

Lithium Isotope Effect Accompanying Chemical Insertion of Lithium into Graphite

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Z. Naturforsch. **57 a**, 857–862 (2002); received April 10, 2002

Lithium was chemically intercalated from 1-methoxybutane solution of lithium and naphthalene into graphite and *vice versa*, and lithium isotope fractionation accompanying those intercalation and deintercalation processes was observed. ^6Li was always preferentially fractionated into the graphite phase. The single-stage lithium isotope separation factor upon intercalation was about 1.023 at 25 °C, nearly independent of the structure of the lithium-graphite intercalation compounds formed. A much smaller separation factor was observed for the deintercalation process, suggesting the existence of lithium sites (surface areas) other than the sites between graphene layers of the host graphite. Separation factor data were consistent with the following decreasing order of the ^6Li -to- ^7Li reduced partition function ratio (RPFR): RPFR of 1-methoxybutane solution > RPFR of surface areas > RPFR of metal lithium > RPFR of graphene interlayer sites.

Key words: Lithium Isotopes; Isotope Effects; Intercalation; Single-stage Separation Factor; Lithium-graphite Intercalation Compounds.

1. Introduction

It is well known that alkali metals, halogens, metal halides and so forth can be intercalated in graphite to form various graphite intercalation compounds (GICs) [1]. GICs are layered compounds in which atomic or molecular layers (intercalate layers) are inserted between graphene layers (often called sheets) of host graphite. An important and characteristic property of GICs is the staging phenomenon, which is characterized by intercalate layers that are periodically arranged in a matrix of graphene layers. The staged structure is schematically illustrated in Figure 1a. The stage index n denotes the number of graphene layers between adjacent intercalate layers. It is known that lithium can be intercalated into graphite to form lithium-graphite intercalation compounds (Li-GICs) [2]. Four different staged structures of Li-GICs are known, depending on the concentration of lithium (Stages 1 to 4 in Fig. 1a). The in-plane structure of Stage 1 is illustrated in Figure 1b. The composition of stage-1 Li-GIC is thus LiC_6 .

If there exist large lithium isotope effects upon lithium insertion/extraction, lithium ion batteries may be applied to lithium isotope separation. A common

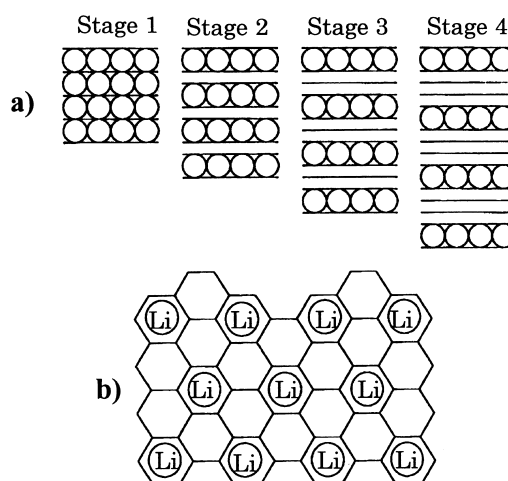


Fig. 1. a) Staged structures of GICs and b) the in-plane structure of stage-1Li-GIC. o: intercalate, —: graphene layer.

lithium ion secondary battery is basically composed of an anode made of a lithium oxide-based compound, a graphite cathode and an organic electrolyte containing lithium salt. It is charged by intercalating lithium ions into graphite and discharged by deintercalating lithium from graphite. Because of their high voltage, high energy density and high safety, lithium

Table 1. Experimental conditions and obtained staged structures and separation factors, *S*, of intercalation experiments at 25 °C.

Run No.	Intercalation time/day	Li/Nap mole ratio	<i>x</i> in LiC _{<i>x</i>}	Stage ^a	<i>S</i>
C20-1	20	1.54	9.0	2	
C15-1	15	1.56	6.3	1, 2	
C10-1	10	3.25	6.8	1, 2	1.027
C10-2	10	3.13	11.0	1, 2	1.023
C10-3	10	3.08	5.9	1, 2, G	1.022
C10-4	10	1.57	7.8	1, 2, G	1.018
C10-5	10	1.21	15.4	2	1.026
C10-6	10	0.77	13.0	2	1.022
C07-1	7	2.18	8.0	1, 2	1.023
C06-1	6	1.49	8.7	1, 2, G	
C03-1	3	1.98	6.3	1, 2	
C03-2	3	1.63	8.7	1, 2	
C03-3	3	1.22	7.6	1, 2, G	
C03-4	3	0.81	8.7	1, 2	
C03-5	3	0.79	12.2	1, 2	
C03-6	3	0.60	380	G	
C03-7	3	0.49	240	G	1.010
C03-8	3	0.39	590	G	1.011
C03-9	3	0.36	69.0	G	

^a 1 = stage-1 phase, 2 = stage-2 phase, G = graphite phase.

ion secondary batteries are nowadays widely used as energy sources of such electronics as personal computers and portable telephones.

