

⁷Li-NMR and Thermal Analysis for Lithium Inserted into Artificial Carbon Material

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Lithium inserted into artificial carbon has been synthesized as a function of the Li concentration. The characteristics of these prepared compounds were determined from the studies using X-ray diffraction(XRD), solid nuclear magnetic resonance (NMR) spectrophotometric and differential scanning calorimeter(DSC) analysis. X-ray diffraction showed that lower stage intercalation compounds were formed with increasing Li concentration. In the case of the AG3, most compounds formed were of the stage 1 structure. Pure stage 1 structural defects of artificial graphite were not observed. ⁷Li-NMR data showed that bands are shifted toward higher frequencies with increasing lithium concentration; this is because non-occupied electron shells of Li increased in charge carrier density. Line widths of the Li inserted carbon compounds decreased slowly because of non-homogeneous local magnetic order and the random electron spin direction for located Li between graphene layers. The enthalpy and entropy changes of the compounds can be obtained from the differential scanning calorimetric analysis results. From these results, it was found that exothermic and endothermic reactions of lithium inserted into artificial carbon are related to the thermal stability of lithium between artificial carbon graphene layers.

Keywords : Lithium, Artificial carbon, Intercalation, XRD, DSC, ⁷Li-NMR.

Introduction

Three kinds of carbon were used for commercial cells : graphite, soft carbon and hard carbon.¹⁻⁵ Graphite intercalates up to a maximum of one lithium per six carbon atoms under ambient conditions. Graphitic carbon is highly anisotropic, at least locally, because it consists of well-developed graphene layers. Such anisotropy leads to non-homogeneous surface structures, as either the basal or edge surface can be exposed, depending on the arrangement of graphene layers near the surface. Therefore, the surface area alone cannot control the irreversible intercalation capacity, unless these two surface types have identical reactivities. In spite of graphite being a three-dimensional ordered crystal structure, soft carbon and artificial graphite do not completely form three-dimensional orders. Soft carbon is called a "graphitizing carbon" because it is graphitized by heat treatment above 2000 °C. Li_xC₆ synthesized with artificial graphite, which are Li-compounds, were obtained by the intercalation reaction and deintercalation process results in Li_(x-y)C₆ intercalates, where the values of x and y depend on the structure of host carbon and determine the quantities of lithium transferred during the intercalation and deintercalation process. Carbon materials vary widely in their internal structure, and it has been found that the microscopic and macroscopic structures greatly influence the chemical and electrochemical properties of the carbonaceous intercalation compounds.

The first use of ⁷Li-NMR in 1946 with Li⁺ aqueous solutions led to solid state Li-graphite studies in 1975 the first systematic synthesis of graphite-Li compounds.⁶ The first ⁷Li-NMR spectra of LiC₆ compounds⁷ revealed that Li-

graphite compounds, having large paramagnetic shifts and temperature independence, are true alloys with a completely new and different intercalation bonding. It was found that the lithium atom is above and under the centers of two superposed C-hexagons. This is completely different from the C-Li bond, where the Li-atom is fixed only to one carbon, like H in C-H, and in which the ⁷Li-NMR line remains within a few ppm shift/Li⁺ in LiCl.

In the present study, the Li-AGICs were synthesized by reacting artificial graphite with lithium at elevated temperatures and pressures. The structural transition and thermal decomposition with Li concentration dependence were also examined by X-ray diffraction and DSC analysis. And, to obtain direct information on the chemical state of Li-artificial graphite intercalation compounds, ⁷Li-NMR spectra of lithiated artificial graphite were taken.

Experimental Section

Materials. The lithium artificial graphite intercalation compounds (Li-AGICs) were synthesized from artificial graphite as a host material and lithium metal as a guest material. The results of elemental analysis (Ce 1110 Elemental analyzer, USA) for the artificial graphite are listed in Table I. Resultant used artificial graphite has a carbon content of 98.622(± 1.21)%. Lithium metal (Stream Chemicals, Inc., U. S. A) of dispersion type was used as an intercalant.

