Estimation of the Na Insertion/Extraction Reaction Rate as the Na Chemical Diffusion Coefficient in Low-Temperature-Fired Soft Carbon

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ABSTRACT

The development of SIB has attracted attention as a substitute for LIB. Low-temperature-fired soft carbon (LFSC) has been the target of study as SIB's useful negative electrode material. We estimated Na chemical diffusion coefficient D_{chem} using the same approach and samples of previous report on LIB. The approach was potential step chronoamperometry (PSCA) method, and the samples were mesophase-pitch-based carbon fiber fired at four different low temperatures (600, 700, 800 and 950°C). The PSCA measurements by using a single LFSC fiber electrode were performed in an electrolyte of propylene carbonate (PC) containing 1 M NaClO₄ at room temperature in a glove box filled with dried Ar. The largest D_{chem} value we obtained with four pristine LFSC was about 10⁻⁹ cm²/sec. The D_{chem} values depended not only on firing temperature of LFSC but also on the nature of LFSC's surface. The effective surface treatment promoted Na insertion/extraction reaction rate on the carbon surface. The largest Na D_{chem} value we obtained after surface treatment was 10⁻⁸ cm²/sec. This Na D_{chem} value was close to the Li D_{chem} value (10^{-7.5} cm²/sec) by previous report, which suggests possibility of SIB's practical use.

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1. Introduction

Public demand has become stronger for rechargeable batteries with high power and long cycle life. Lithium-ion battery (LIB) provides high working voltage, specific capacity, and cyclability, and has long been applied to portable appliances such as laptop computers and mobile phones. Moreover, in recent years, LIB has widened its application range to vehicles such as electric vehicles (EV), hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEV).^{1,2} Li is one of the rare metals mined at limited places, and this wide application of LIB as well as political issues has raised its price. Accordingly, research and development of next-generation battery has prospered in search of the substitute of Li, such as Mg, Ca and Na.^{3–11} Na, relatively easily available on the earth, is low in cost and has property similar to Li. In addition, metallic Na's redox potential is -2.71 V vs. SHE, which is only 0.3 V higher than that of metallic Li. Therefore, the development of Sodium-ion battery (SIB) is expected as one of the most promising next-generation battery.^{6–11}

The main type of negative electrode material used in LIB is graphite. However, graphite can't be utilized for SIB negative electrode, for the amount of Na that can be inserted into the graphite layers is limited.⁶ One of the active research target as a negative electrode material of SIB has been hard carbon.^{7–11} This is because hard carbon's non-crystallized structure with cavities promotes Na insertion/extraction. D. A. Stevens et al.,⁸ S. Komaba et al.¹⁰ and K. Gotoh et al.¹¹ described Na's accommodation mechanism in hard carbon and reported its insertion/extraction characteristics.

Meanwhile, low-temperature-fired soft carbon (LFSC) has also attracted attention as a negative electrode material in LIB.^{12–16} The highest capacity of LFSC is reported up to 900 mA h/g, which is

over twice that of graphitized carbon.¹² LFSC is assumed to have two phases: one is oriented, and the other, non-oriented, which gradually changes according to the firing temperature rise. This structure is similar to that of hard carbon. LFSC's larger capacity compared with that of graphite is due to these two phases. Therefore, we can expect LFSC to have high storage property of Na like hard carbon. And in that case, LFSC could be useful negative electrode material of SIB. The accommodation mechanism of Li and Na in LFSC heated at 1000°C by in situ X-ray scattering scan was reported by D. A. Stevens et al.⁸ In their report, the Na insertion/extraction into/from the oriented phase of LFSC occurred at a positive potential region (1.0–0.1 V vs. Na/Na⁺). The Na insertion/extraction into/from the non-oriented phase occurred at a negative potential region (less than 0.1 V vs. Na/Na⁺).

