

A Study on the Deintercalation Reaction of Li-Graphite Intercalation Compounds

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Li-graphite intercalation compounds (GICs), synthesized at elevated temperature and pressure, were allowed to decompose spontaneously in the atmosphere. The decomposition processes were analyzed by X-ray diffraction, DSC analysis, FT-IR measurements, UV/VIS spectrophotometry. The deintercalation reaction of the Li-GICs ceased after 6 weeks and only the residual compounds could be observed. A strong exothermic reaction was observed at 300 °C in thermal decomposition, and relatively stable decomposition curves were formed. A few endothermic curves have been observed at 1000 °C. After 6 weeks deintercalation reaction time of GICs, many exothermic and endothermic reactions were accompanied at the same time. In addition the reactions of the functional groups such as aromatic rings, nitrogen, -CH₃, -CH₂ etc. of GDIC obtained by the above reaction were confirmed by FT-IR spectrum. UV/VIS spectrophotometric measurement clearly shows the formation of a minimum energy value (R_{\min}) for the compounds between Li-GICs as a starting material and Li-GDICs obtained until after 3 weeks of the deintercalation reaction, while they were no clear energy curves from 4 weeks of reaction time, because of the formation of the graphite structure, of high stages and of the Li compounds surrounding the graphite in the deintercalation reaction.

Introduction

Recently in putting the lithium secondary battery with a high energy density and high output to practical use, the reversibility between the charge and discharge of lithium intercalation compounds which are used as the anode becomes of interest as an important factor for the battery mechanism.^{1,2} Graphite has a layer structure, and the distance between two layers is about 3.35 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 the case of such Li-graphite intercalation compounds which are used as an anode for lithium battery the intercalation and deintercalation processes have to be performed easily.^{3,4} Li_xC₆ which is a Li-graphite intercalation compounds are obtained by the intercalation reaction and the deintercalation processes result in Li_(x-y)C₆ intercalates, where the values of x and y determine the quantities of lithium transferred during the intercalation and deintercalation process. In general, there are electrochemical as well as chemical methods to synthesize Li-GICs.^{5,6} The chemical method can be classified in two processes, which are Chemical Vapour Deposition (CVD), and the reaction of lithium and graphite under pressure.^{7,8} The reversibility between the intercalation and deintercalation process can act as an important factor for the battery mechanism in lithium intercalation compounds obtained by such methods.

Generally, the intercalation reaction occurs relatively smoothly in the case of graphite intercalation compounds. However, various problems are encountered in deintercalation process, and the poor stability of the graphite intercalation compounds is the crucial factor for industrial use and space or aircraft application of these materials.⁹

In this study, we have synthesized the Li-GICs by reacting graphite with lithium at elevated temperature and pressure.

The influence of O₂ and N₂ during the deintercalation process was studied in which such synthesized compounds decompose spontaneously. The properties of each decomposed compound obtained during such reaction processes have been also examined by X-ray diffraction, DSC analysis, FT-IR measurement and UV/VIS spectrophotometric method.

Experimental Section

Materials. We have synthesized the lithium graphite intercalation compounds (Li-GICs) from natural graphite as a host material and lithium metal. First, natural graphite (Sangjin, Korea) chemically purified with flake size between 0.074-0.149 mm. Resultant purified natural graphite has a carbon content of 98.08(±1.51)%. Lithium metal (Strem Chemicals, Inc., U.S.A.) was used as an intercalant and for controlling the reaction atmosphere gases such as Ar, O₂ and N₂ with 99.999% purity have been used.

Preparation of Li-GICs. Li-GICs were synthesized by exposing a mixture of graphite and lithium (30 wt %) to temperature and pressure. The synthesis reaction was performed in argon atmosphere at 200-220 °C and under a pressure of 350-400 kg/cm² with a reaction time of 10-12 hours.

