

# Intercalation of lithium into natural graphite flakes and heat-treated polyimide films in ether-type solvents by chemical method

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## Abstract

X-ray diffraction and Raman spectroscopy have been used to study the intercalation of Li into natural graphite flakes and heat-treated polyimide films (HTT = 1800–3000 °C) by chemical method in various ether-type solvents. Here, naphthalene was used as a dissolving agent for Li, and the solvents were tetrahydrofuran (THF), 2-methyltetrahydrofuran (MeTHF), 2,5-dimethyltetrahydrofuran (diMeTHF), 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), 1-methoxypropane (MP), 1-methoxybutane (MB) and diethyl ether (Et<sub>2</sub>O). First, to elucidate the effects of the solvents, natural graphite flakes were used as a host material. By use of THF, DME and DEE, co-intercalation of Li and these solvents occurred to form ternary Li–solvent graphite intercalation compounds (GICs), but binary Li–GICs without solvents were obtained in MeTHF, diMeTHF, MP, MB and Et<sub>2</sub>O solvents. These results were confirmed by (00 $l$ ) X-ray diffraction patterns. Second, co-intercalation of Li and THF into the heat-treated polyimide films was studied mainly by use of the Raman scattering results. As a result, co-intercalation of Li and THF occurred to form Li–THF–GIC for highly graphitized polyimide films heat-treated above 2400 °C, while only Li was found to be intercalated into the less graphitized films heat-treated below 2100 °C. © 1997 Published by Elsevier Science S.A.

**Keywords:** Intercalation; Graphite. Chemical method; Lithium; Co-intercalation

## 1. Introduction

Lithium–graphite intercalation compounds (GICs) have been extensively studied these days [1–5] because of the recent development of secondary Li-ion batteries in which carbon materials have been used as the negative electrodes. In Li-ion batteries, ternarization (co-intercalation) of Li and solvent is one of the important problems to be clarified. Inaba and co-workers [6,7] made in situ electrochemical scanning tunneling microscopy (STM) observations of the basal plane of highly oriented pyrolytic graphite (HOPG) in 1 M LiClO<sub>4</sub>/ethylene carbonate–diethyl carbonate (EC:DEC, 1:1 by volume). From STM images, they observed an intercalation of a solvated lithium ion and discussed the surface film formation mechanism.

In addition to the electrochemical method mentioned above, chemical method has been used for co-intercalation of alkali metals and solvents such as tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) and hexamethylphosphoric triamide (HMPA) [8–12]. These solvents are polar, and hence they can co-intercalate into graphite with alkali metals. Mizutani et al. [13,14] have studied the co-intercalation of

various polar solvents such as 2-methyltetrahydrofuran (MeTHF), 2,5-dimethyltetrahydrofuran (diMeTHF) and 1-methoxybutane (MB) into natural graphite by a solvent method. Using these solvents, they observed formation of binary alkali metal–GICs.

In Li-ion batteries, less crystallized carbon materials have been focused recently because the batteries give higher capacity than those using highly crystallized carbon materials such as natural graphite. Less crystallized carbon materials have some amounts of defects which are usually electron acceptors, and the defects may cause a change in the Fermi level of the carbon materials [15]. Lowering the Fermi level favors intercalation of donors while it is unfavorable for that of the acceptors. In this point, co-intercalation of solvents (electron acceptor) should be affected by the degree of crystallinity of carbon materials.

As mentioned above, studies of co-intercalation of alkali metal with solvent into graphite and carbon materials is of technological importance and interesting. In the present work, to elucidate the effects of solvents, co-intercalation of Li with various ether-type solvents into natural graphite has been studied by a chemical method. The co-intercalation of Li with

THF into carbon materials prepared by the heat-treatment of polyimide films at different temperatures is also studied.

## 2. Experimental

Using various ether-type solvents, intercalation of Li into natural graphite flakes and heat-treated polyimide films (HTT = 1800, 2100, 2400 and 3000 °C) has been studied by X-ray diffraction (XRD) and Raman spectroscopy. Here, the solvents are THF, MeTHF, diMeTHF, DME, 1,2-diethoxyethane (DEE), 1-methoxypropane (MP), MB and diethyl ether (Et<sub>2</sub>O), which were dehydrated over molecular sieves.