In the view of Li diffusion in LFSC and Li insertion/extraction reaction rate into/from LFSC, H. Kataoka et al. reported the possibility of the rapid movement of Li between two different phases of LFSC by NMR study.¹³ Y. Saito et al. reported the diffusion coefficient of Li in LFSC fired at different temperatures by the pulsed gradient spin echo NMR method.¹⁴ The value in LFSC fired at 800°C was about 10^{-7.5} cm²/sec. O. Omae et al. reported the chemical Li diffusion coefficient D_{chem} in LFSC fired at 800°C by potential step chronoamperometry (PSCA).¹⁵ The detail of PSCA method is shown as follows. 1) A cylindrical glass cell containing a two-electrode system was used for PSCA measurements. 2) The single carbon fiber (LFSC fired at 800°C) was used as a working electrode and metallic Li foil was used as the counter electrode. 3) Propylene carbonate (PC) containing 1 M LiClO₄ was used as an electrolyte solution. 4) The potential was kept at 10 mV (vs. Li/Li⁺) for inserting Li into carbon electrode. 5) The potential was stepped from 10 mV to 100 mV for extracting Li from carbon to electrolyte

solution and the current-time curve was recorded. 6) Similarly, the potential was stepped every 100 mV from 100 mV to 800 mV. 7) The obtained current-time curves were analyzed by the Cottrell equation. Their value of D_{chem} in sufficiently surface modified LFSC was $10^{-7.5} \text{ cm}^2/\text{sec}$.

Since these two values obtained by two different methods were almost the same, the value can be reliable. However, the information of diffusion coefficient of Na in LFSC fired at different temperatures has not been obtained yet.

In this paper, we try to estimate Na chemical diffusion coefficient D_{chem} using the same approach (the Cottrell equation for analysis and PSCA by using a single carbon fiber electrode) and samples (mesophase-pitch-based carbon fiber: Melblon series) as O. Omae et al., for the PSCA method is simple with convenience. We compare our Na D_{chem} with O. Omae et al.'s Li D_{chem} , trying to examine Na character.

2. Experimental

2.1 Materials

The structure of LFSC depends on the firing temperature. The non-oriented-micro-crystal in LFSC is gradually changed to oriented-crystal like a graphite structure with the increase of firing temperature. Hence some LFSCs namely Melblon 600, Melblon 700, Melblon 800 and Melblon 950 (Product of Petoca Materials, Co., Ltd., approx. $10 \mu\text{m}$ in diameter), mesophase-pitch-based carbon fiber felt, were used as a negative electrode material. The number means the firing temperature. For example, Melblon 700 is fired at 700°C , and Melblon 800 is fired at 800°C . The SEM (Scanning electron microscopy) images of Melblon series are shown in Fig. 1. A single carbon fiber was picked out from the integrated fiber felt and used for the test electrode. The sample fiber was heated at 300°C in vacuum for 1 hour as a pretreatment in order to remove the absorbed contaminants like a H_2O on its surface.

Figure 1. Scanning Electron Microscopy (SEM) images of the Melblon series. (a) Melblon 800 ($\times 200$), (b) Melblon 800 ($\times 1000$), (c) Melblon 600 ($\times 1000$), (d) Melblon 700 ($\times 1000$), (e) Melblon 950 ($\times 1000$).

Figure 2. Schematic figure of the two-electrode-cell system.

2.2 Electrochemical measurements

A cylindrical Pyrex glass cell with a two-electrode system was used for the measurements (Fig. 2). A 15-mm-long sample fiber was fixed on one end of a 0.5-mm-diameter Ni wire with conductive carbon paste, and 5-mm of the sample fiber is vertically immersed into an electrolyte as a negative electrode (W.E.). Using a single carbon fiber is advantageous for obtaining the most reliable data, and we can avoid the ambiguity of electrode size, the interference of binder and loosening the electrical contact in the coated type electrode. Pure metallic Na was used as a counter (C.E.) and reference electrode (R.E.).