Deintercalation of Li-GICs. In order to study the reactivity of Li-GICs under O₂ and N₂, we made the Li-GICs as minimal size as possible. These compounds were oxidized under 2 : 8 of O₂ and N₂ for the slow reaction. Small quantities of these oxidized Li-Graphite Deintercalation Compounds (Li-GDICs) were used for characterization.

Analysis and Measurement. X-ray diffraction patterns were taken by Debye-Scherrer camera using an X-ray generator from Rich. Seifert & Co (ISO-DEBYEFLEX 3000) and Cu K α radiation. Each substance obtained after intercalation and deintercalation reactions was filled as densely as possi-

ble into a capillary with a diameter of 0.3 mm so that texture phenomena could not occur. Each sample prepared by this method was filmed with a Debye-Scherrer camera, and the obtained films were interpreted by analyzer. The results of X-ray diffraction analysis are shown in Figure 1.

A DSC (Differential Scanning Calorimeter) analyzer (NETZSCH, Germany) has been used to confirm the thermal stability and reactivity under N_2 of the Li-graphite intercalation compounds. Al_2O_3 was used as a standard material and a Pt crucible was used for the reaction. The range of the measuring temperature of the DSC analyzer is from room temperature to 1400 °C.

In order to identify the functional groups of Li-GDICs formed by the oxidation of Li-GICs under O_2 and N_2 , we have used a FT-IR spectrometer (MIDAC) by KBr pellets in the range of 400 and 4500 cm^{-1} .

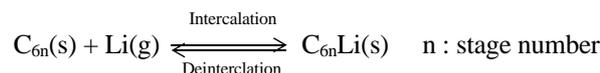
UV/VIS spectrophotometer (PU 8700 Series, UNICAM, PU 8710/01, FALCAN-SCAN) with the diffuse reflectance accessory was used to determine the electron energy state of the Li-GDICs. Li-GDICs obtained after each oxidation time were put into the quartz cell and the reflectance values (R, %) were measured. Before this measurement we have calibrated the apparatus to the standard state by baselining with pure $BaSO_4$ at first. The measurement was performed between in the range 1.37-4.96 eV (Wavelength: 900-250 nm).

Result and Discussion

Generally, alkali metals are intercalated into the graphite interlayer spacings with formation of donor-type intercalation compounds. And it is characteristic that the most of the intercalation compounds form residual compounds when they are decomposed spontaneously in the air or oxidized electrochemically with some parts of the intercalants

remaining in the interlayer spacings.^{10,11} Because the vapour pressure of the heavy alkali metals of K, Rb and Cs is relatively higher than that of lithium, the properties of the graphite intercalation compounds with lithium and of those with the heavy alkali metals are quite different. For example, the graphite intercalation compounds with heavy alkali metals can be easily decomposed, while Li-graphite intercalation compounds can be relatively stable for a long time in the air.¹² 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 (H_2O), O_2 , etc.

Intercalation and deintercalation processes of Li-graphite intercalation compounds can proceed as follows:



In the intercalation process, the temperature and pressure are the decisive factors, while in the deintercalation reaction the oxidative factors have to be considered as mentioned above. The structural changes occurring during the decomposition process of the graphite intercalation compounds can be detected by X-ray diffraction, and the results are shown in Figure 1. After 1 hour contact with the gas, the initial pure stage 1 compound turned into a mixture of stage 1 and stage 2 compounds with d_{001} values of 3.71 Å and 7.07 Å, respectively. In this case, the characteristic gold color of the stage 1 compound disappeared, and a blue color was observed instead. After 1 week, similar features as found after 1 hour were observed, and a marked increase of the number of reflections.

The X-ray reflection analysis obtained after two weeks shows that the reflections for stage 2 were reduced in intensity while those for stage 5 began to appear, and that most peaks for nonintercalated graphite appeared. From this result, we can conclude that the oxidation process proceeded considerably during this reaction time of two weeks. After 3 weeks, the reflections for stage 2 decreased still more, while those for stage 5 increased, and the (G112) reflection for the nonintercalated graphite appeared in addition. After 4-5 weeks, the reflections for stage 1 disappeared completely, the (3s007) reflection for stage 3 was formed, and stage 5 was dominant. After 6 weeks, only the reflections for stage 5 can be observed while all other stages disappeared, and after more than 6 weeks the pattern did not. No additional peaks for nonintercalated graphite have been obtained, either.

