Na$  and  $C_3Na$  at  $T=450^\circ C$  and  $P=15-50$  kbar, thereby indicating complete interaction of sodium with graphite, and refuted the notion concerning the impossibility of formation of Na-GICs of low stages. Recently, Udod et al. [11] have suggested that the limiting composition of the high pressure phase of Na-GICs at 40 kbar is  $NaC_2$  having a two-layer package of intercalate.

However, most work was phenomenological in nature because of the complex deintercalation reaction. Therefore, more detailed information about the stage transformation characteristics is required for improved understanding of intercalation and deintercalation behavior of Li, K and Na-graphite deintercalation compounds (GDICs). In this work, the observation of deintercalation of Li, K and Na-atom from GICs is reported under consideration of a deintercalation mechanism of the intercalants between carbon layers. The structure change, thermal stability and temperature dependence during their deintercalation reactions will be discussed.

## 2. Experimental

Li-GICs were synthesized with natural graphites as a host material and a lithium metal. For this purpose, we have chemically purified the natural graphite (Sagjin, Korea) with a flake of size between 0.074-0.419 mm. The resultant purified natural graphite has the carbon contents of 98.08 ( $\pm 1.51$ ) %. As an intercalant lithium in form of metal (Strerm Chemicals, Inc., U. S.A.) was used. For controlling the reactions, atmosphere gases such as Ar,  $O_2$  and  $N_2$  with a purity of 99.999 % have been used. Li-GICs were synthesized by the chemical method under temperature and pressure with the lithium metal (30 wt%) and the chemically purified natural graphite. The samples were reacted at temperatures of  $200-220^\circ C$ , under pressures of ca.  $350-400$  kg/cm<sup>2</sup> in argon atmosphere for 18-20 h. In order to investigate the reactivity of the Li-GICs under the atmosphere of  $O_2$  and  $N_2$ , we have made the Li-GICs as minimal in size as possible. The compounds were then oxidized under a condition of the ratio 2:8 for  $O_2$  and  $N_2$  for the slow reaction. Some quantities of the oxidized Li-GDICs were characterized.

K-GICs were synthesized in the evacuated and sealed modified two-bulb pyrex tube. It was manipulated in a vacuum glove-box. For avoiding the oxidation, the prepared K-GICs were put into liquid paraffin in a dry inert gas atmosphere. Deintercalation reactions of the K-GICs were performed by spontaneous reductions under a long term exposure to air in a



n:stage number

For the intercalation process the temperature and the pressure have to be considered, while for the deintercalation reaction the oxidative factors have to be considered as mentioned above. Structural changes occurred during the decomposition process of the Li-GICs could be confirmed by the development of (*hkl*) interference for the Li-GDICs shown in Fig. 1. From the Fig. 1, pure stage 1 of graphite intercalation compounds was formed at first. After contact with the gas for 1 h, the pure 1 stage compounds was not formed any more, but stage 1 and 2 compounds are mixed for 3.71 Å and 7.07 of  $d_{001}$  values, respectively. In this case the characteristic gold color for the stage compounds has been disappeared, while the blue color has been appeared. From the results obtained after 1 week, almost the same feature is observed as the result obtained after 1 h with an increasing of the reflections.

According to the X-ray reflection analysis obtained after two weeks, the reflections for stage 2 reduced, the reflections for stage 5 began to appear and most of the peaks for the nonintercalated original graphite appeared. From this result, it is noted that the oxidation proceeded considerably during this reaction time of two weeks. After 3 weeks, the reflections for stage 2 reduced more than after 2 weeks, those for stage 5 increased, and the additional ( $d_{112}$ ) reflection for the nonintercalated original graphite appeared. From the X-ray analysis for the

compounds obtained after 4 weeks, the reflections for stage 1 disappeared completely, (3s007) reflection for stage 3 are formed and those for stage 5 appeared predominantly.

After 5 weeks, the same features were formed as those after 4 weeks. After 6 weeks, only the reflections for stage 5 could be observed, while all the others disappeared. After more than 6 weeks the unchanged same features are observed in X-ray reflection. And no additional peaks for the nonintercalated original graphite have been obtained.

If the deintercalation reaction was performed completely, the reflections for all stages disappeared and only those for the nonintercalated original graphite should appear.

However, according to the experimental results after more than 6 weeks, the reflections for stage 5 still exist, while no peaks for the original graphite have been formed. Consequently, it is assumed that Li-ions which could not decompose from the interlayer still exist between the graphite layers and form the Li-residue compounds. It could be explained as follows; An oxide compound of  $\text{Li}_2\text{O}$  will be formed by the reaction of oxygen ( $\text{O}_2$ ) on the surface area of Li-GICs with the Li-ions which exist between the layers. The Li-ions do not decompose from the interlayer so that the Li-residue compounds could be formed. The decomposition of Li-GICs could proceed as follows:

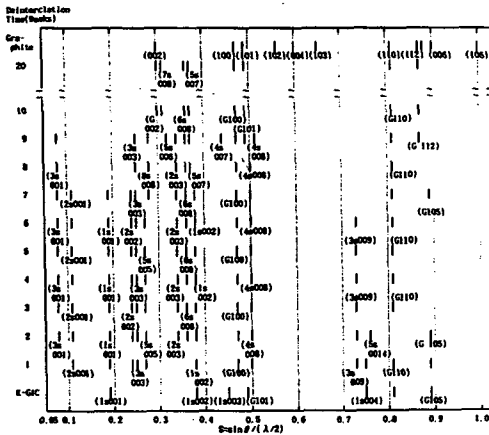
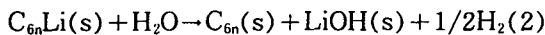


Fig. 2. Development of  $(hkl)$  reflections for the potassium-graphite deintercalation compounds. (1s:stage 1, 2s:stage 2, 3s:stage 3, 4s:stage 4, 5s:stage 5, 6s:stage 6, 7s:stage 7, G:graphite).



