Deintercalation and Thermal Stability of Na-graphite Intercalation Compounds

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Abstract

Na alloyed graphite intercalation compounds with stage 1 and 2 were synthesized using the high temperature and pressure technique. Thermal stability and staging transitions of the compounds were investigated depending on heating rates. The thermal stability and temperature dependence of the deintercalation compounds were characterized using differential scanning calorimeter (DSC) analyzer. Enthalpy of formations were confirmed at temperatures between 25 and 500°C, depending on the various heating rates. The structure changes of Na alloyed graphite compounds during the deintercalation reaction of sodium ions and interlayer spaces of the graphite were identified by X-ray diffraction (XRD). Diffractograms of stages with non-integral (00{l}) values were obtained in the thermal decomposition process, and stacking disorder defects and random stage modes were observed. The average value of the interlayer C-C bond lengths were found approximately 2.12 Å and 1.23 Å from the diffractions. Based on the stage transition, the degree of the deintercalation has an inverse-linear relationship against the heating rate.

Keywords: Na-graphite Intercalation Compounds, Thermal Stability, Stage Transition, DSC, Enthalpy of Formation, XRD, C-C Bond Length

1. Introduction

A great deal of attention has been given to the preparation of the graphite intercalation compounds (GICs), which were formed by the insertion of atomic or molecular layers of guest chemical species, called as intercalants, between layers of the host material. The stability of the graphite intercalation compounds is a crucial factor in the practical industrial and space or aircraft application [1]. Many theoretical studies on the stability have been reported dealing with the mechanism of staging and disorders of stage [2-4].

Generally, the intercalation reaction occurs relatively smoothly when graphite intercalation compounds nothing, but the alkali metal graphite intercalation compounds with poor stability. Among the GICs with alkali metal intercalants, Na-graphite compounds have been recognized to be significant because they are thermodynamically less stable than the K-, Rb-, and Cs compounds [5-7]. Asher [7] reported the lamellar compound of sodium and graphite having an ideal formular \( \text{C}_6\text{Na} \), in which sodium was intercalated in every eighth interplanar gap appeared to be analogous to the K-, Rb-, and Cs-graphite lamellar compounds. Blash \textit{et al.} [8] synthesized the GICs such as \( \text{C}_2\text{Na} \) and \( \text{C}_3\text{Na} \) with sodium at \( T=450^\circ\text{C} \) and \( P=15-50 \text{ kbar} \), thereby indicating complete intercalation of sodium with graphite, and refuted the notion concerning the impossibility of formation of Na-GICs of low stages. The unusual sodium behavior in the intercalation with graphite had been explained by the thermodynamic instability of GICs at the synthesis temperature [9]. According to previous report, Udod \textit{et al.} [10] have suggested that the limiting composition of the high pressure phase of Na-GICs at 40 kbar is \( \text{Na}_2\text{C} \) having a two-layer package of intercalant. It was established that high pressure treatments do not lead to a monolayer structure. However, no detailed studies of the deintercalation behavior of the Na-GICs have been reported at present. In this work, Na-GICs of low stages were synthesized using natural graphite and investigated the deintercalation and thermal stability depending on the heating rates.

2. Experimental

Natural graphite flakes (Sangjin, Korea) with a size between 100 and 200 mesh (approx. 0.149~0.074 mm), were used as a starting host material. They were purified by alkali melting method as one of the chemical treatment such as \( \text{K}_2\text{CO}_3 \) or \( \text{Na}_2\text{CO}_3 \). The carbon content obtained from elemental analysis was 98.08 ± 1.15%. The results of elemental analysis are listed in Table 1. As a intercalant, we used sodium in form of metal (Aldrich Chemicals, Inc., U.S.A.) and controlling the reaction atmosphere gas as Ar with the
posed spontaneously in the air or oxidized electrochemically
pounds to form residual compounds when they are decom-

ced spacings with formation of electron donor-type intercalation
ment, 0.21~0.25 g of GICs were weighed in dry box. Al_2 O_3
the Na-graphite intercalation compounds. For the measure-

cal method under temperature and pressure with sodium
purity of 99.999%. Na-GICs were synthesized by the chemi-

cal method under temperature and pressure with sodium
metal and natural graphite. Thirty percent of sodium metal
was put in stainless steel container. The synthesis has been
performed at the temperature between 650 and 700°C, under
the pressure of ca. 350~400 kg/cm² and under the argon
atmosphere for 18~20 hours. The thermal stability, stage
transition and temperature dependence of the deintercalation
of the Na-GICs were investigated depending on various
heating rates.

