

Impedance measurements of low temperature mesophase carbon fibers during lithium insertion/extraction

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Abstract

Surface modifications with three different procedures were performed on an integrated felt of mesophase carbon fiber (MCF) fired at 600 °C. The surface modification procedures were (1) heating in acetylene black powder under a low pressure of oxygen (MOT), (2) vacuum deposition of Ag film on the fiber surface and (3) vacuum deposition of Ag film on the fiber, followed by heating under low pressure of oxygen. The performance of Li insertion/extraction reaction was found improved by any of these modification treatments.

The cause of the improvement was examined mainly with impedance spectroscopy analysis (EIS). EIS spectra revealed that both the film resistance and the charge-transfer resistance were decreased remarkably by these surface modifications. Among the three modification procedures, MOT revealed the best improving effect. By comparing the EIS data with the results obtained from the double layer capacity measurement, we concluded that the major cause of the increase in the reaction rate is the activation of the reaction site.

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1. Introduction

The anode material most commonly used in the practical Li-ion batteries is highly graphitized carbon. However, in order to respond to the urgent demand of the third generation of the IT equipments, that is to double the capacity of the power sources, the active material should be replaced by another new material having far higher specific capacity. As the candidate silicon and other metals or the alloys are extensively studied due to their extraordinary high Li accommodation capacity [1]. But several critical issues have to be overcome for the practicalization, indicating the realization program is not short term.

On the other hand, carbonaceous materials prepared at moderate temperature have acceptable large capacity for practical use, implying that the practicalization may be attained in a shorter time since battery makers have been acquainted with manipulating carbonaceous materials. With

this background mesophase carbons prepared at lower temperature are now paid attention [2,3]. Especially, a carbon fired at around 600 °C appears to be the most attractive since its Li accommodation capacity is as large as 900 mAh g⁻¹ [4–7]. However, it has not been used yet practically in Li-ion batteries. Two major causes are considered to prevent the practical use: the one is its low rate in Li charge/discharge reaction [8], and the other, the large hysteresis [9–14]. On the latter issue, we have found that the hysteresis in the mesophase carbon can be reduced by an appropriate heat-treatment followed by taking a good electrical contact among the active material particles on the prepared electrode [15–17].

In an attempt to improve the rate of charging/discharging performance, we have examined a surface modification technique based on mild oxidation treatment (MOT) [18–20] that revealed to be quite effective for the mesophase carbon fired above 800 °C. The evaluation of the improvement was performed by potential step chronoamperometry (PSCA). The obtained data were tentatively expressed as the chemical diffusion coefficient D_{chem} of Li in carbon (Fig. 1) as a function

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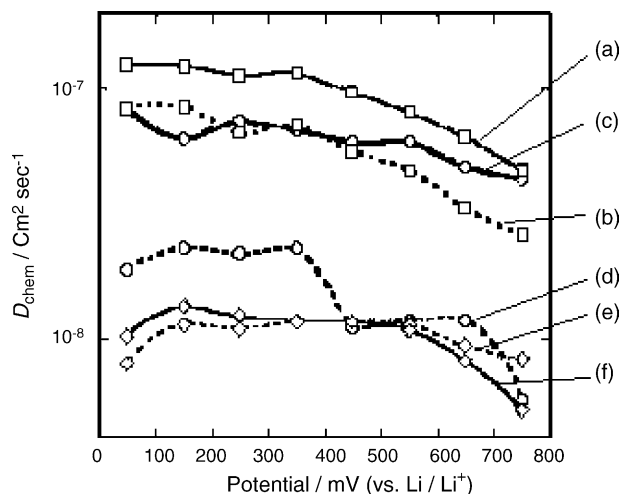


Fig. 1. Chemical diffusion coefficient (D_{chem}) of lithium for mesophase carbon fibers (MCF) fired at low temperature during Li extraction reaction [21]. The firing temperature is indicated after hyphen. (a) Modified MCF-1000; (b) pristine MCF-1000; (c) modified MCF-800; (d) pristine MCF-800; (e) pristine MCF-600; (f) modified MCF-600.

of potential stepping voltage [20,21]. The D_{chem} values were increased remarkably after the MOT treatment, indicating that electrochemical reaction is controlled by the surface process instead of diffusion process in the carbon matrix. In contrast, a 600 °C fired carbon showed no improvement. If, however, the evaluated slow value is due to the slow electron transfer reaction, we can enhance the reaction rate by some effective modification method other than MOT. On the other hand, if the slow rate is due to the slowness of the Li mass transfer in the carbon matrix, only one solution is possible for responding to the required charge/discharge rate is to adjust the particle size of the active material.