Intercalation of Li was carried out by a solvent method; Li was dissolved into the above solvents using a dissolving agent of naphthalene, followed by immersing natural graphite flakes and heat-treated polyimide films into the solutions in a small reaction tube of Pyrex glass. After the reaction tube was sealed completely, the tube was stirred for 1 h to 7 days. For XRD measurements, the sample was taken out from the reaction tube into liquid paraffin, and was immediately wrapped with a thin polyethylene film to prevent from its oxidation by atmospheric air and moisture. XRD data were collected with Cu K $\alpha$  radiation monochromatized by HOPG. Typical working conditions were 35 kV and 20 mA, and a scanning speed was 2°/min with a time constant of 0.5 s. For Raman measurements, the sample was put into an optically flat Pyrex glass cell under an argon atmosphere. Raman spectra were excited by using a 514.5 nm line of argon ion laser, and the scattered light was collected in a backscattering geometry.

## 3. Results and discussion

### 3.1. Types of GICs obtained in various ether-type solvents

By use of THF, DME and DEE, co-intercalation of Li and these solvents occurred to form ternary Li–solvent–GICs, while only binary Li–GIC was synthesized when MeTHF, diMeTHF, MP, MB and Et<sub>2</sub>O were used. Fig. 1 shows the XRD pattern of the GICs prepared in a solution of Li–DEE for 7 days. Here, PE denotes peaks due to polyethylene film. From the peak positions of 7.90, 15.8, 23.8, 31.9, 40.1, 48.6, 57.4 and 66.7° in  $2\theta$ , a value of the  $c$ -axis repeat distance is determined to be  $I_c = 1.12$  nm. This great value of  $I_c$  indicates the co-intercalation of DEE into graphite, and the GIC is identified as stage 1. Formation of the ternary Li–DEE–GIC is reported for the first time. Formation of Li–THF–GIC and Li–DME–GIC was also observed, and the  $c$ -axis repeat distances were in good agreement with literature data [16,17]. Fig. 2 shows a typical XRD pattern of binary Li–GICs prepared in an Li–MP solution for 7 days. The number on the peaks correspond to the (00 $l$ ) index. From the (00 $l$ ) XRD pattern, the  $I_c$  value of the GIC is determined to be 0.371 nm, indicating that the resultant GIC is the binary stage 1 Li–GIC.

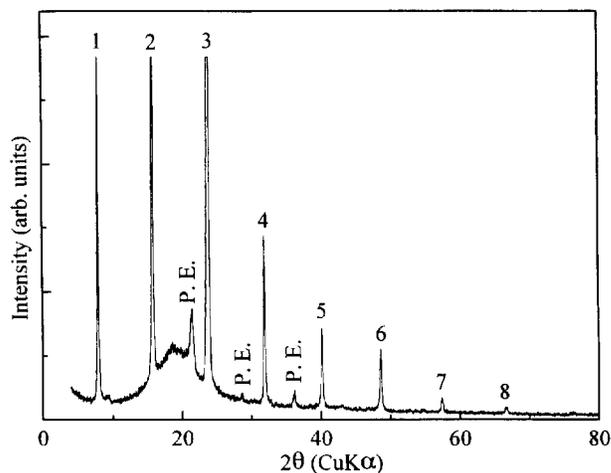


Fig. 1 XRD pattern of GIC prepared in an Li–DEE solution for 7 days. PE denotes polyethylene film. Numbers on peak correspond to the (00 $l$ ) index