Intercalation and deintercalation of lithium can be carried out not only electrochemically but also chemically. In this paper we report on the observation of lithium isotope effects accompanying chemical insertion/extraction of lithium into/from graphite.

2. Experimental

2.1. Graphite and Reagents

Natural graphite flakes with grain sizes of 180 μm or larger, specific surface areas of 0.62 m²/g and crystallite sizes of about 42 nm were used as host material for lithium intercalation. Lithium foils, 1 mm thick and with a purity of 99.8%, were purchased from Honjo Metals Co. Ltd. The other reagents were of analytical grade and were used without further purification except hexane, which was used after dehydration with molecular sieves.

2.2. Intercalation

Li-GICs were synthesized according to the method described in [3]. 2.5 mmol of naphthalene and a certain amount of lithium foil were placed in 10 cm³ of

Table 2. Experimental conditions and obtained separation factors of deintercalation experiments at 25 °C.

Run No.	Deintercal. time/day	Before deintercal. <i>x</i> in LiC _{<i>x</i>}	After deintercal. <i>x</i> in LiC _{<i>x</i>}	Stage ^a	<i>S</i>
C03d	3	9.7	1, 2	G	1.003
C07d	7	8.0	1	G	1.007

^a 1 = stage-1 phase, 2 = stage-2 phase, G = graphite phase.

1-methoxybutane, and the mixture was stirred at 25 °C for 24 h under an atmosphere of dried argon, yielding a lithium-naphthalene-1-methoxybutane (Li-NM) complex. The formation of the Li-NM complex was confirmed by the color change of the solution from transparent to deep blue [4]. After the formation of the complex, 0.2 g of graphite flakes, wrapped in a stainless net, were put in, and intercalation commenced. The operation for intercalation with stirring was continued at 25 °C for several days. The Li-GIC thus obtained was separated from the 1-methoxybutane solution, washed thoroughly with dehydrated hexane. The Li-GIC and the 1-methoxybutane solution were then subject to measurements.

The experimental conditions are summarized in Table 1. The intercalation time ranged from 3 to 20 days. The amounts of lithium metal used for the synthesis of Li-GICs were chosen such that the molar ratio of Li to naphthalene (Li/Nap ratio) of 1-methoxybutane solution became 0.36 to 3.25.

2.3. Deintercalation

The Li-GICs were first synthesized under the conditions of the intercalation experiments, Runs C07-1 and C03-3. Then, using these Li-GICs, deintercalation experiments were conducted.

0.2 g of Li-GIC wrapped in a stainless net and 2.5 mmol of naphthalene were placed in 10 cm³ of 1-methoxybutane at 25 °C, and deintercalation commenced. The operation for deintercalation with stirring was continued at 25 °C for several days to obtain a partially-deintercalated Li-GIC. It was separated from the 1-methoxybutane solution, and both were subject to subsequent measurements.

The experimental conditions are summarized in Table 2.

2.4. Measurements

Powder X-ray diffraction (XRD) patterns of Li-GICs were obtained to determine the staged struc-

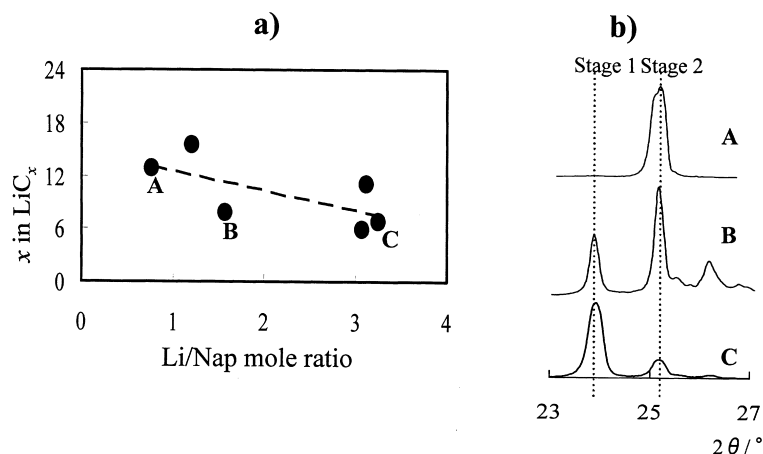


Fig. 2. Plot of x in LiC_x against the Li/Nap mole ratio at the intercalation time of 10 days; and b) examples of XRD patterns. A, B and C in b) correspond to A, B and C in a).