If the deintercalation reaction run to completion the reflections for all GIC stages have got to disappear, and only those for the nonintercalated original graphite must appear. But according to the experimental results after more than 6 weeks, the reflections for stage 5 still exist and not all peaks of the original graphite have been formed. This indicates that some lithium still remain in the interlayer space and forms the Li residue compounds. This could be explained as follows; the oxide compound, Li_2O , formed by the reaction of oxygen (O_2) which exist on the surface area of Li-GICs with the Li-ions which exist between the layers, and this Li_2O can

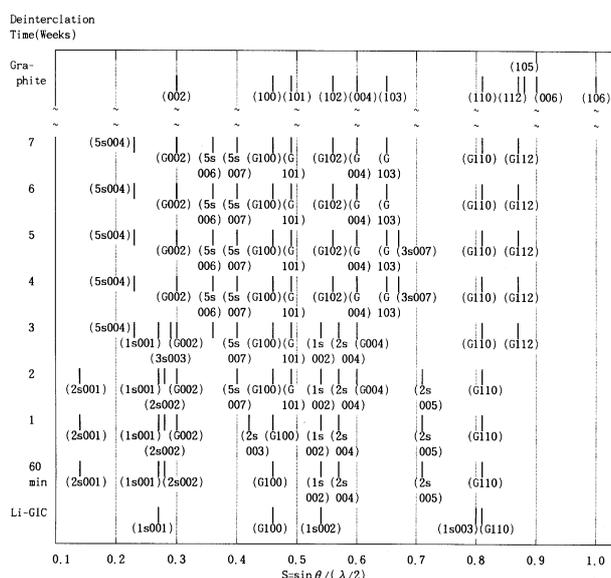


Figure 1. Development of (hkl) Reflexes for the Lithium-Graphite Deintercalation Compounds. *1s: stage 1, 2s: stage 2, 3s: stage 3, 4s: stage 4, 5s: stage 5, 6s: stage 6, 7s: stage 7, G: graphite

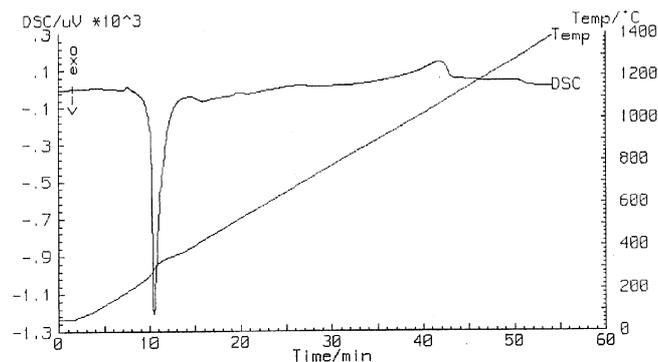


Figure 2. The Analysis of Thermal Decomposition of Li-GIC.

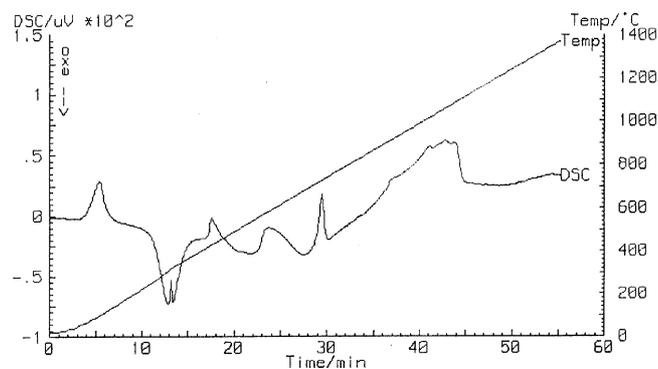
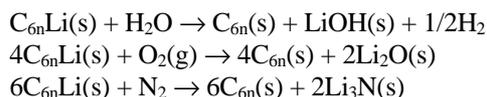