Preparation of Li-AGICs. Li-AGICs were synthesized by exposing a mixture of artificial graphite and lithium by volume percentage (10, 20, 30%) to temperature and pressure. The synthetic reaction was performed in argon atmosphere at 200-220 °C and under a pressure of 350-400 kg/

Table 1. The Results of Elemental Analysis for Artificial Graphite as Host Material

Sample	Elements (%)					Specific gravity
	C	H	N	S	O	
AG	98.622	0.3750	0.4438	0.0000	0.5781	2.10

cm² with a reaction time of 7-9 hours. Synthesized samples were named AG1, AG2 and AG3, respectively.

Analysis and Measurement. X-ray diffraction patterns were taken using an X-ray generator (Shimadzu XD-D1, Japan) and Cu K α radiation. Each substance obtained after intercalation reactions was filled as dense as possible into a sample holder. The results of X-ray diffraction analysis are shown in Figure 1. The Li-AGICs were kept in liquid paraffin, where they were washed by dimethoxyethane and evaporated

to dryness under a vacuum for 30 minutes at room temperature. After drying, these samples were introduced into an NMR sample tube (5 mm diam.) and the sample was sealed by an epoxy resin. All procedures for sample preparation were performed in an argon-filled dry box and set into a wide line probe of solid-state ⁷Li-NMR spectrometer (DSX400, Bruker, Germany). NMR spectra of the Li intercalated samples were measured with LiCl as an external standard. All measurements were performed under an argon atmosphere at ambient temperature (27 °C). A Differential Scanning Calorimeter (DSC) analyzer (NETZSCH, Germany) was used to confirm the thermal stability and reactivity under N₂ of the Li-AGICs. Al₂O₃ 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 was from room temperature to 1400 °C.

Result and Discussion

The literature^{8,10} cites difficulty in forming the stage 1 compound initially during the intercalation of intercalant ions in the graphite interlayers. The reaction of intercalation proceeds as follows: the order is stage 4(LiC₃₆), stage 3(LiC₂₇), stage 2(LiC₁₂₋₁₈) and stage 1(LiC₆),¹¹ and many intermediate stages with stacking disorders existing between each stage.¹² In using highly graphitic carbon materials like natural graphite, Li atoms can be intercalated into the carbon layers up to the so-called LiC₆ state. In this state, Li atoms are located over every three benzene rings. The preparation of highly graphitic carbon materials is technologically so difficult that they are prepared by heat treatment at high temperature (2800-3000 °C) to achieve a high crystallinity. But, the structure of highly oriented carbon material (artificial graphite) is quite different from that of the natural graphite. The structural changes occurring during the intercalation depend on lithium concentration, which is detected by X-ray diffraction. The results for the structural changes during intercalation are shown in Figure 1. The X-ray reflection analysis of the obtained samples shows that the reflections of stage 2 for the sample of AG1, and mixed reflections of stage 1 and stage 2 for the sample of AG2 were observed. The (G002), (G100), (G004) and (G110) reflections for the nonintercalated artificial graphite appeared, in addition, for the samples of AG1 and AG2. In the case of AG3, the reflections for stage 1 with the characteristic gold color appeared completely, but the structure of only pure stage 1 with structural defects of artificial graphite is not observed.