Therefore, the evaluation of the reaction rate is quite important for the purpose of identifying whether the 600 °C fired carbon can be improved or not. The rate data obtained from impedance spectra (EIS) is not based on the measure-

ment of current decay so that it is worthwhile to evaluate the rate based on EIS [22]. In the present study, we adopted EIS method for evaluating the charge-transfer rate at MCF before and after the surface modification treatment.

2. Experimental

An integrated carbon fiber felt of MCF-600 (Petoca Materials, 600 °C fired carbon) was used as a test active material. The felt was cut into 2 mm-thick and 10 mm × 10 mm square pieces and heat-treated in vacuum at 250 °C in advance. Three kinds of surface modifications were employed: (1) heating 10 min at 500 °C in acetylene black powder under a low pressure of oxygen (mild oxidation treatment: MOT); (2) vacuum deposition of a 400 Å-thick Ag film on the felt; (3) vacuum deposition of a 400 Å-thick Ag film on the felt, followed by heating at 340 °C under low pressure of oxygen.

The test electrode was prepared by sandwiching the felt specimen with a folded Ni expanded metal sheet, the peripherals of which being spot-welded for obtaining tight fixing. A Ni wire was spot-welded at one corner of the expanded metal sheet and used as a lead-wire.

Electrochemical measurements were conducted in an electrolyte solution of pure propylene carbonate (PC) containing 1 M LiClO_4 (Tomiya Chemicals, the contaminant water being less than 20 ppm). A Hokuto Denko Potentiogalvanostat (Type HA 151) was used as the power source. Impedance measurement was performed with an automatic impedance analyzer IM-6 (Zahner). All the measurements were conducted at an ambient temperature in a glove-box filled with dried Ar.

3. Results and discussion

We examined at first how MOT affects the CV of the present sample. Fig. 2 shows CVs taken before and after the

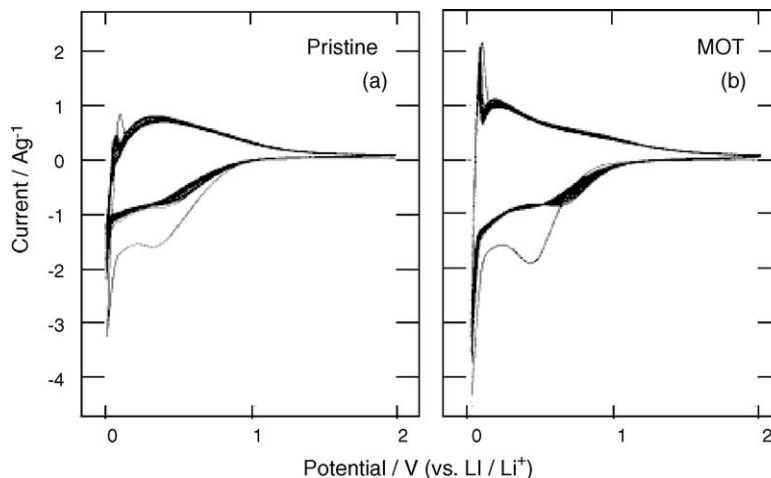


Fig. 2. Cyclic voltammograms of MCF-600 in PC. Sweep rate: 1 mV s⁻¹: (a) pristine and (b) MOT-treated for 10 min at 500 °C.

MOT treatment. In Fig. 2, we can recognize the improvement due to MOT not only in the current peak height increase but also the reduction of hysteresis. This means that the MOT is effective to the performance improvement even for 600 °C-fired carbon, being in contrast to the tendency in D_{chem} . The major cause of the improvement by MOT may be ascribed to the burning-off of surface contaminant, which retards the surface reaction.

