

Structural transition of alkali metal-graphite deintercalation compounds

Won-Chun Oh and Young-Shin Ko

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

Chang-Sung Lim and Keun Ho Auh

Ceramic Materials Research Institute(CMI), Hanyang Univeristy, Seoul 133-791, Korea

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].

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[2]. Li-graphite intercalation compounds which are used as an anode for the lithium battery the intercalation and deintercalation process has to be performed easily.

The synthesized K-GICs are very unstable under temperature, pressure, humidity(OH and O₂ 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.[3] extensively investigated the chemical properties of K-GICs for various gas atmosphere. Therefore, many authors[4, 5] have tried to study on the stability of GICs to solve this problem.

Asher[6] reported the lamellar compound of sodium and graphite having an ideal formula C₆₄Na in which sodium was intercalated in every eighth interplanar gap appeared to be analogous to the K-, Rb-, and Cs-graphite lamellar compounds. Recently, Udod et al.[7] have suggested that the limiting composition of the high pressure phase of Na-GICs at 40 kbar is NaC₂ having a two-layer package of intercalate. However, no detailed studies of the deintercalation behavior of the Na-GICs have been reported at present.

Experimental

In this research, we have synthesized the lithium graphite intercalation compounds(Li-GICs) with the natural graphite as a host material and the lithium metal. As an intercalant we have used lithium in form of metal(Strem Chemicals, Inc., U.S.A.) and for controlling the reaction atmosphere gases such as Ar, O₂ and N₂ with the purity of 99.999% have been used. The reaction synthesis has been performed at the temperature of 200-220°C, under the pressure of ca. 350-400 kg/cm² and under the Argon atmosphere for 18-20 hours. In order to know the reactivity of Li-GICs under the atmosphere of O₂ and N₂ we have made the Li-GICs as minimal

size as possible, and these compounds were oxidized under the condition of the ratio 2 : 8 of O₂ and N₂ for the slow reaction.

The K-GICs were synthesized in the evacuated and sealed modified two-bulb pyrex tube. The prepared K-GICs by this modified method were put into liquid paraffin for avoiding oxidation in atmosphere under the dry inert gas atmosphere. Deintercalation reaction of these K-GICs was performed by spontaneous reduction under long term exposure to the air in the closed chamber at constant temperature and humidity. Stage transitions of K-GDICs(Graphite Deintercalation Compounds) were observed by X-ray diffraction method.

As an intercalant, sodium was used in form of metal. The Na-GICs were synthesized by the chemical method using high temperature and pressure in a stainless steel at temperatures between 650 and 700°C at approximately 45 kbar. The thermal stability and the temperature dependence of the deintercalation compounds were characterized using differential scanning calorimeter(DSC) analyzer. The structure changes of Na-GICs during the deintercalation reaction of Na ions and the interlayer spaces of the graphites were identified by XRD.

Deintercalation and gas reaction of Li-GICs

The graphite intercalation compounds with heavy alkali metals can be easily decomposed, while Li-graphite intercalation compounds can be stable relatively for a long time on the air. Such a stability of Li-GICs can be caused not only by the reactivity of lithium metal but also by the oxidation factors such as the reaction with humidity(H₂O), O₂, etc.

The structural change occurred during the decomposition process of the graphite intercalation compounds can be confirmed by the X-ray diffraction method and their results are shown in Fig. 1. From the Fig. 1, we can see that we have become pure stage 1 graphite intercalation compounds at first, but after contact with the gas for 1 hour, we don't have become pure 1 stage compounds any more, but mixed stage 1 and 2 compounds for which we have obtained 3.71Å and 7.07 of d₀₀₁ values, respectively. From the results obtained after 1 week, we can observe almost the same feature as that obtained after 1 hour and much increases of the reflections.