Figure 3. The Analysis of Thermal Decomposition of Li-GDIC.

act in such a way that the Li-ions does not decompose from the interlayer so that the Li-residue compounds could be formed. The decomposition process of Li-GICs can proceed as follows:



According to the analysis of thermal decomposition of Li-GICs, a strong exothermic reaction was observed at 300 °C and relatively stable decomposition curves was formed. A weak endothermic signal has been observed at 1000 °C. However, after 6 weeks deintercalation reaction, the DSC plots show several combined exothermic and endothermic peaks. These results are shown in Figure 2 and 3.

The reactions of the functional groups such as aromatic rings, nitrogen, -CH₃, -CH₂ etc. of Li-GDIC obtained by the above reaction have been confirmed by FT-IR spectrum. In Figure 4, we can see for example the peaks of 2922 cm⁻¹ for -CH₃ group, 1578 cm⁻¹ for aromatics rings, 2355 cm⁻¹ for the nitrogen etc. The vibrational frequencies and important functional groups are summarized in Table 1. The strong C-H signal is a large resolved signal at $\nu > 3000$ cm⁻¹. CH₃ and CH₂ give rise to two C-H vibrationals(asymmetric and symmetric stretch vibration: ca 2962 + 2872 cm⁻¹ and 2926 + 2853 cm⁻¹, respectively). It is likely that the C-H wagging vibrations are due to hydrogenation of graphite edges.

The analysis results for the electronic energy state of the Li-GDICs measured by the UV/VIS spectrophotometer are shown in Figure 5. From this figure, we can observe the

Table 1. The functional groups and the corresponding IR vibrational frequencies in the infrared spectra of the Li-GDIC

Functional groups	IR vibrational frequency (cm ⁻¹)	
-CH ₃	$\nu_{\text{C-H}}$	2922 + 2853
	$\delta_{\text{-CH}}$	1433*
-CH ₂	$\nu_{\text{C-H}}$	2918*
	$\nu_{\text{C=C}}$	1577
Aromatic rings	$\gamma_{\text{C-H}}$	860
		636
Aromatic rings containing isolated hydrogens		1010
		3566
Free -OH(hydrogen bonded)	ν	3566
Aromatic rings containing adjacent hydrogens	$\gamma_{\text{C-H}}$	750
		2355
Nitrogen containing adjacent hydrogens		2355

*Overlaped peaks

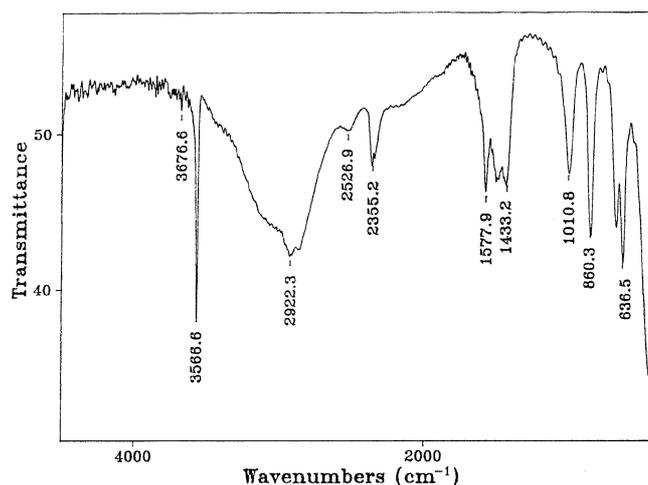


Figure 4. FT-IR Spectrum of Li-GDIC after 6 weeks.

