

Determination of Diffusion Rate and Accommodation State of Li in Mesophase Carbon for Anode Materials by NMR Spectroscopy

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Diffusion coefficients of Li in mesophase carbon of anode materials, independent of the interfacial transport effect, were directly measured first using the pulsed gradient spin echo NMR method. Disordered carbons fired at temperatures lower than 1500 °C consist of two phases: one is a crystalline phase comprising a number of roughly oriented microcrystalline of graphene layers; the other is a disordered phase comprising a number of cavities caused by mismatching space and edge regions among crystalline phases. A single component was shown by NMR spectra and the diffusion coefficient of Li in disordered carbon at 100 °C, indicating that Li accommodated in the phases can move between each other rapidly compared with measuring NMR frequency at that temperature. The observed diffusion coefficient increased with the increase in charged Li content in disordered carbons, indicating that Li is first accommodated into the disordered phase; then, with increasing charging level, Li would dominate the ordered phase in which Li diffusivity is more rapid than that in the disordered phase. The observed diffusion value of Li of ca. $3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ confirmed the feasibility of disordered carbons for anode materials, which have large Li storage capacity, by improvement of interfacial reaction sites with electrolyte materials.

Introduction

For application as anodes in Li secondary batteries, carbonaceous materials have been studied extensively because of their safety and high reversibility during electrochemical insertion and extraction of Li.^{1–3} Although graphitized carbons are generally used in batteries because of their reliability, cost, and convenience, their theoretical value of the Li storage is limited to 372 mA h g⁻¹, which is too low to be applied to next generation batteries having doubled energy density. In contrast, Li storage capacity of some disordered carbons prepared by heating mesophase carbons at lower temperatures has been reported to be as high as 900 mA h g⁻¹,³ which is attractive for providing high capacity batteries. These materials, however, have not been utilized in conventional batteries for several reasons. One major reason is the poor power capability attributable to these materials' intrinsic nature.^{4–7} Dahn et al. assumed that Li is trapped at the stable site once it is accommodated in the carbon structure, resulting in a slower rate of Li extraction process because of increased activation energy.⁴ Takami et al. assumed the semiconductive nature of disordered carbon, which slows the rate of extraction of Li from the carbon.⁵

However, we reported in our previous preliminary investigation that the rate of Li transfer in the interior structure of disordered carbon is presumed to be rather rapid.⁸ It is well-known that disordered carbons consist of two different phases.

One is a crystalline phase comprising a number of roughly oriented microcrystallites of graphite-like structure having a few graphene layers. The other is a disordered phase comprising a number of cavities existing as a result of mismatched space among roughly oriented microcrystallites; it may be considered to be a space surrounded by edge planes of several less-oriented microcrystallites.^{4,9} Although both phases can accommodate Li, large Li storage capacity of disordered carbons is attributed to the disordered phase. We previously pointed out from the features of ⁷Li NMR spectra that Li can move away from the disordered site and into interlayer spacing of the microcrystallite and vice versa fast enough to giving a single peak which is an average of two phases. This indicates that the rate-determining process during the electrochemical reaction of Li insertion and extraction in disordered carbons is not an interior process, but a process occurring at the carbon/electrolyte interface. Most papers that address determination of the diffusion coefficient of Li in carbon have been based on electrochemical measurements such as impedance spectroscopy, potential step chronoamperometry, or current step chronopotentiometry, by which effects of the interfacial process are inevitable.^{10–14} It is acceptable that these results did not necessarily obtain the real diffusive feature of Li in the anode materials.

Provided that the Li mass transfer process in the carbon interior is rapid, the carbon can be utilized as an anode material of practical batteries because the electrochemical reaction rate can be enhanced by activating the surface reaction site. Accordingly, evaluation of the Li mass transfer rate by a method that is independent of the interfacial transport process is essential for practical applications as well as for investigation of the Li migration mechanism. The present study measures the self-diffusion coefficient of Li using a spectroscopic method of

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pulsed gradient spin echo (PGSE) NMR. This approach offers the advantage that diffusion behavior of Li in the carbon material is observed independently of electrochemical Li insertion and extraction processes across the interface. The present paper provides the first direct measurements of the Li diffusion coefficient in carbon anode materials.