tures. Samples for XRD measurements were prepared under an atmosphere of dried argon. An aliquot of a Li-GIC and an appropriate amount of liquid paraffin were placed on a glass plate for XRD measurements and mixed well, and the plate was then wrapped with Parafilm to protect Li-GIC from moisture in the air, since Li-GICs are in general unstable against water. The plate was then mounted on the XRD apparatus, a Rigaku RINT2100V/P X-ray diffractometer, and the XRD pattern was recorded.

The lithium content of a Li-GIC was measured to determine the chemical composition of the Li-GIC, *i. e.*, the x in LiC_x . An aliquot of the Li-GIC was heated at 800 °C for 10 h in an electric furnace and the resultant lithium oxide was dissolved in dilute hydrochloric acid. The lithium concentration of this hydrochloric acid solution was measured with a Dainiseikoshia SAS727 atomic absorption spectrometer operated in the flame photometric mode.

In order to determine the ^7Li -to- ^6Li single-stage separation factor, S , accompanying intercalation and deintercalation, the $^7\text{Li}/^6\text{Li}$ ratios of the Li-GICs and Li-NM complexes were measured mass-spectrometrically. Samples for mass spectrometry were prepared as follows: As for Li-GIC, a portion of hydrochloric acid solution containing lithium chloride used for the determination of the lithium content underwent cation and anion exchange to obtain a lithium hydroxide solution. Hydriodic acid was added to this solution, and the resultant lithium iodide solution was subject to mass spectrometric determination of the $^7\text{Li}/^6\text{Li}$ ratio after the concentration of lithium was adjusted to 0.15 mol/dm³. As for the Li-NM complex, unreacted metal lithium was first separated from the 1-methoxybutane solution containing the Li-NM

complex. A small portion of the solution was then heated at 800 °C for 10 h in an electric furnace, and the resultant lithium oxide was dissolved with dilute hydrochloric acid. This hydrochloric acid solution underwent the same treatment as Li-GIC. The $^7\text{Li}/^6\text{Li}$ ratio of the samples was determined by the surface ionization technique with a Varian Mat CH-5 mass spectrometer or a Finnigan Mat 261 mass spectrometer. The procedure of the lithium isotopic measurements is described in [5]. S is defined as $S = (^7\text{Li}/^6\text{Li})_{\text{sol}} / (^7\text{Li}/^6\text{Li})_{\text{graphite}}$.

In addition to the separation factors accompanying the intercalation and deintercalation processes, S values between Li-NM complexes and unreacted lithium metal were also determined. In this case, S is defined as, $S = (^7\text{Li}/^6\text{Li})_{\text{sol}} / (^7\text{Li}/^6\text{Li})_{\text{metal}}$.

3. Results and Discussion

3.1. Chemical Intercalation and Deintercalation

It is reported that only lithium is inserted in graphite from 1-methoxybutane solution of lithium and naphthalene [3]. In the present study, no evidence for the insertion of the solvent or naphthalene is found by XRD measurements. The chemical compositions and staged structures of the Li-GICs are summarized in the 4th and 5th column of Table 1, respectively.

In Fig. 2a), the chemical composition of Li-GIC, *i. e.*, x in LiC_x , is plotted against the Li/Nap ratio of the 1-methoxybutane solution when the intercalation time is 10 days (Runs C10-1 to C10-6). The Li/Nap ratio was varied between 0.77 and 3.3. A loose and shallow negative correlation, larger Li/Nap ratios yielding smaller x values, ranging from 15.4 to 5.9, is observed

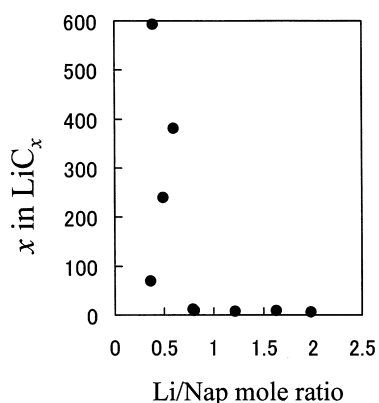


Fig. 3. Plot of x in LiC_x against the Li/Nap mole ratio at the intercalation time of 3 days.

between the Li/Nap ratio and x . The XRD patterns of the selected Li-GICs are shown in Figure 2b). The relative peak height corresponding to the stage-1 Li-GIC increases and that of the stage-2 Li-GIC decreases with decreasing x in LiC_x . Thus, the results of the chemical and XRD analyses are consistent. No peaks corresponding to stage-3 or -4 Li-GIC are observed in the XRD patterns (5th column of Table 1), indicating that lower stage Li-GICs cannot be synthesized under the experimental conditions of the runs shown in the first part of Table 1.