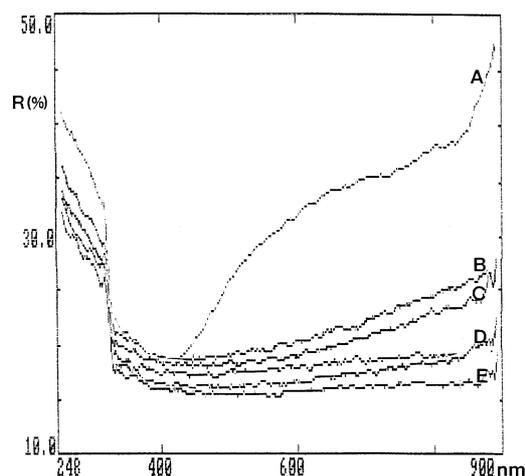


Figure 5. Evolution of UV/VIS reflectance spectra between 248-900 nm for Li-GDICs; A→Li-GIC, B→Li-GDIC after 1 hour, C→Li-GDIC after 1st week, D→Li-GDIC after 2nd week E→Li-GDIC after 3rd week, F→Li-GDIC after 4th week.

clear minimum value of reflectance (R_{min}) obtained for the original graphite(A) and more or less clear reflectance val-

ues obtained for the compounds after 2 and 3 weeks. But because of the formation of the graphite-like structure and of the mixed stages, no clear spectra could be observed from after 4 weeks. All these results are in good agreement with those obtained by X-ray diffraction. The formation of R_{\min} values has been shifted from 408.0 nm for stage 1 compounds(A) to 448.8 nm for the compounds after 1 hour(B) and also to 448.9 nm for those after 1 week(C). Therefore, there was almost no change in R_{\min} values up to 1 week. But the compounds obtained after 2 and 3 weeks showed the R_{\min} values of 479.2 nm and 504.0 nm, respectively, from which we can interpret that the R_{\min} values shifted gradually to lower energy levels with the deintercalation time. An interpretation of the reflectance minimum values for the compounds obtained after more than 4 weeks is not easy because of the unclear minimum value status in each corresponding spectrum. The occurrence of this unclear R_{\min} values could be caused by various factors such as structural changes, mixed stages, disordering of energy region by lithium oxides formed in Li-GDICs. From Figure 5, we can see the relationship between the energy state and the concentration of the intercalants that the clearer spectrum be observed and the R_{\min} values be formed in the higher energy region with the concentration of the intercalants.

Conclusion

Li-GICs (Li-Graphite Intercalation Compounds), synthesized by the reaction of temperature and pressure, have been spontaneously decomposed in the atmosphere. The decomposition processes were analyzed by X-ray diffraction, DSC analysis, FT-IR measurement and UV/VIS spectrophotometry.

1. X-ray diffraction analysis shows that the d_{001} -values of stages 1 and 2 were 3.71 Å and 7.06 Å, respectively. After 6 weeks, the deintercalation reaction of the Li-GICs has ceased and only residual compounds could be observed.

2. Strong exothermic reaction has been observed in thermal decomposition of Li-GICs and relatively stable decomposition curves were formed at 300 °C. A few endothermic signals were observed at 1000 °C. However, there were many exothermic and endothermic reactions occur one after

the other after 6 weeks deintercalation reaction time.

3. The results of the FT-IR measurement for the conforming the reactivity of these residual compounds under the mixed gases of O₂ and N₂, show the peaks at 2922 cm⁻¹ for -CH₃ group, 1578 cm⁻¹ for aromatic rings, 2355 cm⁻¹ for the nitrogen etc.

4. UV/VIS spectrophotometric measurement suggests that the formation of the minimum energy value (R_{\min}) for the compounds between Li-GICs as a starting material and Li-GDICs obtained by up to 3 weeks deintercalation, while there were no clear energy curve after 4 or more weeks of reaction time because of the disordered energy region caused by the formation of the graphite structure, high stages and the Li compounds surrounding the graphite with the deintercalation reaction.

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