

# Faradaic adsorption of Li on carbon. A novel concept for the capacity of the anode of the Li-ion secondary batteries

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## Abstract

Use of Faradaic adsorption (FAd) of lithium on the carbon surface is a novel concept proposed by us for providing an additional capacity for the carbon anode of Li-ion secondary batteries. Since the capacity is, in general, proportional to the effective specific surface area, implying that an active carbon having a very high specific surface area is expected to provide a very large adsorption capacity. Issues in the FAd process have been found in its poor reproducibility and cycleability. In the present paper, the condition to obtain a stable high current CV peak was examined in detail. We found that cleaning the surface and maintaining a good electrical contact are the most important key factors. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Active carbon fiber; Surface treatment; Faradaic adsorption; Li-ion battery; Anode

## 1. Introduction

A large number of studies have been performed with the aim of enlarging the Li dope/undope capacity of carbonaceous materials for the anodes of Li-ion batteries. Most of them appear to be concentrated on the improvement of the internal structure, but only a few are concerned with the surfaces [1–7]. Since the electrochemical reaction takes place at the electrode/electrolyte interface, we have given attention to the surface and examined how the modification of the interface is effective in assisting to increase the electrochemical reaction rate. We have found that the surface modification is quite effective for realizing the ability against heavy current load without significant loss of capacity [8–12]. During the course of the surface modification treatment of carbonaceous materials, we occasionally found the appearance of a new peak positioned at a slightly negative potential with respect to that of main deintercalation peak. The peak is generally very sharp and considerably sensitive to the surface condition of the material. After a precise examination of the condition, we attributed it to the Faradaic adsorption (FAd) of Li on the carbon surface [11,13,14]. Since the site density of the FAd can be assumed to be independent of the internal structure, the amount is expected to be proportional to the specific

surface area. This implies that the amount of the FAd on an active carbon having a greater specific surface area will be very large. Assuming that the site density of Li adsorption is the same as that of hydrogen on a Pt electrode (i.e.,  $\sim 200 \mu\text{C}/\text{cm}^2$ ) a charge density as high as 580 mAh/g is expected to be obtained for an active carbon having a specific surface area of  $1000 \text{ m}^2/\text{g}$ . The value being over 1.5 times of the ideal charge of graphite, is an attractive as the capacity of the anode of Li-ion secondary batteries. However, at present, it is difficult to utilize the FAd for the anode capacity because the peak is very unstable. In the present study, in an attempt to realize the use of the FAd as the capacity of the anode, we have searched in order to find favorable conditions where a large stable FAd peak can be obtained.

## 2. Experimental

### 2.1. Materials

Carbon fiber felt samples prepared from mesophase pitch at various temperatures were made of Petoca (Melbion series) with a mean fiber diameter of about  $10 \mu\text{m}$ .

Active textile type carbon fibers (Kuraray made, Kuractive #2000) were used, the BET specific surface area being  $2000 \text{ m}^2/\text{g}$ .

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## 2.2. Surface treatment

Prior to the measurement, all the materials were heat-treated at 150°C for 1 h in vacuo and were regarded as pristine samples.

Mild oxidation is effective in order to clean up the surface by burning off the contaminated surface layer of the carbon sample. This was done by covering the sample with a sufficient amount of acetylene-black powder in a crucible and heating at a desired temperature around 500°C in air for a few minutes. The heating temperature and time were controlled depending on the thermal stability of the sample.

Metal evaporation on the carbon surface is effective in enhancing the stability between the carbon and electrolyte interface. Among many metals, Ag was examined due to its excellent effect on a graphitic fiber.

## 2.3. Test electrode

Preparation of the test electrode was carried out as follows: A carbon sample textile was cut into a 1-mm thick square of size  $1 \times 1 \text{ cm}^2$  and sandwiched between two Ni sheets, whose rims were spot-welded at several points to maintain a good electrical contact. In order to examine the effect of electrical contact to the appearance of the FAd peak, we chose two kinds of conducting sample holder. One was a 50-mesh Ni grid and the other, a Ni expanded metal. The former had sufficient mechanical strength, but the contact with the carbon specimen is insufficient because of the round surface of each wire. The latter had a flat face giving a large contact area, but the mechanical strength is not enough to hold the sample tightly. We adjusted the contact by adjusting the number of spot-welding points.