Experimental Section

Pitch-based mesophase carbon fibers of about 7 μm diameter having a radical structure (Melblon; Petoca Materials Ltd., Japan) were used as starting materials. They were fired at 600–3100 $^{\circ}\text{C}$ for 10 h under an Ar atmosphere. Then, Li was inserted into the fired carbons, electrochemically changing the content by changing the charged potential. The carbon fiber was polarized in an electrolysis cell from the open-circuit potential to the negative potential side. Reaching the desired setting potential, it was held for at least 30 h at that potential to reach to the equilibrium condition. The test electrode was placed on a three-compartment Pyrex glass cylindrical cell having a three-electrode system and filled with an electrolyte of propylene carbonate or a mixture of ethylene carbonate and diethyl carbonate containing 1 M LiClO_4 . Pure metallic Li foils were used for reference and counter electrodes. The Li-doped sample thus obtained was washed with pure DEC and squeezed into an NMR sample tube of 5 mm diameter, followed by vacuum-drying and sealing.

Diffusion coefficients of Li were measured using pulsed gradient spin echo NMR.¹⁵ The principle of this technique is extracting the translational migration component from all relaxation processes associated with a probed species. The difficulty in diffusion measurement of Li in carbon materials compared with that in liquid-phase samples is attributed to the fast spin–lattice and spin–spin relaxations (e.g., $T_1 = 0.5$ s, $T_2 = 1.0$ ms at 25 $^{\circ}\text{C}$ in the mesophase carbon fired at 3100 $^{\circ}\text{C}$), which make it difficult to extract the diffusion process due to the fast echo decay. Then the measurement temperature was set to 100 $^{\circ}\text{C}$ to increase the relaxation times and diffusion coefficient to obtain the reliable data. The diffusion coefficient of ^7Li was measured on a JEOL ECP 300 W spectrometer at 117 MHz. The stimulated echo sequence was used for this application.¹⁶ The half-sine-shaped gradient pulse was applied twice in sequence after the first and third 90° pulses to detect attenuation of echo intensity according to the migration property of the probed species.¹⁷ Typical values of field gradient pulse parameters were $g = 10.6$ T m^{-1} for the pulse strength, $\delta = 0$ –1 ms for the pulse width, and $\Delta = 50$ ms for the interval between the two gradient pulses. In the present study, we avoided the MAS method since evaluation of the self-diffusing behavior requires no use of mechanical spinning. The NMR spectra represented here were obtained from the simple integration of observed echo signals during the diffusion measurement. Therefore, the width of spectra and the S/N ratio are not necessarily optimized. We thought this measurement condition was enough to see the relative changes of chemical shift and intensity with accumulated Li or carbon firing temperature.

Results and Discussion

Figure 1 represents ^7Li NMR spectra obtained with a well-graphitized carbon fired at 3100 $^{\circ}\text{C}$ for several different insertion amounts of Li. Decrease in the charging potential corresponds to increase in the inserted amount of Li in the carbon. Potential application of 5 mV corresponds to full occupation of Li in the ordered carbon material. The accommodation amount of Li in the graphitized carbon fiber at various potentials was evaluated

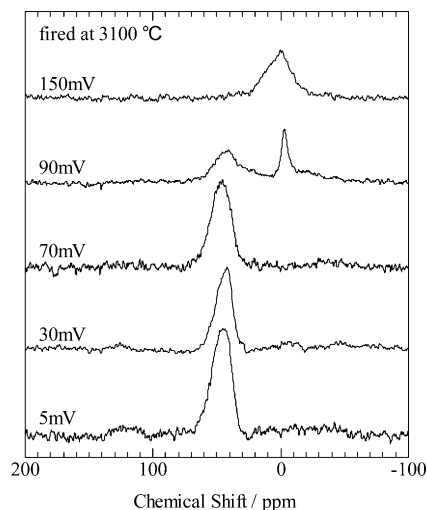


Figure 1. ^7Li NMR spectra of heat-treated carbon at 3100 $^{\circ}\text{C}$ and charged at 5, 30, 70, 90, and 150 mV. Spectra were measured at 100 $^{\circ}\text{C}$.

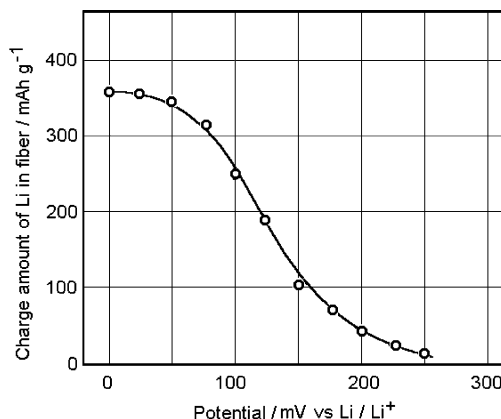


Figure 2. Potential dependency of the amount of accommodation of Li in the graphitized carbon fiber (Melblon 3100). The amount was obtained by integrating the CV obtained with a very slow potential scanning rate of 0.01 mV s^{-1} .

