

## 칼륨-인조 흑연 층간 화합물의 고온열적 안정성과 Deintercalation

오원춘 · 이영훈 · 고영신\*  
한서대학교 화학과  
\*서울교육대학교 탄소화학연구소  
(1997. 8. 1 접수)

### Thermal Stability and Deintercalation of K-synthetic Graphite Intercalation Compounds at Elevated Temperatures

Won-Chun Oh, Young-Hoon Lee and Young-Shin Ko\*

Department of Chemistry, Hanseo University, Chungnam 352-820, Korea

\*Institute of Carbon Chemistry, Seoul National University of Education, Seoul 137-742, Korea

(Received August 1, 1997)

**요 약:** 변형된 two-bulb pyrex관을 사용하여 K-SGICs(인조흑연 층간화합물)를 합성하였다. 흑연과 칼륨을 반응시키기 위하여 two-bulb관내에 압력을  $10^{-3}$  torr로 유지하여 주었다. 변형된 방법에 의하여 얻어진 K-SGICs는 유동 파라핀 내에서 25~1400°C 사이에서 열처리하여 deintercalation을 시켰다. K-SGICs의 온도 의존성과 열적 안정성을 DSC 분석기에 의하여 특성화하였다. K-SGIC의 엔탈피와 엔트로피 형성은 여러 온도에 의존하는 열역학적 발열반응과 deintercalation을 확인하여 계산하였다. 칼륨 이온의 deintercalation 반응이 일어나는 동안 K-SGICs의 구조변이와 열적 안정성을 XRD에 의하여 확인하였다.

**Abstract:** K-SGICs(synthetic graphite intercalation compounds) were synthesized in a modified two-bulb pyrex tube. The pressure in the two-bulb tube was maintained at approximately  $10^{-3}$  torr for the reaction of potassium and graphite. Deintercalation process of the K-SGICs obtained by the modified method was heat-treated by keeping in liquid paraffin between 25°C and 1400°C. The thermal stability and the temperature dependence of the K-SGICs were characterized using differential scanning calorimeter(DSC) analyzer. Enthalpy and entropy for K-SGIC formations were calculated by confirming the deintercalation and thermodynamic exothermic reactions depending on the various temperatures. The structure changes and thermal stability of K-SGICs during the deintercalation reaction of potassium ions and the interlayer spaces of the synthetic graphite were identified by X-ray diffraction(XRD).

**Key words:** Potassium, Synthetic graphite, Deintercalation, Stability, Enthalpy and entropy, DSC, XRD

#### 1. INTRODUCTION

A tremendous worldwide growth in research activity in recent years have been witnessed in the field of graphite intercalation compounds (GICs). Many questions concerning the origin of the kinetics of staging formation and transitions, the complex

structure of modulated intercalate layers in higher stage compounds, the vibrational excitations and diffusion of the intercalates, are crucial factors in the practical industry and space or aircraft applications.<sup>1</sup> The GICs are categorized according to their charge transfer and the number of different atomic or molecular species within the host galleries. GICs in which

the intercalates donate electrons to the host graphite layers are called donor compounds, while those which extract electrons from the host are labeled as acceptor compounds. For donor compounds, many theoretical studies on their stability have been reported dealing with the mechanism and kinetics of the intercalations and the staging transitions concerning with structural staging mechanisms and stage disorders.<sup>2,3</sup>

However, the donor compounds such as Li-, K-, Rb-, Cs-GICs are extremely unstable and pyrophoric in the atmosphere of air with high humidity.<sup>4-9</sup> In a previous study,<sup>10</sup> the stability of K-GDICs (graphite deintercalation compounds) were reported. The investigation aimed at providing the synthesis of the K-GICs by a modified two-bulb, structural stability and stage transition in the K-GDICs. This investigation of the deintercalation of the K-GICs using natural graphite flakes was performed by spontaneous oxidation during long term exposure to air in a closed chamber at ambient temperature of  $25 \pm 1$  °C and humidity of  $60 \pm 2\%$ , respectively, by keeping in liquid paraffin.