A noticeable reduction peak due to the initial irreversible process is recognized on the CV even after the MOT (Fig. 2 (b)). The cause of the irreversible peak will be discussed here. The MOT process exposes the sample carbon in the atmosphere containing oxygen at moderately higher temperature resulting in oxidation of the carbon surface. The surface covering oxygen thus formed is supposed to be reduced during the Li insertion process causing to give large irreversible capacity. We can estimate the amount of the capacity by referring to the amount of the charge due to the adsorption of hydrogen fully covering Pt surface. The value is well known to be $210 \mu\text{C cm}^{-2}$ of flat Pt. Thus, the reduction charge corresponding to full coverage of oxygen is about $400 \mu\text{C}$ and this value may be not so much different from the value on the surface of carbon. Since the specific surface area of the present sample is $1.5 \text{ m}^2 \text{ g}^{-1}$, the irreversible capacity due to the oxygen fully covering over the carbon surface is estimated to be less than 1% of the full extraction capacity of the sample. As shown in Fig. 2, the surface area after MOT increased by about two times to pristine. The amount of the capacity due to the surface oxygen on MOT treated carbon is estimated still as low as 1–2% of the total capacity. Therefore, the large irreversible capacity shown in Fig. 2 (b) can be ascribed to the reduction decomposition of the electrolyte,

which can possibly be suppressed by some surface treatment [17,20,23].

Let us consider the cause of the rate enhancement due to surface modification. In general, three major causes are possible in consideration: the first is the increase in the electric conductivity by the removal of the surface contaminant, the second is the enlargement of the effective surface area and the third is the activation of the reaction site. Which one is the major cause, will be discussed together with the results obtained from Nyquist plots and SEM image examination.

SEM photographs of the treated fibers are shown in Fig. 3. It is rather difficult to recognize the surface change after simple MOT (Fig. 3 (a and b)). Covering with a 400 Å-thick Ag film revealed smooth surface that was difficult to differentiate the covered- or bare-surface. Partial scratching of the Ag film on the surface enables us to recognize the presence of the deposited film (Fig. 3 (c)). Heating the Ag covering sample in reduced air pressure gave rise to dramatic change to form a number of Ag spots (Fig. 3 (d)).

The enlargement of the surface area by simple MOT could be recognized by measuring the double layer capacity. Fig. 4 shows cyclic voltammograms of the carbon sample taken in the double layer region (2–3 V versus Li/Li⁺) before and after the simple MOT treatment. As seen in Fig. 4, the double layer charging current after MOT increased by about twice, suggesting the surface area was enlarged by about two times.

The Nyquist plots of surface modified carbon felt samples fired at 600 °C are shown in Fig. 5 for the case during Li extraction, where we see two kinds of hemi-circle, i.e., preceding smaller one in the low impedance region followed by larger one. The former is due to the surface film resistance and the latter, the charge-transfer resistance. Fig. 5 shows