According to the X-ray reflection analysis obtained after two weeks we can see that the reflections for stage 2 reduced while those for stage 5 began to appear and that most peaks for the nonintercalated original graphite appeared. From this result, we can believe that the oxidation process proceeded considerably during this reaction time of two weeks. After 3 weeks, we can observe that more reflections for stage 2 reduced, while those for stage 5 increased, and that the additional (G112) reflection for the nonintercalated original graphite appeared. From the X-ray analysis for the compounds obtained after 4 weeks, we can see that the reflections for stage 1 disappeared completely, (3s007) reflection for stage 3 are formed and those for stage 5 appeared dominantly. After 5 weeks, we have become the same features as those after 4 weeks. After 6 weeks, we could observe only the reflections for stage 5 and all the other ones disappeared, and after more than 6 weeks we have obtained the unchanged same features in X-ray reflection as those after 6 weeks. And no additional peaks for the nonintercalated original graphite have been obtained either.

S	N	H	C	Ash
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and 7.06 Å, respectively. After 6 weeks, the deintercalation reaction of the Li-GICs has ceased and only residual compounds could be observed.

In the present study, we have been synthesized K-GICs by modified two-bulb method. This paper presents experimental results of the structural stability and stage transition in the K-GDICs. From the X-ray diffraction analysis we can assume that the K-GDICs after more than 10 weeks could be regarded as the very stable K-graphite residue compounds.

Synthesized Na-GICs with stage 1 and 2 using the high temperature and pressure technique. This paper presents experimental results of the deintercalation reaction and thermal stability depending on the heating in the Na-GICs. The structure changes of Na-GDICs depending on the heating rates were identified by XRD.

From the above data, we can suggest a stage transformation by considering the deintercalation mechanism of the intercalants between the carbon layers. As a deintercalation process, stage transformation could be considered irregular deintercalation of a GDICs with disordered stages.

The cokes obtained from bituminous coal were used in this study. The result of the

REFERENCES

Experiment

- [1] H. Endo, M. S. Dresselhaus, G. Dresselhaus, Ext. Abs. Graphite intercalation compounds : Science and applications, Mater. Res. Sci., 15, 1988
 - [2] B. Scrosati, J. Electrochem. Soc., 139, 2776, 1992
 - [3] N. Daumas, A. Herold, Bull. Soc. Chim. Fr., 5, 1598, 1971
 - [4] R. Schögl, H. P. Boehm, Carbon, 22, 351, 1984
 - [5] W. C. Ock, J. H. Cho, J. S. Lee, Carbon, 34, 209, 1996
 - [6] B. C. Asher, J. Inorg. Nucl. Chem., 10, 238, 1959
 - [7] I. A. Udod and V. K. Genchel, High pressure Res. 8, 581, 1992
 - [8] A. Herold, Bull. Soc. Chem., 999, 1955
- Activated carbons are the microporous carbonaceous adsorbents which are prepared from carbon-containing source materials such as wood, coal, lignite, petroleum and sometimes synthetic high polymers. [1-2] Activated carbons shows an ability to adsorb hydrocarbons of the gas phase. Activated carbons are used in the purification of many kinds of gas phases like hexane, benzene, toluene, etc. [3] In this study, cokes from bituminous coal were activated for the purpose of intercalation and deintercalation.

Introduction

***Inst. of Car. Chem. Seoul Nat'l. Univ. of Ed, Seoul 137-070, Korea
 **Institute of Ceramics Technology, Seoul 152-023, Korea
 *Dept. of Inorganic Materials Eng., Paj Chai Univ., Daejeon 302-735, Korea
 Dept. of Mater. Eng., Hansoo Univ., Seosan 352-820, Korea
 In-Ki Kim, Han-Jun Oh, Jin-Seok Jang, Hee-Nam Youn, Young-Shin Ko***