Therefore, more detailed information about the stability and deintercalation behaviour at elevated temperatures are required to understand the deintercalation mechanisms. In present work, we have synthesized K-GIC using synthetic graphites and investigated the deintercalation reaction and thermal stability at elevated temperatures.

## 2. EXPERIMENTAL

For experimental studies on GICs two main types of host graphite material are used: natural graphite and synthetic graphite. The most commonly used host material in GIC research is a synthetic form of graphite. In this study, we have synthesized graphite powders as a host material by heating petroleum cokes at 2300°C for 10 h. The synthesized graphite has a purity of  $98.05(\pm 1.66)\%$  and a crystallite size of 0.074–0.177 mm in diameter. This is a textured polycrystal with a well defined c-axis and random a- and b-axis orientation. As an intercalant, potassium was used in form of metal manipulated in a glove-

box under a dry inert gas. Liquid paraffin was used as stabilization agent for K-SGICs (synthetic graphite intercalation compounds).

The potassium GICs were synthesized in a modified two bulb pyrex tube, evacuated and sealed with vacuum grease, in which 3–4 g of graphite sample and the appropriate amount of potassium metal were placed. The pressure in the two-bulb tube was maintained at approximately  $10^{-2}$  torr for reaction of potassium and graphite. For degassing, the graphite in the bulb was heated under vacuum before starting the reaction until the temperature of graphite ( $T_g$ ) had reached a high temperature above 150 °C. The other bulb with potassium was also heated under vacuum until the temperature of the intercalant ( $T_i$ ) had reached approximately 250°C. After keeping  $T_i$  at this temperature,  $T_g$  was slowly brought down from high temperature to approximately 230–280°C. At this temperature for both  $T_i$  and  $T_g$ , the reaction was performed. Deintercalation of K-GICs, obtained by this modified method and kept in liquid paraffin, was performed by heating between 25 and 1400°C. The thermal stability and temperature dependence of the K-SGDICs (synthetic graphite deintercalation compounds) were characterized using differential scanning calorimeter (DSC) analyzer (Netzsch, Germany). The structure changes of K-SGDICs during the deintercalation reaction of potassium ions and the interlayer spaces of the synthesized graphites were identified by X-ray diffraction (XRD), Debye-Scherrer camera with an Iso-Debyeflex 3000 generator (Rich Seifert and Co., Germany) was used for the XRD measurement.  $\text{CuK}\alpha$  radiation was used an incident beam. Deintercalated stage stacking and stage numbers were determined by the X-ray structure analysis.

## 3. RESULTS AND DISCUSSION

The thermal stability and temperature dependence of the deintercalation process of potassium-SGICs kept in liquid paraffin by increasing deintercalation temperature under air atmosphere were characterized by means of DSC analyzer. Fig. 1 shows the DSC curve consisting of various kinds of distinct peaks

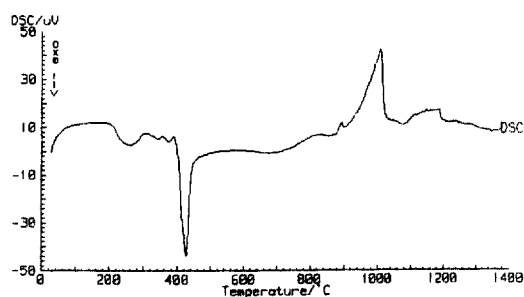


Fig. 1. Differential Scanning Calorimeter analysis of K-SGICs showing the endothermic reaction at the temperatures of 327, 927 and 1252°C and a sharp peak for the exothermic reaction at 479°C caused by a strong deintercalation process of potassium ions from the interlayer space of K-SGICs.