## 2.4. Electrochemical measurements

As an electrochemical evaluation, cyclic voltammetry (CV) was measured in an electrolyte solution of 1 M  $\text{LiClO}_4$  dissolved in propylene carbonate (PC) or a 1:1 mixture (v/v) of ethylene carbonate (EC) and dimethyl carbonate (DMC). Choice of the electrolyte was based on the affinity between the electrolyte and the carbon sample to provide a reversible electrochemical reaction. All the electrolyte solutions were provided by Tomiyama Chemicals, whose water content was less than 20 ppm. A linear sweep CV mainly with a sweep rate of 1 mV/s and sweep range of 0 to 2 V vs.  $\text{Li/Li}^+$  was performed repeatedly. A constant current charge/discharge test with potential range of 1 to 3000 mV vs.  $\text{Li/Li}^+$  was performed if necessary. A Hokuto Denko Potentiogalvanostat type HA-151 was used for the electrochemical evaluation. All the measurements were performed in a dry box filled with argon gas at room temperature.

## 3. Results and discussion

An example of an FAd at a highly graphitized carbon fiber will be shown first. A pristine sample prepared at 3100°C gave only a single large peak on the positive sweep branch of the CV, which is due to the deintercalation of Li from the carbon matrix (Fig. 1(A)). When the sample was heat-treated at 250°C in vacuo for 1 h, a new sharp peak appeared on the negative potential side but close to the main peak (Fig. 1(B)). A similar phenomenon was also observed with a less graphitized carbon fiber samples. The additional sharp peak was very surface sensitive, and attributed to the FAd of Li on the carbon surface.

Since FAd is an electrochemical adsorption reaction, and not a doping reaction which occurs in the interior of carbonaceous material, the capacity is expected to be proportional to the adsorption site density and accordingly to the effective specific surface area. We examined the appearance of FAd peak with an active carbon fiber which has a very high specific surface area but very poor Li intercalation ability.

A test electrode fabricated with an active carbon pristine sample and Ni grids with a loose electrical contact gave no indication of an FAd of Li on the CV curve as shown in Fig. 2(A). Through an accumulation of many experimental data obtained at various conditions, we have recognized that the most important factors effecting the

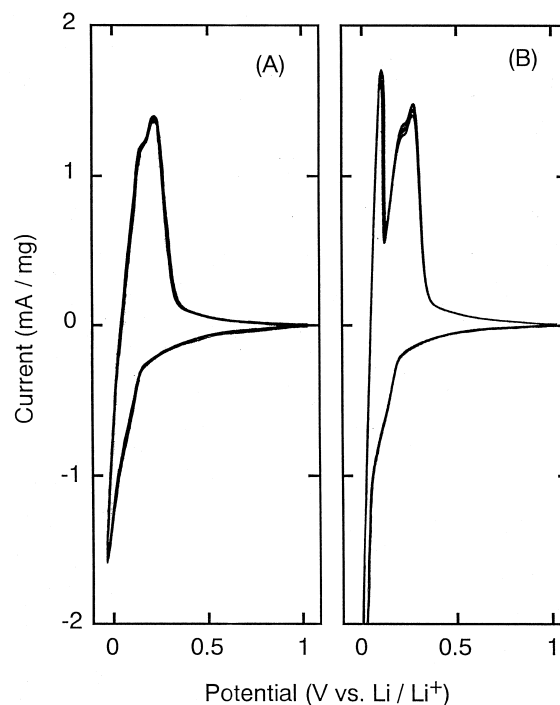


Fig. 1. CV curves of a highly graphitized carbon fiber felt prepared at 3100°C (Melblon 3100) in EC/DMC containing 1 M  $\text{LiClO}_4$ : (A) pristine sample; (B) heat-treated at 250°C in vacuo for 1 h. Potential sweep rate: 1 mV/s.