Preparation of the activated carbon for the canister from cokes

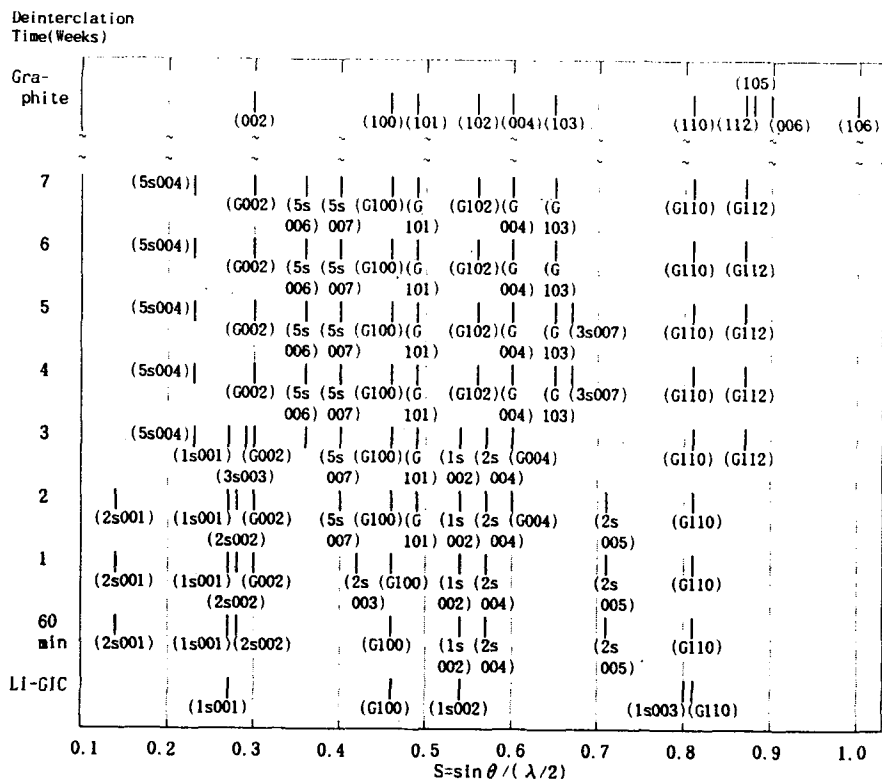


Fig. 1. Development of (hkl) Interference for the Lithium-Graphite Deintercalation Compounds.

* 1s : stage 1, 2s : stage 2, 3s : stage 3, 4s : stage 4, 5s : stage 5,
6s : stage 6, 7s : stage 7, G : graphite

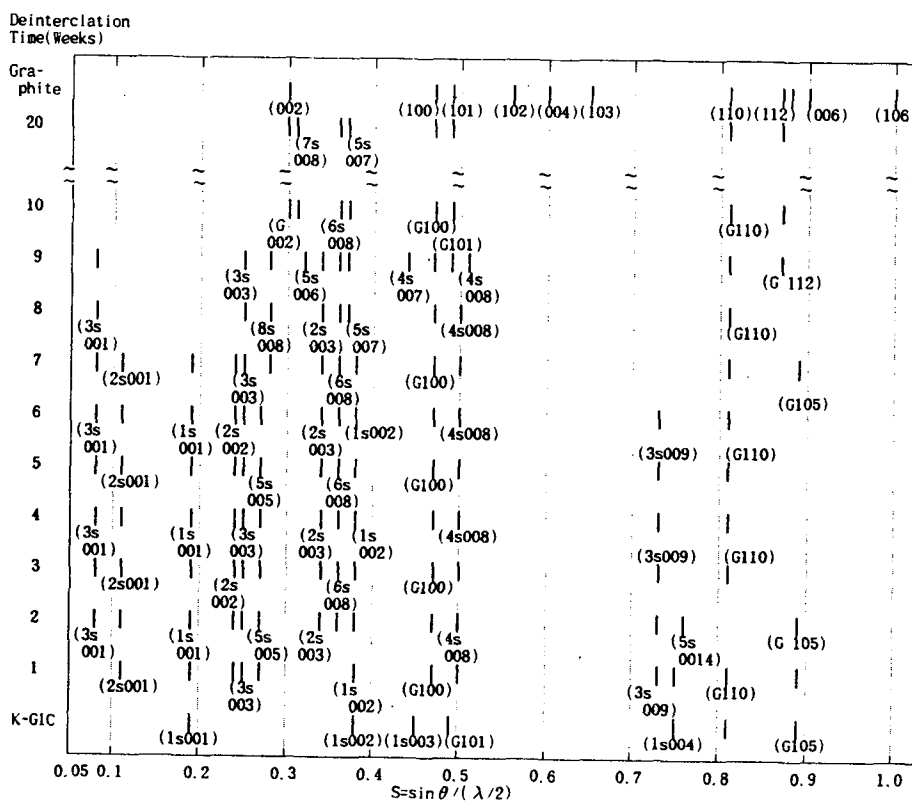


Fig. 2. Development of (hkl) reflections for the potassium-graphite deintercalation compounds.