by integrating the cyclic voltammogram (CV) from positive potential side, which is shown in Figure 2. We can estimate from this result that Li occupation is 70% at 90 mV and 30% at 150 mV. In the spectra, two peaks at around 0 and 45 ppm appeared, changing the intensity ratio depending on the inserted Li content. This changing feature is consistent with ^7Li NMR spectra of Li intercalated in natural graphite.¹⁸ This implies that the well-graphitized carbon fiber sample has very similar structure to that of natural graphite, where a stack of many graphene layers run parallel with each other. These two peaks were assigned to two different layer occupation of Li corresponding to LiC_6 and LiC_9 .^{18,19} We see that LiC_6 peak at ca. 45 ppm becomes dominant with increasing insertion amount of Li. Figure 3a shows diffusion coefficient values of Li in the carbons charged at 5, 30, 70, and 90 mV. The apparent diffusion coefficient decreased rapidly with increase in the Li insertion amount. The absolute diffusion values of less than 10^{-8} $\text{cm}^2 \text{s}^{-1}$ could not be determined because of the measurement limit on this apparatus. Practically, echo intensity for samples charged at 5 and 30 mV showed no change with δ within experimental error. Therefore, we can infer that actual values at 5 and 30 mV are far lower than the value indicated in the figure. Rapid decrease in the diffusion rate with concomitant increase in the accommodation amount can be attributed to the rapid decrease in the numbers of vacant sites available for Li movement.

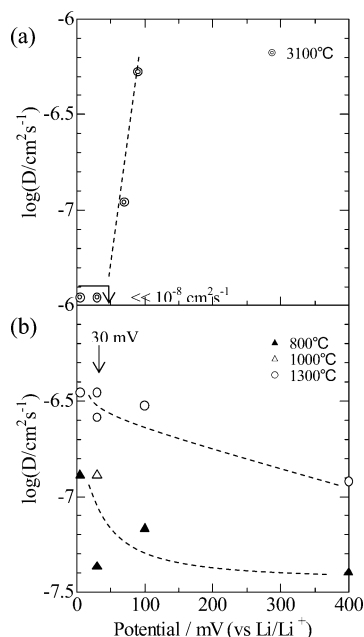


Figure 3. (a) Diffusion coefficients of graphitized carbons heat-treated at 3100 °C. (b) Diffusion coefficients of disordered carbon heat-treated at 800, 1000, and 1300 °C.

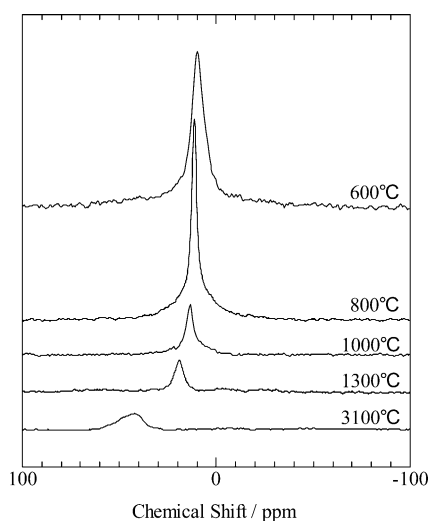


Figure 4. ^7Li NMR spectra of carbons heat-treated at 600–3100 °C and charged at 30 mV. Spectra were measured at 100 °C.

Figure 4 shows NMR spectra of Li which is fully charged in the mesophase carbons fired at several temperatures. All samples, independent of carbon firing temperature, showed only a single peak. That peak position shifted to the higher positive side with increased carbon firing temperature. As already pointed out, the mesophase carbons consist of two different phases: order and disordered phases. The existing fraction between the two phases and, as a result, the ratio of Li accommodation capacity between the two phases depend on the carbon firing temperature. With increasing the firing temperature, the ordered phase becomes dominant.²⁰ Li insertion and extraction reactions for the two phases can be recognized well by regarding the cyclic voltammetry (CV) peak shown in Figure 5. We can see two different types of peaks: one is sharp, centered at around 0.1 V; the other is broad, in the 0.5–1.2 V region. The ratio of the peak height at 100 mV to that at 800 mV is 3.5 for 800 °C fired carbon, while the ratio is 5 for 1000 °C fired carbon. Considering the larger amount of ordered phase fired at higher temperature, it is confirmed that the peak at around 0.1 V