Multinuclear solid-state NMR spectroscopy is a well-suited technique for structural analysis of artificial graphite based anode materials generated from the pyrolysis of petroleum cokes. Several types of ordered carbons reversibly intercalated lithium in excess of the graphite stoichiometry of LiC₆. To verify the enhanced intercalation levels within this class of carbon, it is important to differentiate between the electrochemically relevant lithium species that are truly reversibly intercalated and those lost to traps, such as those located in the passivation layer or associated with structural

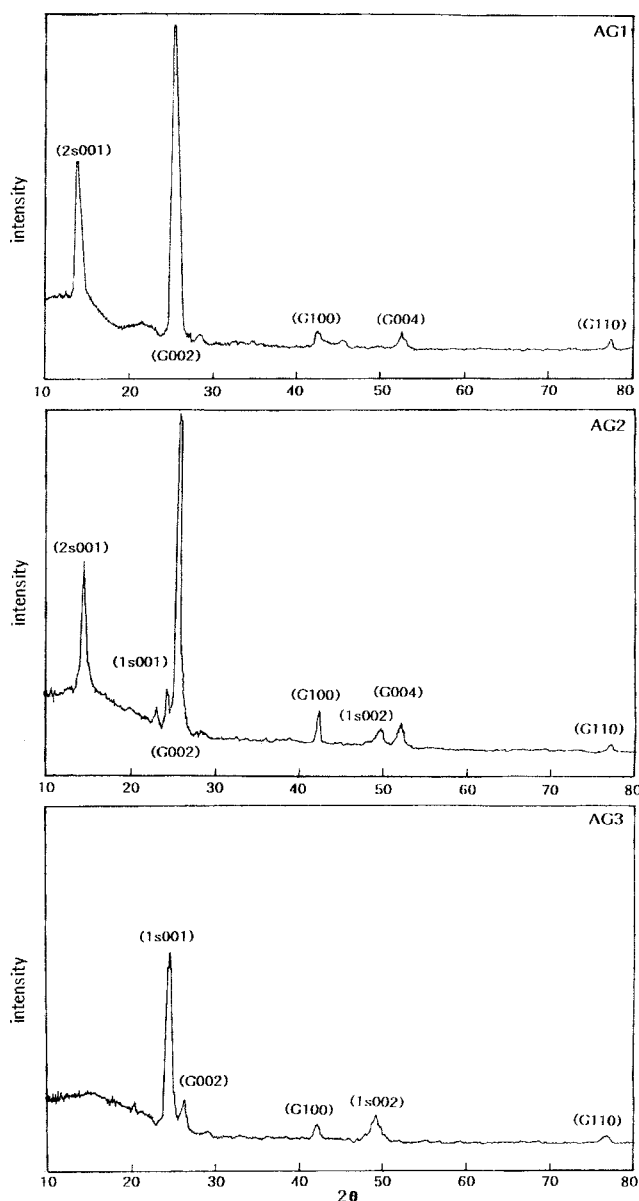


Figure 1. X-ray diffraction patterns of Li-artificial graphite intercalation compounds by Li concentrations.