Propylene carbonate (PC) containing 1 M NaClO_4 was used as an electrolyte. The electrolyte solution with its water less than 30 ppm was provided by Tomiyama Chemicals. Electrochemical measurement was conducted by a linear sweep cyclic voltammetry (CV) with a sweep rate of 0.1 mV/sec and by the current-time curves of potential step chronoamperometry (PSCA). A Bio-Logic Potentiostat-galvanostat type SP-150 was used for the electrochemical measurement. Our focus in this paper is on Na extraction reaction from carbon, which is directly related to the battery power. In PSCA measurement, the potential step range ($5\text{--}700 \text{ mV}$) was determined by current due to Na extraction reaction in CVs. The detail potential step method is shown as follows. 1) For checking the cell condition, 6 cycles of CV measurement with a sweep rate of 0.1 mV/sec was carried out. 2) The potential was kept at 5 mV for 100 hours to insert Na into carbon sample. 3) The potential was stepped from 5 mV to 100 mV , and kept at 100 mV for 1 hour. 4) Similarly, the potential was stepped every 100 mV from 100 mV to 700 mV . All measurements were performed at room temperature in a glove box filled with dried air.

2.3 Apparent diffusion coefficient D_{chem} of Na

The Na chemical diffusion coefficients D_{chem} in the carbon fiber sample were obtained by analyzing the PSCA current decay curves. The current decay curves were recorded by voltage-width, and Cottrell plots were obtained from the curves, some parts of which showed approximately straight lines. The value of D_{chem} was estimated from the inclinations of these straight lines along each curve and the following Cottrell equation:

$$j = nF(D_{chem})^{1/2} C_{Na} / (\pi t)^{1/2}$$

where j [A/cm^2] is the current density; n , the number of electrons involved in the electrode reaction; F [C/mol], the Faraday constant (96485 C/mol); C_{Na} [mol/cm^3], the concentration of Na in the carbon electrode which was estimated by CV measurement; t [sec], the time after the potential step.

Figure 3. Cyclic voltammograms (CVs) of a single carbon fiber with potential sweep rate of 0.1 mV/sec. (a) Melblon 600 in PC containing 1 M LiClO₄, (b) Melblon 950 in PC containing 1 M LiClO₄, (c) Melblon 600 in PC containing 1 M NaClO₄, (d) Melblon 950 in PC containing 1 M NaClO₄.

There are two reasons why the diffusion coefficient D is expressed as the apparent diffusion coefficient D_{chem} .

In a strict sense, the Cottrell equation can be applied unless the rate-determining step of all reactions is controlled by the Na diffusion in carbon electrode. However, it is not clear yet where the rate-determining step happens in this study. The estimated D values may not indicate diffusion coefficient but chemical reaction rate.

This Cottrell equation is applicable for planar electrodes, not for cylindrical electrodes like a carbon fiber. Generally, the diffusion equation for cylindrical electrode should be calculated by adopting the Fick's 2nd law of diffusion. Bansal et al. reported that the Cottrell equation is a limiting case for cylindrical equation and it is accurate only when D is small ($D < 10^{-5} \text{ cm}^2/\text{sec}$), r_0 (the radius of the electrode) is large ($r_0 > 2.6 \text{ mm}$) and t is small ($t < 1 \text{ sec}$).¹⁹ According to Bansal et al.'s report, the diffusion current for cylindrical electrode is increased than that of planer electrode. In this case, the estimated D value is larger than the true D value because of adopting larger current than that of planer electrode. In our study, the estimated D values were not so large. There is possibility that our D values larger than approximately ten times larger than the true D values.

Therefore, the estimated diffusion coefficients are apparent diffusion coefficients, and they are expressed as chemical diffusion coefficients D_{chem} . In this study, it should be kept in mind that the D_{chem} values were not the true D values but apparent D values. These approach followed Omae's procedure.^{15,16} One of our purposes is to compare our Na D_{chem} with O. Omae et al.'s Li D_{chem} , and we used the same approach as O. Omae et al. in order to accomplish our purpose.