corresponds to Li in the microcrystalline phase, and the broad peak between 0.5 and 1.2 V comes from Li extraction from the disordered phase. Bearing in mind that Li accumulation starts from the higher potential and the known relationship $\Delta G = -nFE$ between the Gibbs free energy change ΔG and the potential E with the number of electrons n and Faraday constant F , the energy state of Li accommodated in the ordered phase is inferred to be unstable by a few hundred millivolts in comparison to that of Li in the disordered phase. On the basis of these assumptions, it is expected that the different energy state of Li accommodation would yield different peaks in ^7Li NMR spectra corresponding to each phase. However, only one peak is recognized for all samples. This can be explained by assuming that Li particles, once accommodated in the ordered phase, can move to the disordered phase, and vice versa, with a sufficiently rapid rate compared to the measuring NMR frequency, which cannot differentiate the two separate peaks. Different from graphitized large crystal, microcrystallites of the ordered phase are considered to be suspended in the mesophase carbon skeleton. Thereby, Li accommodated in the microcrystallite is presumed to be able to spill over easily into the disordered region and vice versa for the fully charged condition. This single peak indicates that Li intercalated in mesophase carbon can move freely independent of the fraction of two phases. It is possible to separate the two phases when we measure the spectra at lower temperature.

The peak ca. 0 ppm for the carbon fired at 600 °C is dominated by the disordered phase and the peak ca. 45 ppm is by the ordered phase. The single peak shifting represents the averaged condition changing the fraction ratio of Li between the two phases.

Figure 3b shows diffusion coefficients of Li for the carbons fired at 800, 1000, and 1300 °C as a function of the Li insertion potential. Unfortunately, the values for the 600 °C fired sample were too slow to constitute meaningful data because of their measurement limit explained above. At a fixed potential, the diffusion coefficient was fast with increasing the firing temperature of carbon, from $4.3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in the carbon fired at 800 °C to $3.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ fired at 1300 °C at 30 mV applied potential. Bearing in mind that the Li accommodation in the ordered phase is predominant in the carbon fired at higher temperature and that at more positive insertion potential occupation of Li in the ordered phase is less dominant, we can infer that Li diffusion is faster in the ordered phase than in the disordered phase. Ordered configuration of carbon would appropriate for Li hopping migration through site alignment, resulting in enhanced mobility.

Figure 6 represents the insertion potential dependence of ^7Li spectra for the disordered carbon fired at 800 °C. With a decrease in the insertion potential, i.e., with an increase in the inserted amount of Li, a single peak was shifted toward the positive direction. Actually, it was impossible to estimate the Li occupation rate with applied potential in disordered carbons because ^7Li spectra in the disordered carbon does not show the characteristic feature as stage structures of ordered carbons, and the Li site content depends not only on the carbon firing temperature but also on the carbon precursor structure before firing. The progressive shift of the peak position with Li insertion potential could be explained by the Li occupation fraction change between the two phases in the disordered carbon. As is suggested in the CV peak behavior, Li accumulation starts at more positive potential with the insertion into the disordered phase preferentially. Therefore, the large number of sites in the ordered phase is vacant, and only a restricted number of the