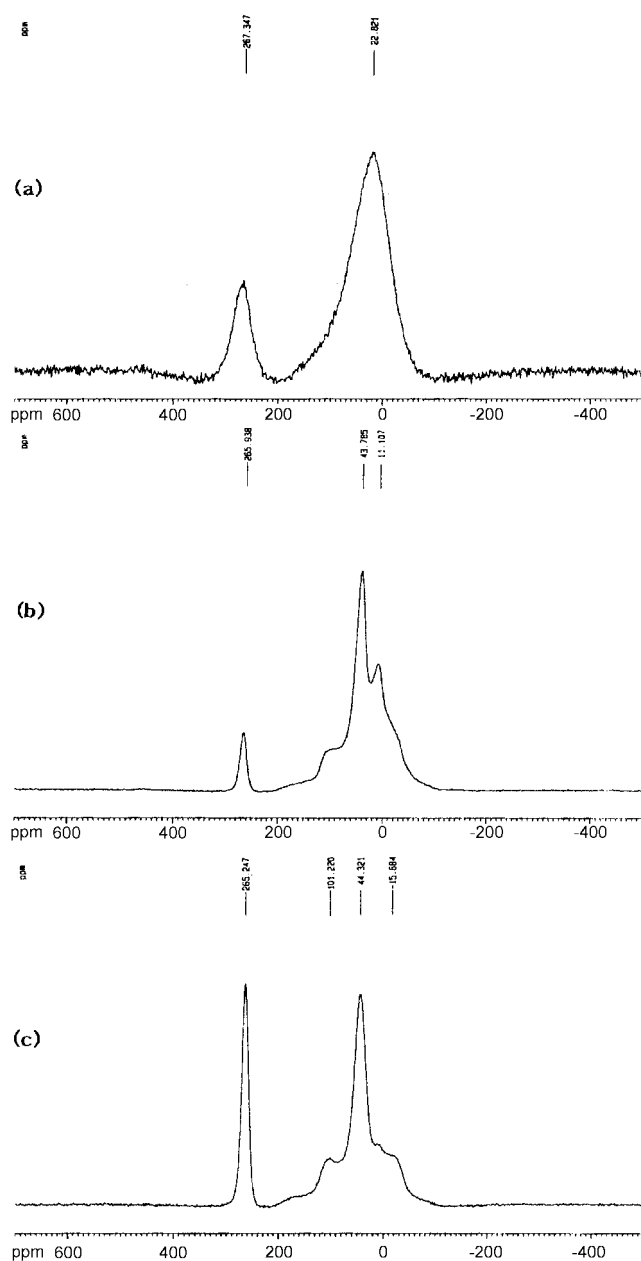


Figure 2. Solid-state NMR analysis for Li-artificial graphite intercalation compounds; (a) AG1, (b) AG2, (3) AG3.

lattice defects within the solid-state microstructure. Figure 2 shows the variations of ⁷Li-NMR spectra of AG1, AG2 and AG3. In the overall tendency, Li-AGICs with increasing lithium concentration show various local site-symmetry. The ⁷Li-NMR spectrum for AG1 shows a clear broad band with strong intensity at 22.28 ppm and another broad band at 267.35 ppm. For AG2, the sample clearly shows band of strong intensity at 11.11 ppm, another one at 43.78 ppm with sharp and strong intensity, an other one at 80.01 ppm and finally one at 265.93 ppm. The AG3 sample clearly shows two bands at 15.68 ppm and 44.32 ppm, and one between the peaks, 101.22 ppm and 265.25 ppm. It is believed that some shifts between 10 and 25 ppm are responsible for adsorbed ionic lithium in the reversible site of the carbon

basal plane. From the results, it was found that observed bands shifted toward higher frequencies with increasing lithium concentration because non-occupied electron shells of Li increased in charge carrier density. I have considered the change in the electronic structure of Li intercalated carbon material as a function of the amount of intercalated Li. Due to the semigraphite structure the pristine artificial graphite has localized states within the bandgap, and these localized states are supposed to consist of the unpaired electrons with π nature existing in the condensed aromatic carbon planes. In the initial intercalated stage (AG1), Li intercalant scavenges these defect levels or, in other words, occupies the localized states with donating electrons. Since the carrier density is reasonably small and Li is a supposition cannot be a reason for outcome. Fully ionized, the NMR signal is observed at almost the same position as that of the LiCl reference without the Knight shift. With further intercalated AG2 and AG3, the electrons transferred from Li atoms to artificial graphite material begin to occupy the conduction band. The intercalation generates conduction electrons and causes the Knight shift. From further study, it has been confirmed that the unpaired electrons begin to be influenced by Li intercalants in an intercalated state over 10% and that metallic nature arises in terms of the Pauli paramagnetic contribution of the ESR spectrum from this range.¹³ Line widths of Li-AGICs decreased slowly because of non-homogeneous local magnetic order and the random electron spin direction of located Li between graphene layers. The large difference in chemical shifts for the middle lower stage compounds (LiC₁₂₋₁₈) is probably caused by the difference in electronic interaction between graphite and Li. Chemical shifts of both 44.78 and 80.01 ppm are interpreted as Knight shifts caused by conduction electron bands. Thus, from the NMR results it is clear that the Fermi contact interaction also works in the present system as well as the spin-orbit interaction as supported by the ESR measurements.¹³ According to Zaghbi¹⁴ *et al.*, the relation between the chemical shifts observed in the "twilight" zone (10-15 ppm) of higher stage compounds, where a subtle distinction might be made in structures with reduced contributions of conduction electron density and simply covalent states. For the LiC₆ compound of the lower stage, a Knight shift of 44.32 ppm (metallic lithium 265.25 ppm) indicates its metallic character, an electrical field gradient at the lithium nucleus site with a quasi-axial symmetry. In a recent ⁷Li-NMR experiment, Sato *et al.* show that there are two kinds of Li sites that give different Knight shift values.¹⁵ This clearly shows the existence of different types of chemical bonding between Li ions with themselves or with carbon atoms in which the electronic structure associated with the edges should be different from that of the bulk. To explain the ⁷Li-NMR spectra, the author tentatively proposes the existence of molecular Li states in LiC₆ in which all hexagonal centers of the honeycomb lattice are occupied by Li atoms to give the LiC₂ stoichiometry.¹⁵ However, a large amount of energy would be needed to put Li atoms in a plane, and even in this case, a three-dimensional structure would be expected to occur.