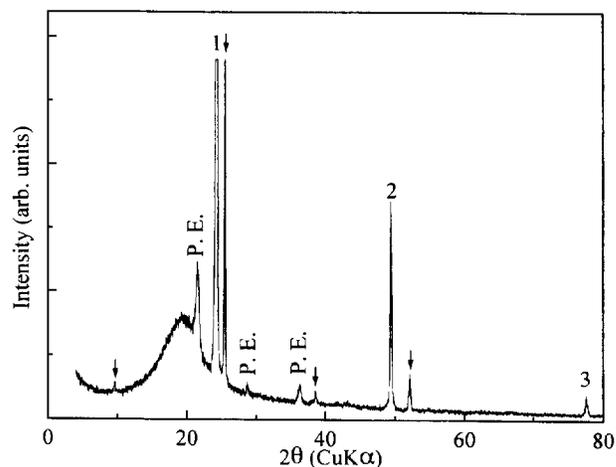


Fig. 2 XRD pattern of GIC prepared in an Li–MP solution for 7 days. PE denotes polyethylene film. Arrows correspond to the binary stage 2 Li–GIC.

In addition to the binary stage 1 Li–GIC, peaks labeled with arrows are observed in Fig. 2. These peaks are assigned as binary stage 2 Li–GIC.

From the above results, synthesized GICs are very dependent on the solvents. To elucidate the difference of the resultant GICs, electron donor numbers (DN) of the above solvents are taken into account. Gutmann's donor numbers (DN) for the solvents THF, DME, MeTHF and Et<sub>2</sub>O have been reported to be DN = 20, 24, 18 and 19.2, respectively [18]. Hence, the interaction between the solvents and Li should increase in the order of DME > THF > Et<sub>2</sub>O > MeTHF. Since a magnitude of interactions between Li and the solvent correspond to the bond strength between Li and the solvent, the present results seem to be quite valid for the Li–DME, Li–THF, Li–Et<sub>2</sub>O and Li–MeTHF systems. Since the Gutmann's donor numbers [18] of the other solvents have not been reported, measurements of <sup>29</sup>Si NMR were carried out to obtain qualitative information on the donor numbers of solvents. A small amount of dimethoxydiphenylsilane was dissolved in 0.5 ml of the solvents used in the present work, and the <sup>29</sup>Si NMR chemical shift caused by the interaction between the silicon and the

oxygen atom of the solvents was measured using JEOL EX-207 spectrometer. The values of the  $^{29}\text{Si}$  NMR chemical shift relative to external tetramethylsilane (TMS) were determined to be  $-29.91$ ,  $-29.86$ ,  $-29.86$ ,  $-29.58$ ,  $-29.63$ ,  $-29.51$ ,  $-29.63$  and  $-29.50$  ppm for THF, MeTHF, diMeTHF, DME, DEE, MP, MB and  $\text{Et}_2\text{O}$ , respectively. When Gutmann's donor number is considered, the value of DME should be higher than that of THF, however, the present result is vice versa. The DME and DEE solvents have two oxygen atoms in molecule which can coordinate to a silicon atom of dimethoxydiphenylsilane. Considering that the values of the  $^{29}\text{Si}$  NMR chemical shift of DME and DEE are relatively lower than that of THF and that the values are close to that of MB whose molecular structure is thought to be similar to that of DME, only one oxygen atom of DME and DEE may be coordinated to silicon atom of dimethoxydiphenylsilane. Hence practical donicities of DME and DEE are not obtained by the present method. For the other solvents of THF, MeTHF, diMeTHF, MP, MB and  $\text{Et}_2\text{O}$  with only one oxygen atom, the values may be reasonable. The chemical shift of THF is the highest, indicating the strongest interaction between THF and dimethoxydiphenylsilane, corresponding to our result of the formation of Li-THF-GIC. It is concluded from the  $^{29}\text{Si}$  NMR chemical shift that the present result can be understood by the interaction of Li and the solvents except solvents with two oxygen in a molecule which can coordinate to Li.

Table 1 summarizes the GIC types obtained in the above solvents, Gutmann's donor number [18] and the values of  $^{29}\text{Si}$  NMR chemical shift.

### 3.2. Types of GIC obtained for various heat-treated polyimide films

To elucidate the effect of the degree of crystallinity, heat-treated polyimide films (HTT = 1800, 2100, 2400 and 3000  $^\circ\text{C}$ ) were used as the host materials. Co-intercalation of Li and THF into the films was studied mainly by use of Raman scattering observation. Raman spectra of Li-GICs prepared from the films in MeTHF were also measured for comparison.