3. Results and Discussion

The CV measurement results of Melblon 600 and Melblon 950 showed characteristic of Li and Na's insertion/extraction reaction into/from typical LFSC (Fig. 3). The CVs were in the 5th cycle. At first, even a single carbon fiber of 10 μm in diameter and 5 mm in length showed excellent cycle performance in CV. Two peaks

appeared on both the cathodic and the anodic branches. According to D. A. Stevens et al.'s report, this may imply that two phases exist in LFSC: one is oriented-phase (positive potential region) and the other is non-oriented-phase (negative potential region). In the case of Melblon 600, Li was inserted into carbon fiber at around 1.20 V (vs. Li/Li⁺) and the current increased suddenly at around 0.35 V (vs. Li/Li⁺) due to Li insertion (Fig. 3(a)). Na was inserted into carbon fiber at around 1.2 V (vs. Na/Na⁺) and the current increased suddenly at around 0.10 V (vs. Na/Na⁺) due to Na insertion (Fig. 3(c)). The insertion potential converted to SHE potential was not so different between Li and Na. In the case of Melblon 950, Li was inserted into carbon fiber at around 1.35 V (vs. Li/Li⁺) and the current increased suddenly at around 0.35 V (vs. Li/Li⁺) due to Li insertion (Fig. 3(b)). Na was inserted into it at around 1.60 V (vs. Na/Na⁺) and two current peaks appeared clearly due to Na insertion (Fig. 3(d)). The drastic difference of these CVs shapes (Figs. 3(b), (d)) might imply that the small and limited amount of Na can be inserted into graphite layers. The CV measurements were carried out by 0.1 mV/sec. This means that the x-axis indicates not only the potential but the time. Since y-axis shows electric current, the quantity of electricity could be estimated. We have estimated discharge capacity by measuring the quantity of electricity and the mass of carbon material (calculated by its density and volume) for reference. The discharge capacities of a single fiber cited from each CVs in Fig. 3 were (a) 388 mAh/g, (b) 433 mAh/g, (c) 258 mAh/g, (d) 171 mAh/g.

The discharge capacities obtained from various LFSC single fiber cited from each CVs are showed (Table 1). For comparison, the capacity evaluated from CVs with fiber felt samples is also shown in Table 1. The felt sample was cut into 3.0 mg $1 \times 1 \text{ cm}$ square sheet, heated at 300°C, and sandwiched in between two Ni expanded sheets. The capacity of single fiber is higher than that of fiber felt at any firing temperature. This indicates that single fiber is more reliable without conductivity loss due to the contact with other carbon fibers. The capacity decreases with the increase of firing temperature. This tendency also implies the difficulty of Na insertion into the oriented phase.

Table 1. The discharge capacities of a single fiber and felt fiber cited from CVs.

	Discharge capacity mA h/g			
Sample	Mel. 600	Mel. 700	Mel. 800	Mel. 950
Fiber felt	163	108	152	128
Single fiber	258	226	182	171

Figure 4. Discharging current decay curves of a single carbon fiber (Melblon 700) obtained in PC containing 1 M NaClO₄ by PSCA. (a) 5–100 mV, (b) 200–300 mV, (c) 400–500 mV, (d) 600–700 mV.

The Na insertion/extraction reaction depends on the potential, and PSCA method was applied for evaluating potential dependence of diffusion as D_{chem} . The current decay curves of Melblon 700 are shown in Fig. 4 in different potential stepping ranges. The current is highest with stepping in the range of 5–100 mV. The Cottrell plots obtained from the current decay curves and its linear approximation for current vs. $t^{-1/2}$ were shown in Fig. 5.

Figure 6 shows the D_{chem} values of various firing temperature LFSCs. Among all the four LFSCs, Melblon 700 showed larger D_{chem} values (ca. 10^{-9} cm²/sec). Melblon 700 and Melblon 800 showed larger values than Melblon 600 and Melblon 950. The D_{chem} values of Melblon 600 were small in spite of its highest discharge capacity (Table 1). The reason of this is not yet elucidated. The correlation is not clear between D_{chem} values and potential step ranges, excepting for potential step range of 5–100 mV. Except Melblon 800, the D_{chem} values estimated from potential step range of 5–100 mV are clearly higher than 100–700 mV (Figs. 6(a), (b), (d)). This may indicate that Na extraction reaction rate from non-oriented phase is higher than that from oriented phase with each LFSC. In such a case, the largest D_{chem} value could be expected with Melblon 600, but in fact, the D_{chem} value with Melblon 600 was small. The different surface condition and inter structure in each LFSC might complicate the matters. In the case of Melblon 800, the unfavorable surface condition might have brought different potential dependency (Fig. 6(c)). All the LFSC's D_{chem} values of Na are smaller than those of Li by O. Omae's report.¹⁵