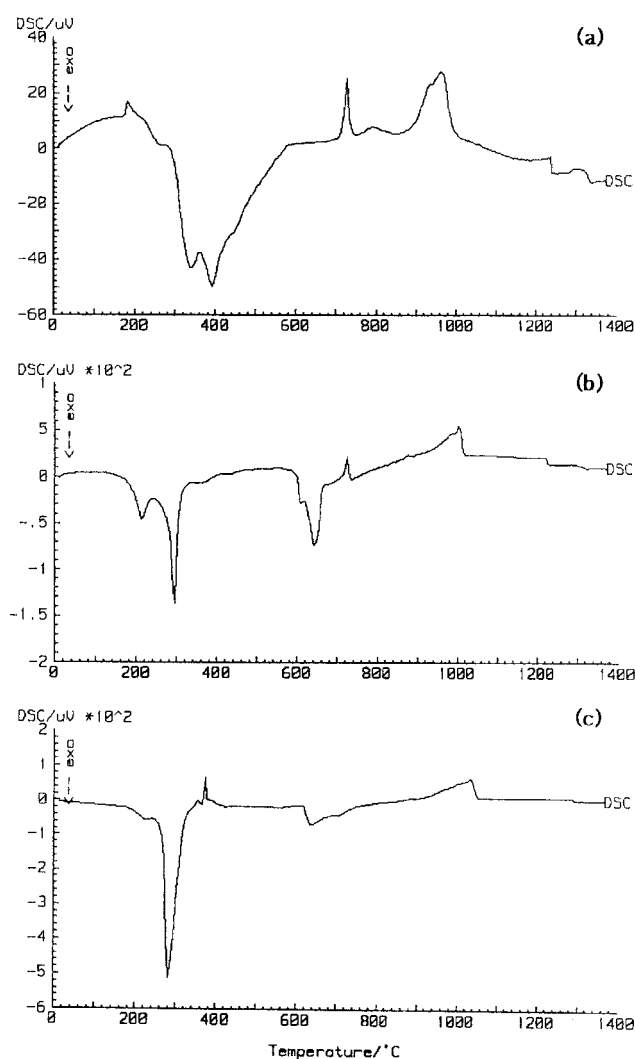


Figure 3. Thermal analysis of Li-artificial graphite intercalation compounds by DSC; (a) AG1, (b) AG2, (c) AG3.