Fig. 3(a) and (b) shows the Raman spectra of the GICs prepared from the films heat-treated at 3000  $^\circ\text{C}$  in Li-THF and Li-MeTHF solutions for 7 days. The Raman active  $E_{2g}^{(2)b}$  mode frequencies determined by Lorentzian line shape analysis were 1604 and 1598  $\text{cm}^{-1}$  in Fig. 3(a) and (b), respectively. Since the polyimide films heat-treated at 3000  $^\circ\text{C}$  are highly graphitized, the resultant GICs prepared from

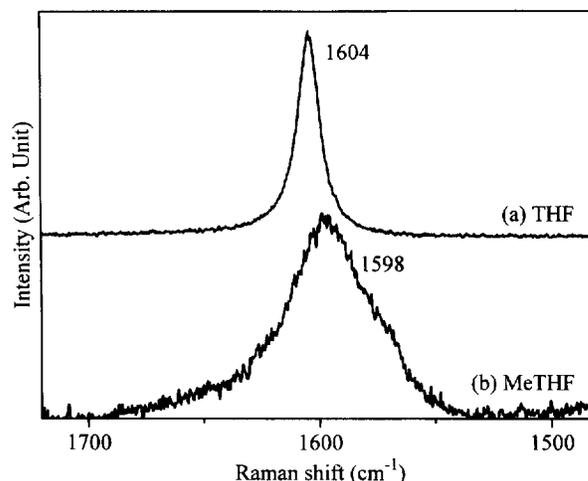


Fig. 3. Raman spectra of GICs prepared from polyimide films heat-treated at 3000  $^\circ\text{C}$  in (a) Li-THF and (b) Li-MeTHF solutions for 7 days. The number on the peak refers to the Raman active  $E_{2g}^{(2)b}$  mode frequency determined by Lorentzian line shape analysis.

the films are the same as those prepared from natural graphite mentioned above. Hence, the Raman active  $E_{2g}^{(2)b}$  mode frequency of 1604  $\text{cm}^{-1}$  corresponds to the ternary stage 1 Li-THF-GIC and that of 1598  $\text{cm}^{-1}$  to the binary stage 1 Li-MeTHF-GIC, which are also confirmed by XRD. The Raman active  $E_{2g}^{(2)b}$  mode frequencies are determined to be 1604 and 1597  $\text{cm}^{-1}$  for the GICs prepared from the films heat-treated at 2400  $^\circ\text{C}$  in Li-THF and Li-MeTHF solutions, respectively. Similar to the results of the films heat-treated at 3000  $^\circ\text{C}$ , the formation of ternary stage 1 Li-THF-GIC and binary stage 1 Li-GIC is observed.

As is mentioned above, for the graphitized films heat-treated above 2400  $^\circ\text{C}$ , there is a clear difference in Raman active  $E_{2g}^{(2)b}$  mode frequencies of the resultant GICs prepared in Li-THF and Li-MeTHF solutions. In contrast, for less graphitized films heat-treated at 1800 and 2100  $^\circ\text{C}$ , the peaks associated with the Raman active  $E_{2g}^{(2)b}$  mode were observed at 1592 and 1599  $\text{cm}^{-1}$ , respectively, irrespective of the kind of solvent. Fig. 4(a) and (b), for example, shows the Raman spectra of the GICs synthesized from the films heat-treated at 2100  $^\circ\text{C}$  in the Li-THF and Li-MeTHF solutions for 7 days. As is shown in Fig. 4(a) and (b), the Raman active  $E_{2g}^{(2)b}$  mode frequencies are the same for the GICs prepared in both solutions. As is mentioned before, less crystallized carbon materials have some amounts of defects which are electron acceptors, and therefore the defects lower the Fermi level of the carbon materials [15]. The lowering of the Fermi

Table 1  
GICs obtained in various solvents, Gutmann's donor number (DN) [18] and  $^{29}\text{Si}$  NMR chemical shift <sup>a</sup>

Solvent	THF	MeTHF	diMeTHF	DME	DEE	MP	MB	$\text{Et}_2\text{O}$
Type	Ternary	Binary	Binary	Ternary	Ternary	Binary	Binary	Binary
DN	20	18		24				19.2
chemical shift (ppm)	-29.91	-29.86	-29.86	-29.58	-29.63	-29.51	-29.63	-29.58

<sup>a</sup> Values of the  $^{29}\text{Si}$  NMR chemical shift are given relative to external TMS.