Someone may doubt the reliability of all the D_{chem} values in Fig. 6, for the Cottrell equation for planer electrode was applied into the calculation of D_{chem} values and all D_{chem} values may be unreliable and meaningless values. However, the reliability of these D_{chem} values can be confirmed by the following simple calculation. Figure 5(a) is the Cottrell plot obtained by the potential step of 5–100 mV in Melblon 700. The value of x-axis that we were based in

Figure 5. Cottrell plots of Fig. 4. (a) 5–100 mV, (b) 200–300 mV, (c) 400–500 mV, (d) 600–700 mV. **Figure 6.** Chemical diffusion coefficient D_{chem} of Na for a single carbon fiber fired at low temperature during Na extraction reaction. (a) Melblon 600, (b) Melblon 700, (c) Melblon 800, (d) Melblon 950.

defining of the slope is about 0.1, which is approximately 100 sec. Figure 6(b) shows Na D_{chem} of Melblon 700, and the D_{chem} value in 5–100 mV is estimated at about 2.0×10^{-9} cm²/sec. In general, the thickness of the diffusion layer L is considered to be the square root of $D t$ (D : diffusion coefficient, t : time), namely $L^2 = D t$. The square root of 2.0×10^{-9} cm²/sec times 100 sec equals 4.5 μm (the thickness of the diffusion layer), which is almost the same as the radius of carbon fiber electrode. Although the radius of carbon fiber electrode is not utilized in our Cottrell equation, the estimated value of the diffusion layer corresponds to the radius of carbon fiber electrode.

If the rate-determining step of Na insertion/extraction reaction were surface reaction such as electron transfer reaction etc., the obtained D_{chem} values would not be true value. If that is the case, the surface reaction becomes faster and the D_{chem} values might get larger and approximately true value by surface treatment. We tried some effective surface treatment methods in LIB which is reported in:^{15–18} such as mild oxidation treatment (MOT), metal film deposition on carbon surface (MFD) and the combination of MFD and MOT. This paper reports the most effective method we have tried. The concrete method is shown as follows. 1) Melblon 800 is covered with 90 nm-thick Ag film by vacuum deposition, and heated at 350°C in vacuum

Figure 7. CVs of a single carbon fiber (Melblon 800, in PC containing 1 M NaClO₄, potential sweep rate: 0.1 mV/sec) with and without surface modification. (a) Pristine, (b) covered with 90 nm-thick Ag film, (c) heated for 1 hour in reduced air pressure at 350°C after the Ag film deposition, (d) CVs of a vacuum deposited 90 nm-thick Ag film on a Ni plate in PC containing 1 M NaClO₄, potential sweep rate: 0.1 mV/sec.

for 1 hour, 2) Ag on the carbon surface melts and coagulates into tiny drops, 3) Tiny Ag drops spread all over the carbon surface.

The CVs of carbon samples with surface treatment were shown in Fig. 7. In the case of Ag film deposited sample, the peak current was once decreased (Fig. 7(b)). However, in the case of Ag film deposited and heated sample, the peak current drastically increased (Fig. 7(c)). This indicates that the reaction rate on the carbon surface increased. For reference, the discharge capacity cited from CVs in Fig. 7(c) was 320 mAh/g, which could be enough capacity as SIB negative electrode material.

One may suspect that Na insertion/extraction into/from Ag accelerated and gave the increase of discharge capacity. But there would be little probability of that. Na insertion/extraction reaction into/from Ag was not detected in CV measurement (scan rate: 0.1 mV/sec) for 90 nm-thick Ag film on Ni plate (Fig. 7(d)). In addition, if Na insertion/extraction into/from Ag accelerates and contributes to the discharge capacity, the capacity would increase by simple Ag deposition (Fig. 7(b)). The electrode of a single fiber has no adhesion between the each fiber. Therefore, there would also be little probability that conductivity improvement enhanced electrode performance. This surface treatment could have worked to change the factors that slow down the surface reaction.