Generally, alkali metals are intercalated into the graphite interlayer spacings with the formation of electron donor-type intercalation compounds. It is characteristic of the intercalation compounds to form residual compounds when they decompose spontaneously in air and heat, and are oxidized electrochemically with some parts of the intercalants remaining in the interlayer spacings.¹⁶⁻¹⁹ The properties of the carbonaceous compounds with lithium are quite different. Carbonaceous compounds with heavy alkali metals can be easily decomposed, while Li-carbonaceous compounds can be relatively stable for a long time in air and heat. The thermal stability and the deintercalation reaction of the Li-AGICs were characterized using DSC to a temperature of 1400 °C. Enthalpy and entropy formations were calculated by the confirmation of the thermodynamic endothermic and exothermic reactions, depending on the various lithium concentrations, 10, 20 and 30%. Figure 3 shows the enthalpy formation versus various heating rates. Figure 3(a) shows the biggest absolute values for the enthalpy formation of -1.747, -7.508 and 1.016 J/g. These values were formed for a lithium content of 10% at the narrowest temperature ranges

Table 2. Thermodynamic Data of Li-Artificial Graphite Intercalation Compounds

Sample	Temperature range (°C)	Enthalpy (ΔH) (J/g)	Entropy (ΔS) $\times 10^{-3}$
AG1	142.3-437.8(290.1)	-1.747	-3.10
	685.0-808.9(746.9)	-7.508	-10.1
	879.3-1041(960.2)	1.016	0.82
AG2	199.9-332.0(265.9)	-4.021	-7.46
	337.8-419.8(378.8)	2.886	4.43
	615.5-739.5(950.7)	-1.423	-1.51
	900.3-1055(977.7)	1.043	0.84
AG3	200.3-332.0(266.5)	-4.456	-8.26
	364.4-415.8(390.1)	2.111	3.18
	925.5-1074(999.8)	1.110	0.872

* (): Average temperature for the entropy calculation

of 142.3-437.3 °C, 685-808.9 °C and 879.3-1041 °C. Figure 3(b) also shows the largest and smallest absolute values for the enthalpy formation of -4.021, 2.886, -1.423 and 1.043 J/g. These values were also formed by the lithium content of 20% at the narrowest temperature ranges of 199.9-332.0 °C, 337.8-419.8, 615.5-739.59 and 900.3-1055 °C. The DSC plot of AG2 shows several combined exothermic and endothermic peaks. Finally, Figure 3(c) shows the largest and smallest absolute values for the enthalpy formation of -4.456, 2.111, and 1.110 J/g. These values were also formed for the lithium content of 30 % at the narrowest temperature ranges of 200.3-332.0 °C, 364.4-415.8 °C, and 925.5-1074 °C, and relatively stable composition curves were formed. From the XRD and NMR results, it has been confirmed that the concentration of the Li intercalants in the intercalated state affects the stages of each samples. In Table 2, the enthalpy and entropy formations corresponding to each temperature are listed depending on the lithium concentrations. In addition, it was found that the thermal stability of the compounds depends on the diffusion of Li between carbon interlayers with increasing temperature. This was determined from the DSC results.

Conclusion

In the present study, Li-AGICs were synthesized as a function of Li-concentration. The characteristics of these prepared compounds were determined from studies using X-ray diffraction, solid NMR spectrophotometer and Differential Scanning Calorimeter analysis. The following results are reported.

1. From the results of X-ray diffraction, it was found that the lower stage intercalation compounds were formed with increasing Li-concentrations. Mixed stages in these compounds were also observed. In the AG3 case, the compounds in the stage 1 structure were mostly formed, but the structure of only pure stage 1, for concentrating on structural defects of artificial graphite was not observed.

2. From the obtained ⁷Li-NMR data, it was found that observed bands are shifted toward higher frequencies with

increasing lithium concentration because non-occupied electron shells of Li increased in charge carrier density. Line widths of Li-AGICs decreased slowly because of non-homogeneous local magnetic order and the random electron spin direction for Li located between graphene layers.

3. The enthalpy and entropy changes of the compounds can be obtained from the DSC analysis results. From these results, it was found that exothermic and endothermic reactions of Li-AGICs are related to the thermal stability of lithium between artificial graphite layers.

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