In order to synthesize Li-GICs of lower stages (stage 3 and stage 4), the Li/Nap ratio and intercalation time were reduced. The results are shown in Figure 3. The intercalation time was 3 days and the Li/Nap ratio ranges from 0.36 to 1.98 (Runs C03-1 to C03-9). The x value ranges from 6.3 to 12.2, equivalent to that in Fig. 2a), when the Li/Nap ratio is 0.79 or larger (Runs C03-1 to C03-5). The XRD analysis identifies the stage-1, stage-2 and graphite phases and not the stage-3 and stage-4 phases. When the Li/Nap ratio becomes smaller than 0.79, x abruptly becomes large, 69 to 380, showing that very little intercalation occurs. Only the graphite phase is detected in the XRD patterns of those Li-GICs.

In Fig. 4, the x value is plotted against the intercalation time. The Li/Nap ratio is kept almost constant at 1.6 ± 0.1 . As is seen, the chemical compositions of the Li-GICs are nearly independent of the intercalation time between 3 and 20 days and stage-1 and stage-2 Li-GICs are obtained. Figure 4 thus shows that intercalation time of 3 days is long enough for stage 1 and stage 2 Li-GICs to be synthesized.

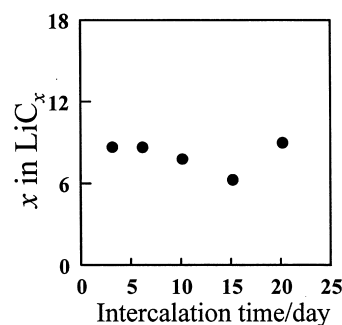


Fig. 4. Plot of x in LiC_x against the intercalation time at the Li/Nap molar ratio of 1.6 ± 0.1 .

To summarize, the stage-1 and stage-2 Li-GICs can be synthesized within 3 days at 25 °C as long as the Li/Nap ratio of the 1-methoxybutane solution is 0.79 or larger. When the Li/Nap ratio is below 0.79, lithium is hardly intercalated within graphite. It seems difficult to synthesize stage-3 and stage-4 Li-GICs by chemical intercalation of lithium from a 1-methoxybutane solution of the Li-NM complex.

The change in chemical composition of Li-GIC accompanying deintercalation is summarized in Table 2. The x values after deintercalation are 10.8 and 10.5 by the chemical analysis, which indicates that the partially-deintercalated Li-GICs should show the stage-2 and/or stage-1 phases. However, the XRD analysis reveals that they have only the graphite phase. This discrepancy contrasts the moderate correlation observed for the intercalation process, as shown in Table 1 and Fig. 2, and indicates that the majority of lithium atoms in the partially-deintercalated Li-GICs of Runs C03d and C07d after deintercalation does not exist between the graphene layers of the host graphite but in some other sites. Candidates for those sites are surface areas of the graphite crystallites, graphite particles, and edge planes. Speciation of lithium at edge planes seems underdeveloped in the case of chemical insertion/extraction of lithium into/from graphite. In the case of electrochemical insertion of lithium from an ethylene carbonates-based solvent, it is reported that stable surface films are formed on the surfaces of graphite by accumulation of decomposition products of the solvated lithium ion and by rupturing of graphite layers [1]. If similar phenomena occur in chemical insertion / extraction, lithium at edge planes may be situated more like lithium in the solution phase than lithium between graphene layers.

3.2. Lithium Isotope Effects

The S values of intercalation experiments are listed in the last column of Table 1. They are all larger than unity, ranging from 1.010 to 1.027, which means that ^6Li is preferentially fractionated into graphite. This tendency of lithium isotope fractionation is the same as those of other chemical exchange methods of lithium isotope separation using amalgam [6 - 9], tin [10], crown ether/cryptands [11, 12] and organic and inorganic ion exchangers [5, 13 - 16]. The S value is nearly constant at 1.023 (the average of the seven data) in the x range of 6 to 15 where the staged structures of Li-GICs are observed (stage 1 and stage 2). Thus, the S value seems to be independent of the staged structure of Li-GIC. That is, the ^6Li -to- ^7Li isotopic reduced partition function ratio (RPFR) [17], $(s/s')f$, of lithium between graphene layers little depends on stage index n . Contrary to this, the S value is much smaller (1.011, the average of the two data) when the staged structure is not observed.