### 3.2. Deintercalation of K-GICs in liquid paraffin

X-ray diffraction data were obtained for several deintercalation times over 20 weeks. The deintercalation of K-GICs occurred continuously upto the 9th week. development of  $(hkl)$  interference for the K-GDICs is shown in Fig. 2. The deintercalation reaction of K-GICs was no more done after the 9th week. We can discuss the effect of the formation of higher-stage K-GDCs by reduction with the change of basal spacing and stage-number. At first, we have obtained the d-value of

5.3528 Å for (001)-interference for stage 1 of the K-GICs. After the 1st week, however, the disordered forms of stage 1, stage 2 and stage 3 for these compounds are observed, and the  $d_{001}$  value for stage 2 is 8.7248 Å, while the  $d_{001}$  value for stage 3 could not be observed. After the 2nd~7th week of the deintercalation time, the transitions of stage 1, stage 2, stage 3, stage 4 and stage 6 are observed, while after more than 10 weeks, only the stage 5, 6 and 7 are observed. After more than 10 weeks the K-GDICs have not been changed any more. From this fact, we can suggest that the K-GDICs after more than 10 weeks could be considered as the very stable K-graphite residue compounds. And we could observe that the long range disorder in layer is accompanied by the reduction of potassium between layers, which occurs from stage 1 ( $C_8K$ ) to stage  $n$  ( $C_{12n}K$ =Residue compound). We can also see stages with non-integral (001) diffraction indicating defect disorder and irregular basal spacings. From this results, the reaction rate is proportional to the amount of  $H_2O$  molecules existing in atmosphere and the K-GICs are very stable in liquid paraffin.

### 3.3. Thermal stability and deintercalation of Na-GICs

The thermal stability and deintercalation reaction of Na-GICs for stage 1 and 2 were characterized using DSC to temperature of 500°C (Fig. 3). The structural

changes of Na-GICs depending on the heating rates were identified by the XRD as shown in Fig. 4. The perfect compound for stage 1 could not be found in the Na-GICs.

A weak diffraction peak could be observed on the (001) interference for the stage 2. The observed compound of  $\text{NaC}_{64}$  for the stages were reported by the previous workers [9,12]. In this study, we could obtained blue and red Na-GICs for stage 1 and 2. Deintercalation compound for stage 1-5 could be found by the deintercalation process of the compounds with the heating to the temperature of  $500^\circ\text{C}$ , in which the stage 3 was a main structure in the deintercalation compounds.

#### 4. Conclusions

Li-GICs were synthesized by a controlling temperatures and pressures and spontaneously decomposed in the atmosphere. The  $d_{001}$ -values of stage 1 and 2 were identified to be 3.71 and 7.06 Å, respectively. After 6 weeks, the deintercalation reaction of the Li-GICs ceased and only residual compounds could be observed.

K-GICs were synthesized by the modified two-bulb method resulting in structural stabilities and stage transitions. The very stable K-graphite residue compounds were observed after 10 weeks.

Na-GICs with stage 1 and 2 were synthesized using the high temperature and pressure technique. The deintercalation reac-

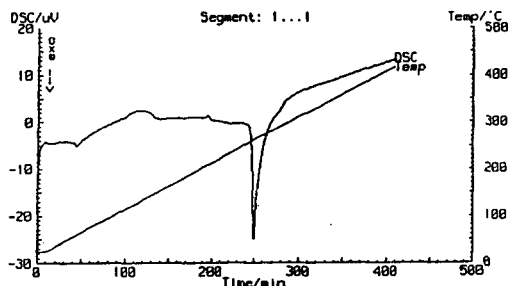


Fig. 3. Differential scanning calorimeter analysis of Na-GDICs showing the endothermic reaction for heating.

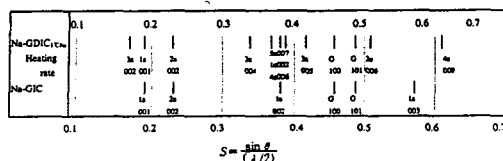


Fig. 4. X-Ray reflection for the deintercalation of Na-graphite intercalation compounds. (1s:stage 1, 2s:stage 2, 3s: stage, 3....., Gs:graphite).

tion and thermal stability of the Na-GDICs were dependent upon heating rates.

Stage transformation characteristics of Li, K and Na-graphite deintercalation compounds could be proposed under consideration of the deintercalation mechanism of the intercalats between carbon layers. As the deintercalation process, the stage transformations could be attributed to irrregular deintercalatuons of the GDICs with disordered stages.

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