A Differential Scanning Calorimeter (DSC) analyzer
(Netzsch, Germany) has been used to confirm the thermal
stability, temperature dependence, and reactivity under N_2
of the Na-graphite intercalation compounds. For the measure-
ment, 0.21~0.25 g of GICs were weighed in dry box. Al_2O_3
of ca. 0.2 g was used as a standard material and a Pt crucible
was used for the reaction. Enthalpy of formation were con-
firm at temperatures between 25 and 500°C, depending on
the various heating rates, 1, 5, 10, 15, 20 and 25 oC/min. The
enthalpy and entropy were calculated by using Netzsch
Instrument software (SW/xxx/65x.01). The structural changes
of Na-GICs during the deintercalation of Na ions and the
interlayer spaces of the graphites were identified by XRD. In
the X-ray diffraction analysis, we can observe more reflec-
tion peaks for most graphite intercalation compounds than
during intercalation that were obtained during the deinterca-
lation process. For the study the structural change of the
graphite deintercalation compounds (GDICs), the Debye-
scherrer camera with an ISO-DEBYEFLEX 3000 generator
(Rich. Seifert & Co) was used for the XRD measurements.
Cu Kα radiation was used an incident beam. Each substance
obtained after the intercalation and deintercalation reactions
were filled in a capillary with the diameter of 0.5 mmΦ as
dense as possible so that the texture phenomena can’t occur.
Each sample prepared in such method was filmed with
Debye-scherrer camera under the condition of 45 kV and 40
mA for 7~8 hours. The films obtained in this way were
interpreted with analyzer.

### Table 1. Elemental analysis of the purified starting natural
graphite

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sangjin</td>
<td>98.08±1.01</td>
<td>0.32±0.01</td>
<td>0.05</td>
<td>0.42±0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

3. Results and Discussion

Alkali metals are intercalated into the graphite interlayer
spacings with formation of electron donor-type intercalation
compounds. It is characteristics of the intercalation com-
ounds to form residual compounds when they are decom-
posed spontaneously in the air or oxidized electrochemically
with some parts of the intercalants remaining in the inter-
layer spacings [4, 11-13]. Because the vapour pressure of
sodium is relatively higher than that of other alkali metals
such as K, Rb, Ce, the properties of the graphite intercalation
compounds with sodium are quite different. The thermal sta-
bility and the deintercalation of the Na-GICs for stage 1 and
2 were characterized using DSC to temperature of 500°C.
Enthalpy and entropy of formations were calculated by the
confirmation of the deintercalation and thermodynamic exo-
thermic reactions. Fig. 1 shows the enthalpy of formation
versus heating rate. Fig. 1(a) shows the biggest absolute
value for the enthalpy of formation of -681.35 J/g. This
value was formed by the heating rate of 1°C/min at the
smallest temperature ranges between 219.9 and 279.9°C. Fig.
1(f) shows the smallest absolute value of -166.63 J/g formed
by the heating rate of 25°C/min at the biggest temperature
ranges between 91.4 and 447.1°C. In Table 2, the enthalpy
and entropy of formation corresponding to each temperatures
are listed depending on the heating rates. Based on the
results, the enthalpy of formation represents the dependence
of the heating rates.

The temperature and pressure are the decisive factors in
the intercalation and deintercalation process. The structural
changes occurring during the thermal decomposition process
of the Na-GICs can be detected by X-ray diffraction device
with the results shown in Fig. 2. The perfect compound for
stage 1 could not be found in the Na-GICs. A weak diffrac-
tion peak could be observed on the (00l) interference for the
stage 2. The observed compound of NaC_64 for the stages
were reported by previous workers [7, 14]. Metrot et al. [15]
gave sorption isotherms for the soft and hard carbons. The
sodium uptake in soft carbon was found to be mainly due to
intercalation. The amount of sodium decreased as the treat-
ment temperature of the cokes increased. In this study, we
could obtained blue and red Na-GICs for stage 1 and 2. The
deintercalation for stage 1~5 compounds could be found by
the temperature of 500°C, in which the stage 3 was a main
structure in the deintercalation compounds. In the case of the
compounds with the heating rate of 5 and 10°C/min, a weak
peak was observed on the lower stage (stage 1 and 2) and
stage 4 and 5, but a peak of original graphite was strongly
revealed. For the heating rate of 15 and 20°C/min, the stage
5, 6 and 8 were main structures, in which the peak of origi-
nal graphite was stronger than other cases. And finally, in the
case of the compounds with the heating rate of 25°C/min, a
very weak peak was observed on the lower stage and stage
5, 6 and 8. The kinetics of final residue compounds charac-
terized by the relation of the deintercalation temperature of
500°C.

During the thermal decomposition process, diffractograms
of stages with non-integral (00l) values were obtained, char-
acteristic of stacking disorder defects and random stage
modes in the Na-GDICs. Table 3 shows the average values
of d_l for the each stage found at the end of each heating rate
Fig. 1. Differential scanning calorimetric analysis of Na-GDICs showing the endothermic reaction on various heating rates (a) 1°C/min (b) 5°C/min (c) 10°C/min (d) 15°C/min (e) 20°C/min (f) 25°C/min.