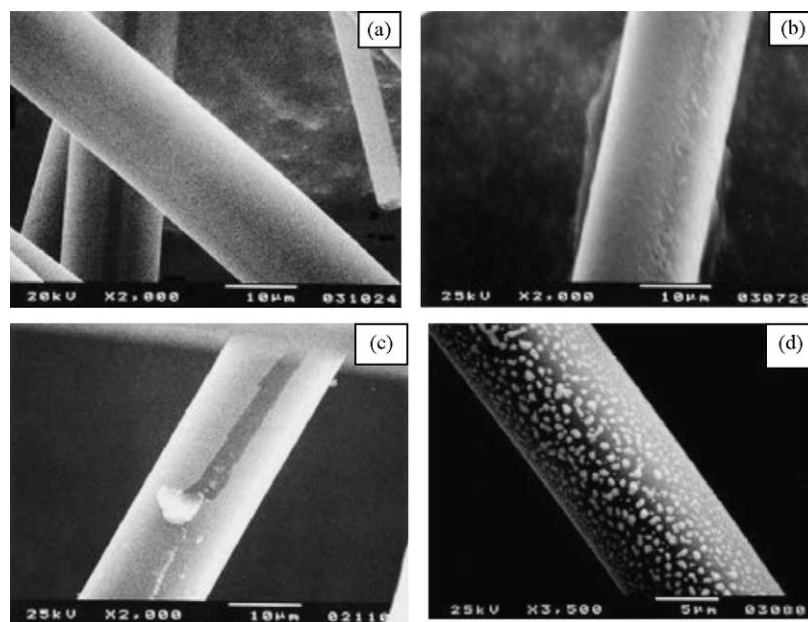


Fig. 3. SEM images of the surface modified MCF-600 fibers. (a) Pristine; (b) MOT-treated for 10 min at 500 °C; (c) covered with a 400 Å-thick Ag film by vacuum deposition; (d) heated for 1 h in reduced air pressure at 340 °C after the Ag film deposition.

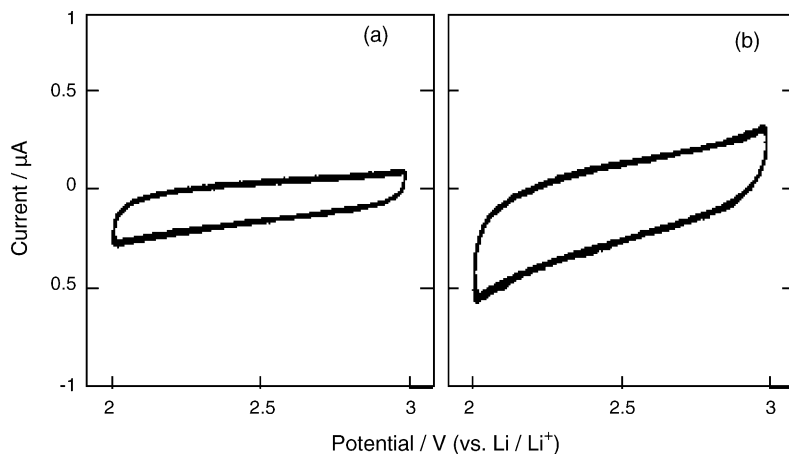


Fig. 4. Cyclic voltammograms of MCF-600 in PC potential sweep rate: 100 mV s^{-1} . (a) Pristine and (b) MOT-treated for 10 min at 500°C .

that not only the film resistance but also the charge-transfer resistance could be reduced remarkably by the surface modification treatment. Similar tendency was found for the Li insertion process as well. This means that the rate of Li insertion/extraction reactions at the 600°C carbon can be enhanced to a great extent by an appropriate surface modification. Thus, we can suggest that the low temperature fired carbon has a possibility to be applied to the practical battery.

In order to examine which of the causes play an important role between the surface enlargement and the activation of the surface reaction site, let us compare the degree of enlargement by the surface treatment. In regard to the surface area enlargement, we refer to Fig. 4, where the degree of enlargement is shown to be two times. In regard to the enhancement of the site activation, we compare the size of the hemi-circle in Fig. 6 for four cases where non-treatment case is included. If we compare the size of hemi-circle between the cases of