for exothermic and endothermic reactions. The endothermic reactions correspond to the peak at temperatures of 327, 972 and 1252°C, respectively, while the exothermic reaction corresponds to the peak at 479°C. Several weak and broad peaks for exothermic reactions are observed below 400°C. These can be recognized with a weak deintercalation of potassium ions from the interlayer spaces of the K-SGICs. In comparison with these weak peaks, a strong and sharp peak for the exothermic reaction is observed near 479°C. It might be caused by a strong deintercalated process of potassium ions from the interlayer spaces of K-SGICs at the temperature region. At temperatures above 562°C, no remarkable peak for the exothermic reaction is appears, since the deintercalation process proceeds slowly.

Enthalpy and entropy formations could be calculated from the deintercalation and thermodynamic exothermic reactions depending on the various temperatures, listed on Table 1. The enthalpy and entropy values decreased by increasing of the temperature to 562.2°C. Based on these results, the enthalpy of formation represents the dependence of deintercalation temperatures to 562°C.

The development of the (*hkl*) reflection for the structure changes of K-GDICs with the temperatures were identified by XRD in Fig. 2. Based on the results, the deintercalation of the intercalants between carbon layers could be recognized by the stage transitions. The intensity of the (001) in-

Table 1. Enthalpy and entropy formations for K-SGICs at various temperatures

Temperature range (°C)	$\Delta H$ ( $J \cdot g^{-1}$ )	$\Delta S$ ( $J \cdot g^{-1} \cdot K^{-1} \times 100$ )
257.5~397.4 (327)	2.21	0.37
397.4~562.2 (479)	-7.15	-0.99
869.3~1075 (972)	10.87	0.87
1075~1225 (1150)	2.44	0.17

\* ( ): average temperature for  $\Delta S$  calculation.

terference for the stage 1 and (002)-interference for the stage 2 of K-SGICs are very strong. Thereby the perfect stage 1 for the K-GICs using synthetic graphites could not be obtained while the perfect stage 1 for the K-GICs using natural graphite could be obtained. After heat treatment of K-SGICs at 200°C the interference for stage 1 exhibits a mixed state with stage 2 and 3 in the case of the heat treatment at 400°C the higher stages 4 and 5 were observed as mixed states including lower stages 1 and 2. Higher stages occur with the lower stages at this temperature because large amounts of the potassium ions could be deintercalated from the interlayer space of K-SGICs. After heat treatment at 600°C, the interference for stage 1 completely disappeared and only stage 5 with a weak stage 4 and 2 remained. In the case of the heat treatment at 1000°C, prevalent interferences for the original synthesized graphite nonintercalated were observed with a medium intensity for stage 2, 4 and 5. After heat treatment at 1400°C, the only observed interference was for stage 4. Generally most of the GICs change to the exfoliated graphite if they are heat-treat.<sup>4,5,10</sup> Therefore, it is proposed that the nonintercalated K-SGICs are formed at 1400°C because of the thermal stability in liquid paraffin. From the above results, we can assume that the deintercalation of K-SGICs occurred by diffusion of K-atoms between carbon layers in liquid paraffin molecules, the reaction rate is proportional to heating temperature, and the K-SGICs are very stable under liquid paraffin at high temperature.