* 1s : stage 1, 2s : stage 2, 3s : stage 3, 4s : stage 4, 5s : stage 5,
6s : stage 6, 7s : stage 7, G : graphite

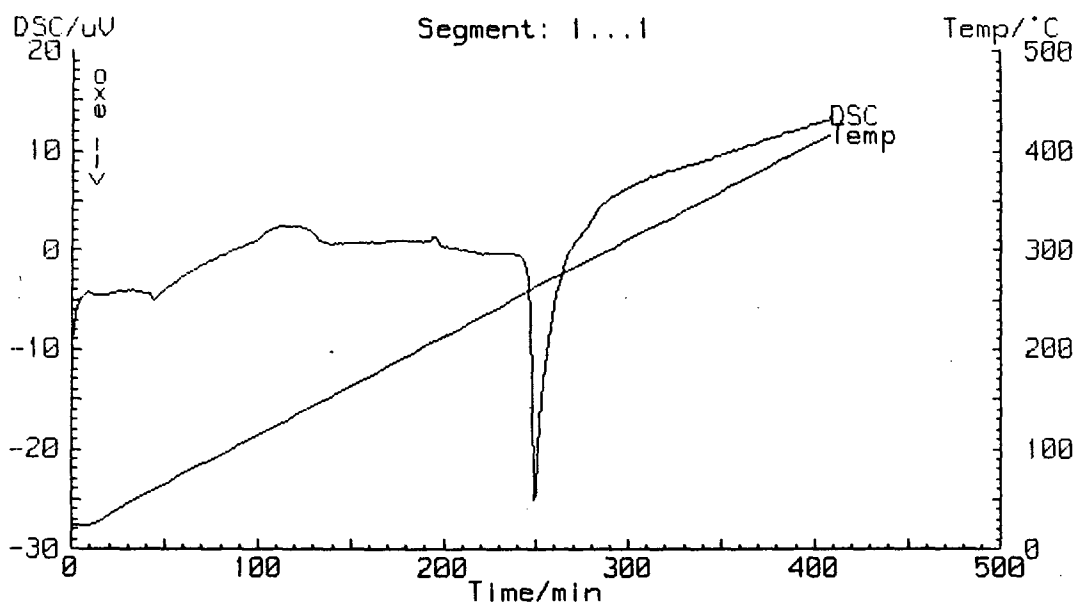


Fig. 3. Differential scanning calorimeter analysis of Na-GDICs showing the endothermic reaction for heating.

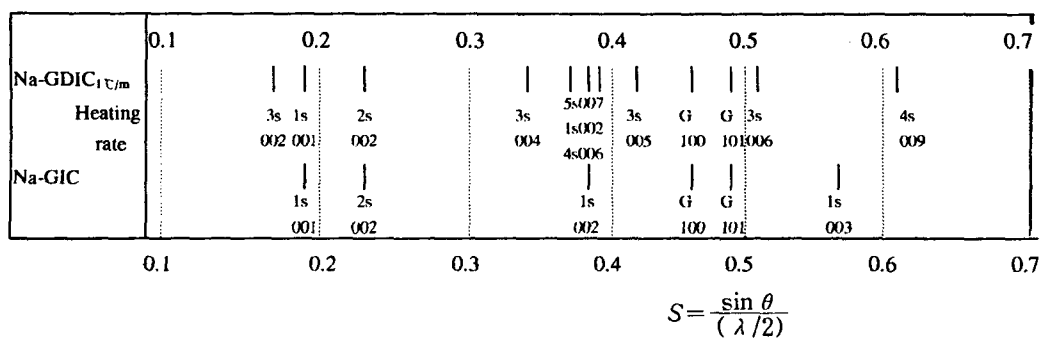


Figure 4. X-ray reflection for the deintercalation of Na-Graphite intercalation compounds.

* 1s : stage 1, 2s : stage 2, 3s : stage 3....., G : graphite