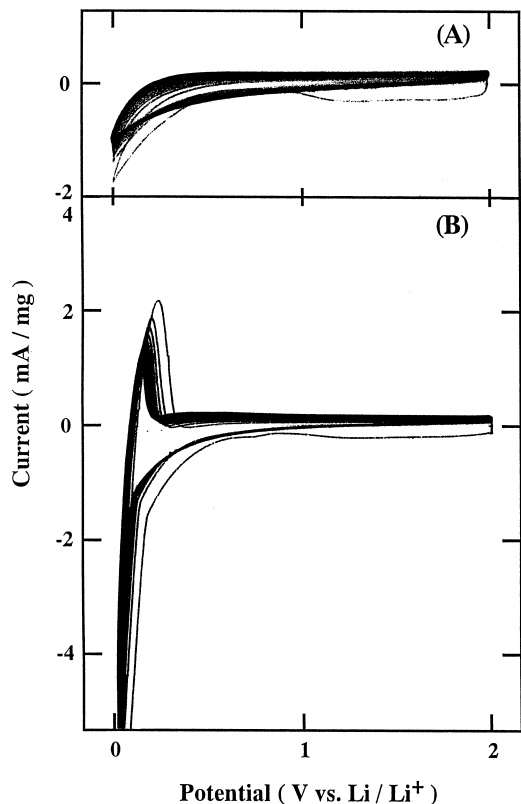


Fig. 2. CV curves of an active carbon fiber (Kuractive #2000) in PC containing 1 M  $\text{LiClO}_4$ . The test electrode was assembled by sandwiching the carbon sample with two types of Ni sheets whose rims were spot-welded at several points: (A) fabricated using 50 mesh Ni grids with a loose electrical contact; (B) fabricated using a fiber sample heat-treated at  $250^\circ\text{C}$  in vacuo for 1 h, and a Ni expanded metal. Good electrical contact could be obtained by a light spotwelding. Potential sweep rate: 1 mV/s.

appearance of FAd peak are: (1) cleanliness of the carbon surface, and (2) a good electrical contact at the working electrode. As an example of the most favorable case, the sample was heated at  $250^\circ\text{C}$  in vacuo and fabricated using a Ni expanded metal with a good electrical contact. We obtained a reproducible appearance of the distinct sharp peak as shown in Fig. 2(B). Comparison was made with these two samples by a constant current charge/discharge test, the results being shown in Fig. 3(A),(B). As seen in this figure, a pristine sample fabricated using Ni grids with a loose electrical contact gave no indication of the FAd which should be recognized by a plateau at about +50 mV. In contrast, sample (B) shows a wide plateau near +50 mV vs.  $\text{Li}/\text{Li}^+$  which is attributed to the FAd of Li. One may ascribe the additional sharp peak on CV to dissolution current of occasionally deposited metallic Li which might possibly be formed if the test electrode should accidentally go beyond 0 V to the negative side during the potential scan. We examined this possibility by comparing two single scan CV curves which were obtained with different potential scan ranges. One was obtained in the potential range positive to 0 V (Fig. 4(A));

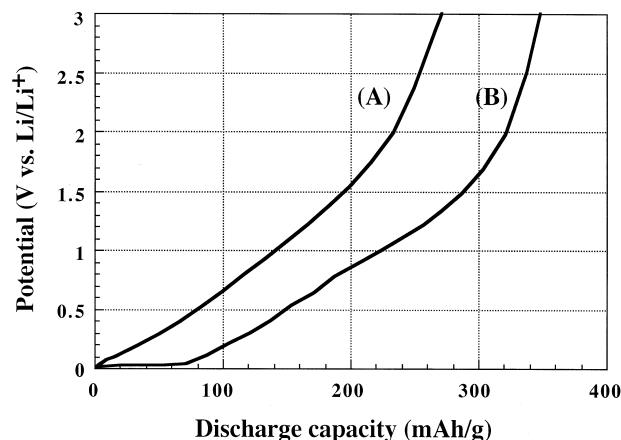


Fig. 3. Constant current discharge curves for an active carbon fiber (Kuractive #2000) in PC containing 1 M  $\text{LiClO}_4$ : (A) electrode was fabricated using 50 mesh Ni grids with a loose electrical contact; (B) electrode was fabricated using a Ni expanded metal with a sufficient electrical contact after heating the specimen at  $250^\circ\text{C}$  in vacuo for 1 h.

and the other was obtained by scanning intentionally negative enough to cause metallic Li deposition ( $-100$  mV, Fig. 4(B)). Fig. 4(A) shows only a single anodic peak