The S values accompanying deintercalation are listed in the last column of Table 2. In this case, ^6Li prefers to be in the graphite phase rather than to be in the solution phase similarly to the case of intercalation, but the S value is much smaller (1.004, the average of the two data).

The experimental observations on the lithium isotopic separation factor mentioned in the last two paragraphs are qualitatively understood in terms of the RPFRs of lithium species involved in the present systems. The chemical and XRD analyses suggest that there are two kinds of sites in graphite where lithium resides, *i. e.*, between graphene layers and at edge planes. Then, the experimentally observed separation factor may be expressed as

$$\ln S = \ln(s/s')f_{\text{sol}} - \ln\{y(s/s')f_{\text{layer}} + (1-y)(s/s')f_{\text{sur}}\},$$

where $(s/s')f_{\text{sol}}$, $(s/s')f_{\text{layer}}$ and $(s/s')f_{\text{sur}}$ are the RPFRs of lithium in 1-methoxybutane solution, between graphene layers of graphite and at edge planes (surface areas) of graphite, respectively, and y is the mole fraction of lithium between graphene layers in graphite. In the two extreme cases of $y = 1$ and $y = 0$, S is given as $S = K_{s/l}$ ($\equiv (s/s')f_{\text{sol}}/(s/s')f_{\text{layer}}$) and $S = K_{s/s}$ ($\equiv (s/s')f_{\text{sol}}/(s/s')f_{\text{sur}}$), respectively, where $K_{s/l}$ and $K_{s/s}$ are the equilibrium constants of

the lithium isotope exchange reactions between the 1-methoxybutane solution and graphene layers and between 1-methoxybutane and edge planes, respectively. The experimental results are consistent with the assumption that the decreasing order of RPFRs of lithium is $(s/s')f_{\text{sol}} > (s/s')f_{\text{sur}} > (s/s')f_{\text{layer}}$, and that the y value is the largest for intercalation experiments where staged structures are observed, the smallest for deintercalation experiments and in between for intercalation experiments where no staged structure is observed.

The S value obtained for the equilibration of metal lithium and the Li-NM complex at 25 °C is 1.018 (average of two data, 1.015 and 1.021). Thus, the RPFR of lithium metal, $(s/s')f_{\text{metal}}$, is expected to be between $(s/s')f_{\text{sur}}$ and $(s/s')f_{\text{layer}}$; $(s/s')f_{\text{sol}} > (s/s')f_{\text{sur}} > (s/s')f_{\text{metal}} > (s/s')f_{\text{layer}}$.

Quantitative estimation of the RPFR values is still difficult because no vibrational mode of lithium species in the graphite-1-methoxybutane system is reported. Molecular orbital calculations may be effective to such systems that lack in vibrational information [18, 19], and we have already started a molecular orbital study along that line.

4. Conclusion

Lithium isotope effects accompanying chemical insertion of lithium from 1-methoxybutane solution of lithium and naphthalene into graphite and chemical extraction of lithium from lithium-graphite intercalation compounds to 1-methoxybutane solution were experimentally observed at 25 °C. The lighter isotope was preferentially fractionated into the graphite phase in every experiment. The value of the single-stage separation factor was 1.023 (the average of seven data) for the chemical insertion accompanying the formation of graphite staged structures, 1.011 (the average of two data) for the chemical insertion without the formation of the graphite staged structure and 1.004 (the average of two data) for the chemical extraction. It was speculated that lithium resided not only between graphene layers but at some other places, such as edge planes of graphite.

Acknowledgements

Natural graphite flakes used in this study were kindly donated to us by Dr. T. Abe, Institute of Atomic Energy, Kyoto University. The use of a mass spectrometer to determine $^7\text{Li}/^6\text{Li}$ isotopic ratios was

kindly offered by Prof. Y. Fujii, Res. Lab. Nucl. Reactors, Tokyo Institute of Technology. The assistance

of Dr. M. Nomura, RLNR-TIT, in the $^7\text{Li}/^6\text{Li}$ isotopic ratio measurements is greatly appreciated.

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