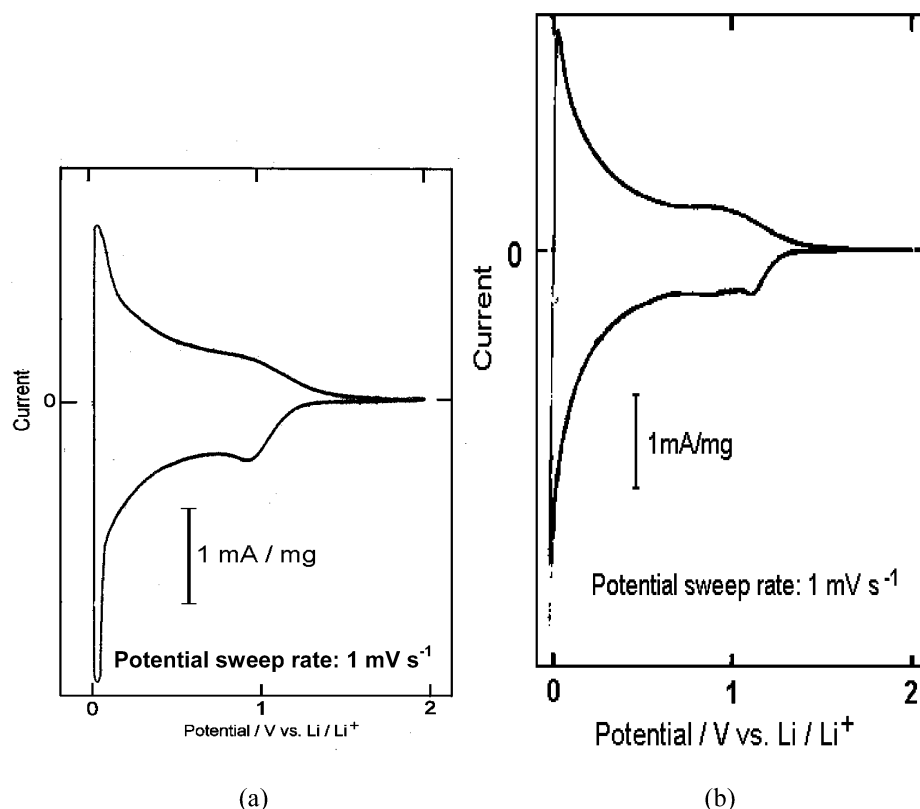


Figure 5. Cyclic voltammetry of mesophase carbon fibers measured in PC containing 1 M LiClO₄ at an ambient temperature with the potential sweep rate of 1 mV s⁻¹: (a) 800 °C fired carbon fiber; (b) 1000 °C fired carbon fiber.

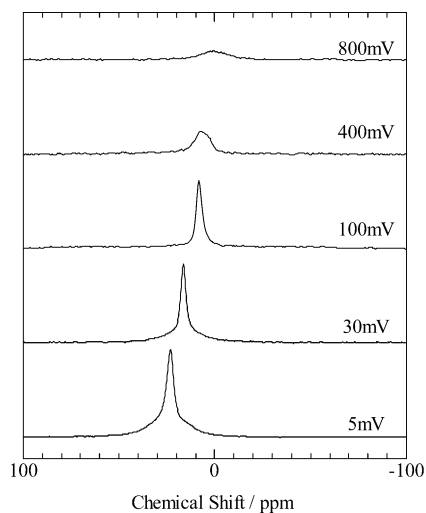


Figure 6. ⁷Li NMR spectra of disordered carbon heat-treated at 800 °C and charged at 5, 30, 100, 400, and 800 mV. Spectra were measured at 100 °C.

disordered sites were occupied at the first of Li accumulation. Then, the small peak at the potential at 800 mV represents the low population of Li in the carbon interior. The broadness of the CV peak corresponding to this NMR peak around 0.5–1.2 V indicates that the energy state of Li in the disordered phase is widely distributed, which is in contrast to that of the ordered phase. When the insertion potential moves from very positive to more negative, the Li site of the ordered phase will begin to be occupied. As we said in Figure 4, once the Li occupies the ordered phase, Li transfer between the two phases is sufficiently rapid enough not to separate the peak during the migration process. Consequently, the peak position changes in proportion to the population ratio between the two phases. As already

discussed, Li diffusion in the ordered phase is rapid compared with that in the disordered phase. As a result, increased occupation of the ordered phase, which corresponds to the direction to more negative potential in Figure 3, revealed an increase in the measured diffusion value, which is absolutely different from the changing feature in a single phase occupation observed in a carbon fired at 3100 °C.

The high capacity of Li in disordered carbon materials is attributable to the disordered phase, whose fraction is reduced through increasing the firing temperature. On the other hand, the ordered phase is advantageous for fast Li migration compared to the disordered phase. Furthermore, in contrast to the fact that Li mobility decreases with increasing inserted Li content in a single graphite phase, Li mobility rather increases in the progress of charging in the disordered carbon. This indicates that Li migration can be promoted even in the Li-rich condition, taking advantage of Li transport process between the different phases of disordered carbons.

Conclusions

We could successfully determine the diffusion coefficients of Li accommodated in graphitized and not well-graphitized carbon by evaluating with NMR spectra measured for Li which is electrochemically inserted in carbon anode materials. This is the first successful determination of the diffusion coefficient of Li in mesophase carbons without using electrochemical method where the disturbances caused by reaction kinetics taking place at the carbon/electrolyte interface is inevitable. Hence, the absolute values obtained in this study are considered to be the most reliable among the literature values reported to date. We found fast exchange of Li between ordered and disordered phases in the not-well-graphitized carbon. As a result, Li diffusion rates of the not-well-graphitized carbons were fairly fast, larger than 10⁻⁸ cm² s⁻¹, which is compatible to the

diffusion rate in the cathode material of LiCoO_2 now being used practically for high-performance batteries.^{21–24} The slow rate of Li extraction suggested previously may be attributed to the rate-determining process of the interfacial reaction. Therefore, we anticipate the increase of the electrochemical reaction rate by appropriate surface modification treatment to activate the reaction site. In addition, we confirmed that mesophase carbon prepared at low temperature can be used as an anode active material of Li ion batteries.

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