#### 4. CONCLUSION

The thermal stability and the temperature depen-

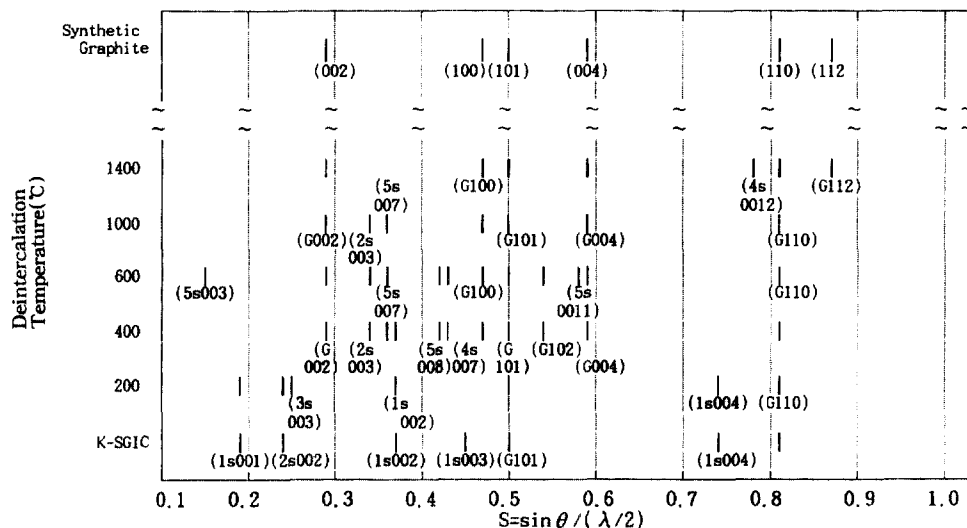


Fig. 2. Development of reflections for the potassium-graphite deintercalation compounds in liquid paraffin in various temperature conditions. \*1s: stage 1, 2s: state 2, 3s: stage 3, 4s: stage 4, 5s: stage 5, 6s: stage 6, 7s: stage 7, G: graphite.

dence of the deintercalation process of K-SGICs kept in liquid paraffin were investigated by increasing deintercalation temperature under air atmosphere. Below 400°C a weak deintercalation of potassium ions from the interlayer spaces of the K-SGICs was observed and a strong deintercalation process occurs near 479°C. Above 562°C, the deintercalation process proceeds slowly. The enthalpy and entropy values decreased by increasing the temperature up to 562.2°C. The smallest value for the enthalpy and entropy formation was  $-681.35 \text{ J} \cdot \text{g}^{-1}$  and  $-9.9 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \times 10^{-3}$ , respectively.

For the structure changes and stability of K-SGICs depending on the temperatures, higher stages 4 and 5 were observed as mixed states including lower stages 1 and 2, because large amounts of the potassium ions were deintercalated from the interlayer space of K-SGICs after heat treatment at 400°C. After heat treatment at 1400°C, the only observed interference was for stage 4. Therefore, it is proposed that the nonintercalated K-SGICs were formed at 1400°C because of their thermal stability in liquid paraffin.

## REFERENCES

1. M. Endo, M. S. Dresselhaus, and G. Dresselhaus,

*Ext. Abs., Graphite Intercalation Compounds: Science and applications, Mater. Res. Soc.*, 145(1988).

2. Y. S. Ko and H. P. Boehm, *Z. Naturforsch*, **39a**, 768(1984).
3. S. H. Anderson Axdal and D. D. L. Chung, *Carbon*, **25**, 377(1987).
4. W. C. Oh, S. J. Cho and Y. S. Ko, *Proc. Carbon '94, Int. Conf. Carbon, Granada/Spain*, 620(1994).
5. W. C. Oh, S. J. Cho, Y. J. Choi, M. K. Kim and Y. S. Ko, *Carbon '95, Int. Conf. Carbon, San Diego/U.S.A.*, 647(1995).
6. D. E. Bergbreiter and J. M. Killough, *J. Am. Chem. Soc.*, **100**, 2126(1978).
7. M. Suzuki and H. Suematsu, *J. Phy. Soc. Japan*, **52**, 2761(1983).
8. P. J. Salzano and S. Aronson, *J. Chem. Phys.*, **42**, 1323(1965).
9. H. Suenatzu, M. Suzki and H. Ikeda, *Phys. Soc. Japan*, **49**, 835(1980).
10. W. C. Oh, S. J. Cho and Y. S. Ko, *Carbon*, **34**, 209(1996).
11. S. H. Anderson and D. D. L. Chung, *Carbon*, **22**, 253(1984).