Detailed mechanism that enhances the reaction rate has not been elucidated yet. F. Kikuchi et al. reported the reason about Li insertion/extraction reaction enhancement for LIB graphite negative electrode.¹⁷ In the case of simple Ag film deposition on graphitized carbon fiber, decrease of surface-film resistance and charge-transfer resistance were detected by impedance measurement. In the case of the combination of Ag film deposition and heating, the surface-film resistance did not decrease much but the charge-transfer resistance drastically decreased. This could imply that the surface was activated by Ag melting and coagulating. We believe that the same phenomena took place in Na insertion/extraction with the combination of Ag film deposition and heating.

The D_{chem} of Na obtained with LFSC was summarized in Fig. 8. One may speculate that the D_{chem} values could be enhanced at the same level by surface treatment at any potential, but the actual

Figure 8. D_{chem} of Na for a single carbon fiber (Melblon 800) with and without surface treatment. (a) Pristine, (b) covered with 90 nm-thick Ag film, (c) heated for 1 hour in reduced air pressure at 350°C after the Ag film deposition.

increase tendency depends on potential range. D_{chem} values are higher in low potential range than in high potential range (Fig. 8(c)). The combined surface treatment was effective in lower potential range, which promoted Na extraction from non-oriented phase, though its mechanism has not been elucidated yet. Simple Ag film deposition treatment eliminated D_{chem} value's potential dependency (Fig. 8(b)). According to these results, the combined surface treatment might have brought out the more fundamental nature of LFSC in Na extraction reaction. Anyway, detailed research for demonstrating the mechanism of the surface treatment should be done. The highest D_{chem} value in Fig. 8 was about 10^{-8} cm²/sec. The surface treatment could remove unfavorable surface reactions. This surface treatment might promote Na insertion/extraction reaction

rate into/from the carbon surface and bring out larger Na diffusion coefficient in LFSC. Altogether, D_{chem} depends on the surface condition of carbon, and the D_{chem} values could become larger. Here, we can conclude that the Na chemical diffusion coefficient D_{chem} in LFSC (Melblon 800) is 10^{-8} cm²/sec at the moment and it could be improved with more effective surface treatments.

4. Conclusion

We estimated chemical diffusion coefficient D_{chem} of Na in Melblon 600, 700, 800 and 950 by PSCA method. Among these LFSCs, Melblon 700 showed larger D_{chem} values (ca. 10^{-9} cm²/sec). We tried several kinds of surface treatments to enhance Na insertion/extraction reaction into/from carbon, and reported the most effective method at the moment. The method was the combination of Ag film deposition and heating in a reduced air pressure. This surface treatment enhanced the D_{chem} value of Melblon 800 (ca. 10^{-8} cm²/sec). This implies that many more surface treatments could improve Na D_{chem} . There is a possibility of Na D_{chem} getting closer to Li D_{chem} , in spite of Na's larger mass and ion diameter than Li. More detailed studies need to be made in order to examine Na character minutely. Recently, L. Xiao et al. reported the Na diffusion coefficient in polyaniline with hard carbon nanoparticle.²⁰ The D_{chem} values obtained by electrochemical impedance spectroscopy were 10^{-10} – 10^{-13} cm²/sec. The electrode was coated type electrode, and their D_{chem} values were much smaller than our D_{chem} values. We ascribe these different D_{chem} values to the following reasons: one is the difference of carbon materials (hard carbon/soft carbon), and the other is electrode type (coated type/single carbon fiber). Simple comparison of D_{chem} values is difficult and sometimes is not suitable, but our using a single carbon fiber is advantageous for obtaining reliable data. We can avoid the ambiguity of electrode size, the interference of binder, and loosening the electrical contact, which could happen in the coated type electrode. Therefore, we believe our results are more reliable. In addition, it is expected that the true Na D_{chem} value in LFSC could be larger than 10^{-8} cm²/sec by adopting more effective surface treatments.

At the moment, we can conclude that the Na D_{chem} in Melblon 800 is 10^{-8} cm²/sec. We will try to estimate D_{chem} in other firing temperature LFSCs with surface treatment to confirm the surface treatment's effects. Many more methods are desired to perform to estimate D_{chem} . The relation between crystal structure of LFSC and D_{chem} are also needed to be examined.

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