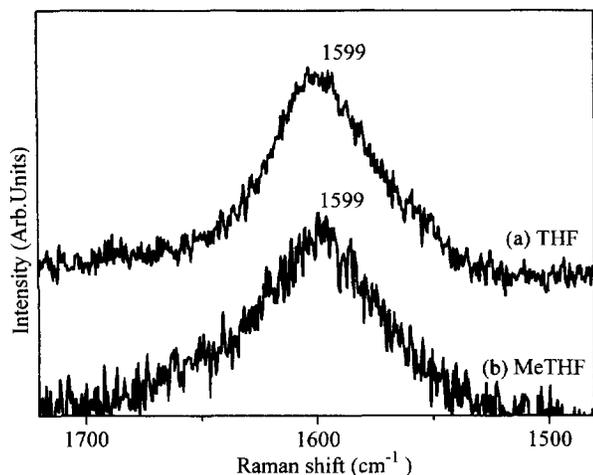


Fig. 4. Raman spectra of GICs prepared from polyimide films heat-treated at 2100 °C in (a) Li–THF and (b) Li–MeTHF solutions for 7 days. The number on the peak refers to the Raman active  $E_{2g}^{(2)h}$  mode frequency determined by Lorentzian line shape analysis.

Table 2  
Raman active  $E_{2g}^{(2)h}$  mode frequencies ( $\omega$ ) and GIC types obtained in Li–THF solution for various heat-treated polyimide films

HTT (°C)	1800	2100	2400	3000
Type	Binary	Binary	Ternary	Ternary
$\omega$ (cm <sup>-1</sup> )	1592	1599	1604	1604

level favors intercalation of donors while it is unfavorable for that of acceptors, and therefore, co-intercalation of solvents (electron acceptor) should be affected by the degree of the crystallinity of the carbon materials. Thus, the resultant GICs are probably binary Li–GICs. XRD patterns for these GICs obtained from the less graphitized films were also measured and weak peaks around 24° in  $2\theta$  were observed. The value is in good agreement with that of (001) XRD peak for binary stage 1 Li–GIC, indicating again that the resultant GICs are likely to be binary Li–GICs. Similar results have been obtained in the K–THF system by Mizutani et al. [19]. For polyimide films heat-treated below 2100 °C, co-intercalation of THF does not occur, and only Li is intercalated into these films. Inagaki and Iwashita [20] studied the intercalation of sulfuric acid into various heat-treated carbons and they concluded that the host carbon materials must have a certain degree of graphitization for the intercalation of sulfuric acid into the host materials and that there must be a criterion on electronic structure of host for the intercalation.

Considering these results [20], co-intercalation of THF in the present work may be affected by the electronic structure of heat-treated polyimide films.

Table 2 summarizes the Raman active  $E_{2g}^{(2)h}$  mode frequencies ( $\omega$ ) and the types of the GIC obtained in the Li–THF solutions for various heat-treated polyimide films.

From the above results, co-intercalation of solvents into carbon materials is mainly affected both by the degree of the

interactions between Li and the solvent and by the degree of the crystallinity of the carbon materials.

#### 4. Conclusions

Intercalation of Li into natural graphite and heat-treated polyimide films in various ether-type solvents has been studied by X-ray diffraction and Raman spectroscopy.

The results are as follows:

1. Co-intercalation of solvents with Li into natural graphite is affected by donicities of the solvents, that is, the interaction between Li and the solvents.
2. Co-intercalation of solvents is also influenced by the degree of the crystallinity of the carbon materials.

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