Table 2. Thermodynamic data of Na-graphite intercalation compounds

<table>
<thead>
<tr>
<th>Na-GDIC Heating rate</th>
<th>Temperature range (°C)</th>
<th>ΔH (J·g⁻¹)</th>
<th>ΔS (J·g⁻¹·K⁻¹)</th>
<th>Degree of deintercalation [-ln(1-X)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-GDIC 1°C/min</td>
<td>219.9~279.9(249)</td>
<td>-681.35</td>
<td>-1.305</td>
<td></td>
</tr>
<tr>
<td>Na-GDIC 5°C/min</td>
<td>140.7~349.9(245)</td>
<td>-526.80</td>
<td>-1.017</td>
<td>1.31</td>
</tr>
<tr>
<td>Na-GDIC 10°C/min</td>
<td>138.4~420.2(279)</td>
<td>-377.61</td>
<td>-0.684</td>
<td>0.96</td>
</tr>
<tr>
<td>Na-GDIC 15°C/min</td>
<td>135.9~422.4(279)</td>
<td>-361.95</td>
<td>-0.656</td>
<td>0.62</td>
</tr>
<tr>
<td>Na-GDIC 20°C/min</td>
<td>135.3~430.3(282)</td>
<td>-169.77</td>
<td>-0.306</td>
<td>0.37</td>
</tr>
<tr>
<td>Na-GDIC 25°C/min</td>
<td>91.04~447.1(273)</td>
<td>-166.63</td>
<td>-0.305</td>
<td>0.26</td>
</tr>
</tbody>
</table>

* ( ) : average temperature for ΔS calculation
Deintercalation and Thermal Stability of Na-GICs

up to the formation of deintercalated compounds. This parameter is calculated using the expression

\[ d_i = \left( \frac{\sum d_i \cdot l_i \cdot \tan \theta_i}{\sum \tan \theta_i} \right) \]

where \( n \) is the number of (00\( l \)) lines relative to each stage in the given diffractogram and where the statistical weight of each value of \( d_i \) is taken as proportionally inverse to the uncertainty in the corresponding value of \( \theta_i \).

It is also possible to obtained \( d_{C-C} \) from the proposed method [4]. The average value of the interlayer C-C bond lengths, from the reflexions at approximately 2.12 Å and 1.23 Å that are found in all the diffractograms, and which are both independent of the interlayer distance and only depend on the C-C bond lengths. The values thus calculated are also given in Table 3.

Based on the stage transitions by XRD, the kinetics of the deintercalation of Na-GICs were studied for heating rates between 1 and 25°C/min, and degree of deintercalation. On the assumption that the deintercalation is heating rate-controlled, the degree of the deintercalation follows a linear relationship. Therefore, the degree of the non-deintercalation (X) and deintercalation (\(-\ln(1-X)\)) are listed for the heating rates in Table 2 [2]. This relation indicates that the deintercalation is heating rate-controlled. The degree of the deinterca-

\[ S = \frac{\sin \theta}{(\lambda/2)} \] (Å⁻¹)

Fig. 2. X-ray diffraction for the deintercalation of Na-Graphite intercalation compounds by heating rates.

Table 3. Average \( d_i \) values for the stages, as calculated from the 00\( l \) lines in the diffractograms and average interlayer C-C distances

<table>
<thead>
<tr>
<th></th>
<th>Average ( d_i ) for the stages (Å)</th>
<th>( d_{C-C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-GIC</td>
<td>5.20  8.56</td>
<td>1.416</td>
</tr>
<tr>
<td>Na-GDIC_1°C/min</td>
<td>5.21  8.55  11.90  15.24</td>
<td>1.414</td>
</tr>
<tr>
<td>Na-GDIC_5°C/min</td>
<td>11.91  15.25  18.59</td>
<td>1.418</td>
</tr>
<tr>
<td>Na-GDIC_10°C/min</td>
<td>8.56  11.90  15.25  18.60</td>
<td>1.419</td>
</tr>
<tr>
<td>Na-GDIC_15°C/min</td>
<td>15.26  18.61  21.94</td>
<td>1.422</td>
</tr>
<tr>
<td>Na-GDIC_20°C/min</td>
<td>18.61  21.96</td>
<td>1.420</td>
</tr>
<tr>
<td>Na-GDIC_25°C/min</td>
<td>11.90  15.24  18.61  21.94  28.66</td>
<td>1.420</td>
</tr>
</tbody>
</table>

*Values in *italics* were determined from single 00\( l \) diffractions and are therefore not averages
laton has a inverse-linear relationship against the heating rate, as plotted in Fig. 3. The deintercalation reaction constant (K) calculated from this relationship is proposed to be $5.8 \times 10^{-2}$/min.

4. Conclusion

In the present study, the Na-GICs were synthesized 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 rates in the Na-GICs. From the DSC result, entropy of formation could be calculated through the confirmation of the deintercalation and thermodynamic exothermic reactions depending on the various heating rates. The enthalpy and entropy of formation represents that the values are dependent upon the heating rates. The structural changes of Na-GDICs depending on the heating rates were identified by XRD. During the thermal decomposition process, diffractionograms of stages with non-integral (00l) values were obtained, characteristics of stacking disorder, defects, and random stage modes. The average value of the interlayer C-C bond lengths, from the diffractions at approximately 2.12 Å and 1.23 Å that are found in all the diffractionograms. The kinetics of final residue compounds characterized by the relation of the deintercalation temperature, and the heating rates. Based on the stage transition, the degree of the deintercalation has a inverse-linear relationship against the heating rate. The deintercalation constant is proposed to be $5.8 \times 10^{-2}$/min.

References