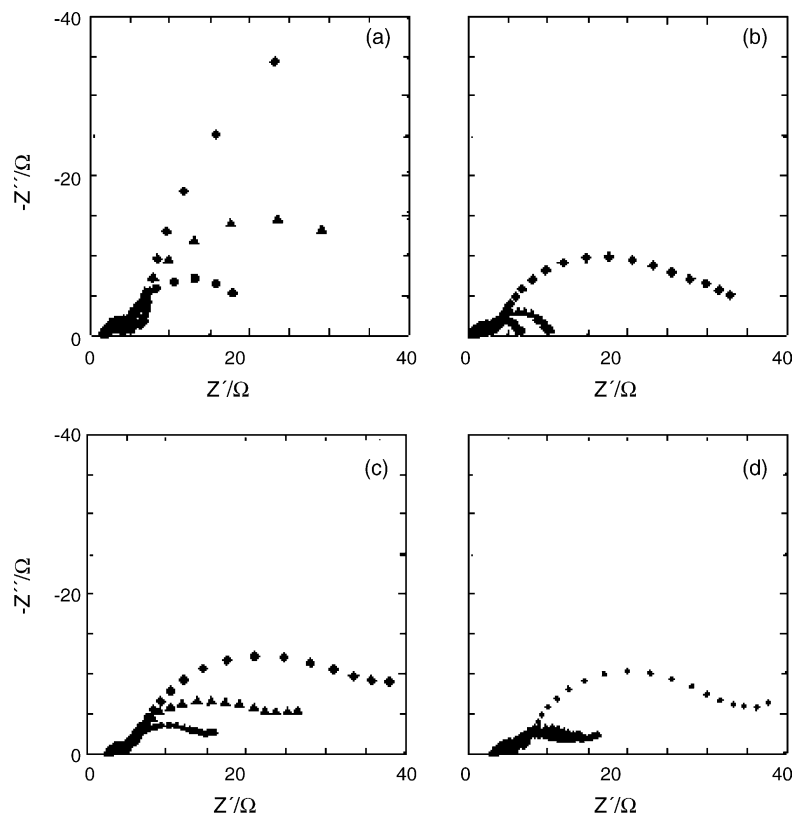


Fig. 5. Nyquist plots of MCF-600 during lithium extraction in PC. (a) Pristine; (b) MOT-treated for 10 min at 500°C ; (c) covered with a 400 \AA -thick Ag film deposition; (d) heated for 1h in reduced air pressure at 340°C after an Ag film deposition. Measured at: (\blacklozenge) $0.6 \text{ V vs. Li/Li}^+$, (\blacktriangle) $0.2 \text{ V vs. Li/Li}^+$, (\bullet) $0.05 \text{ V vs. Li/Li}^+$.

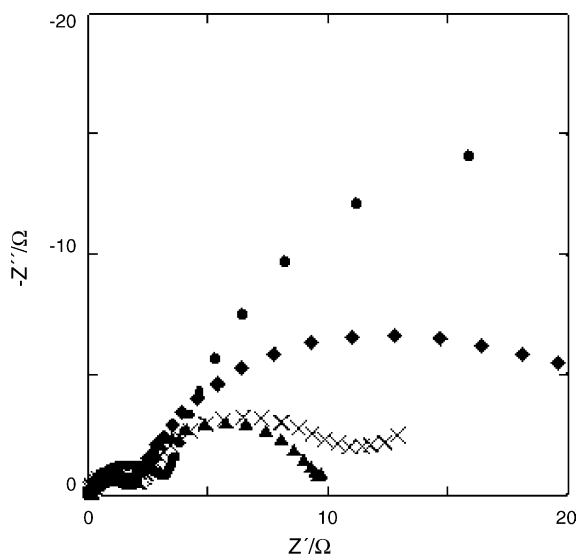


Fig. 6. Nyquist plots for surface modified MCF-600 during lithium extraction in PC. (●) Pristine; (▲) MOT-treated for 10 min at 500 °C; (◆) covered with a 400 Å-thick Ag film deposition; (×) heated for 1 h in reduced air pressure at 340 °C after an Ag film deposition. Measured at 0.2 V vs. Li/Li⁺.

pristine and MOT, we see the degree of reduction of the size is far larger than two. This means that the effect of the site activation is the major contribution to the enhancement of the reaction rate.

Back to the results shown in Fig. 1, we see no change in D_{chem} even after MOT where the activation of the surface site had been recognized. This implies that the overall rate is controlled by the rate of Li diffusion in the carbon matrix. Therefore, for the purpose of increasing the charge/discharge rate with a coated electrode it is necessary to use smaller size carbon particle as the active material.

4. Conclusions

We have been able to show that the 600 °C fired carbon fiber having a very high capacity can be a candidate of the anode material for the next generation of Li-ion batteries provided that it is treated by an appropriate surface treatment. The surface modification treatments by MOT resulted in reducing of both the charge-transfer resistance and the surface film resistance as compared to those of the pristine sample.

For the purpose of attaining high rate charge/discharge performance we have to use small-size particle of the active material.

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