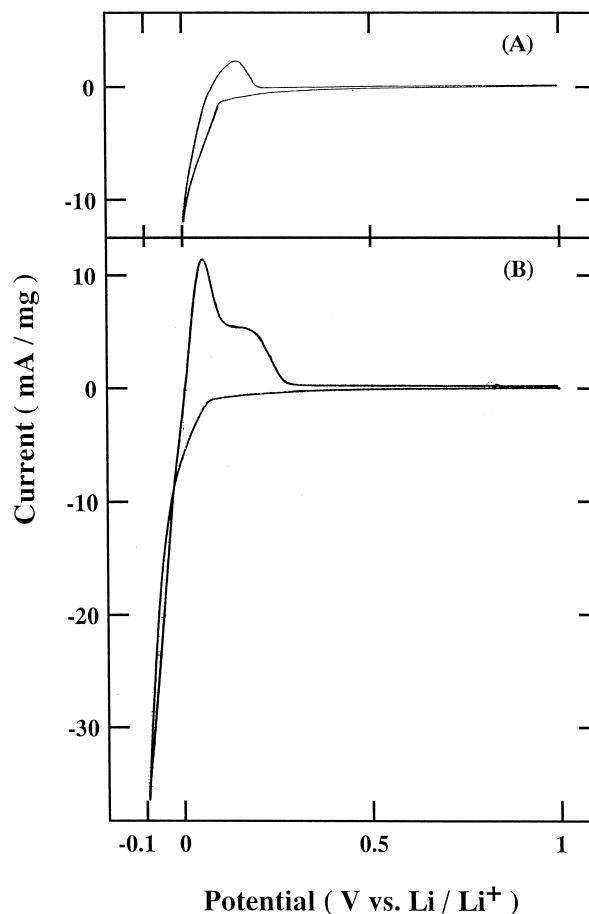


Fig. 4. CV curves of an active carbon fiber (Kuractive #2000) in PC containing 1 M  $\text{LiClO}_4$ : (A) the potential scan range was limited to the positive potential range; (B) the potential scan range was expanded to  $-100$  mV to cause metallic Li deposition. Potential sweep rate: 1 mV/s.

which can well be attributed to the FAd Li at around 150 mV, whereas Fig. 4(B) shows two peaks, though it is not so well separated. The large peak at the negative potential side on the anodic scan branch can be attributed to the dissolution of metallic Li since it never appeared as far as the potential scan range was restricted to the positive region. In contrast, the peak fusing to the major peak at the positive potential side appeared always irrespective of the present potential scan range. Therefore, it can be attributed to the Li formed by FAd. The reason why the peak shape in Fig. 4 is not so sharp is due to the condensed scale of the ordinate.

The FAd capacity corresponding to the peak in Fig. 3(B) was only 50 mAh/g which is far lower than expected. The reason why the value is too low is presumably due to the incomplete cleaning of the surfaces. Mild oxidation is quite effective to burn off the contaminated surface layer of the carbon sample and to enlarge the effective specific surface area. With this consideration we performed mild oxidation by heating the sample at 500°C for 5 min while covering it with a sufficient amount of acetylene-black in a crucible. The CV obtained after the mild oxidation is shown in Fig. 5, where we see an enhanced FAd peak.

Other issues to be solved are the successive degeneration of the observed peak during a cycle repetition and large irreversible capacity of the first charge. We considered that these issues are associated with the gradual

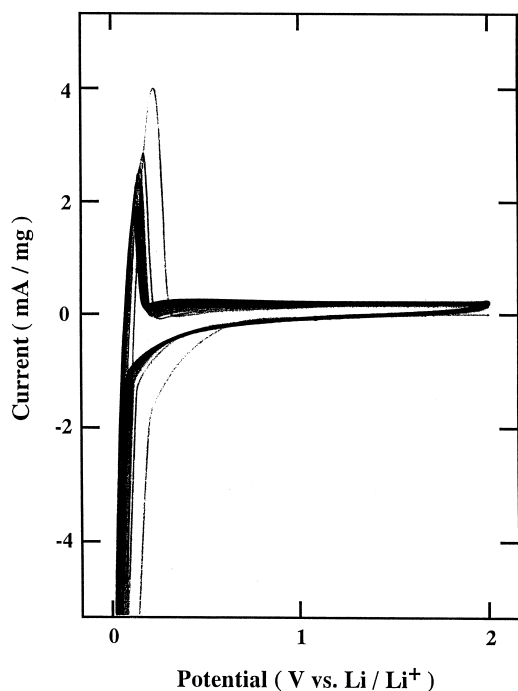


Fig. 5. CV curves of an active carbon fiber (Kuractive #2000) in PC containing 1 M LiClO<sub>4</sub>. Before the measurement, the sample was heat-treated at 500°C and covered with a sufficient amount of acetylene-black for 5 min (Mild oxidation). Potential sweep rate: 1 mV/s.

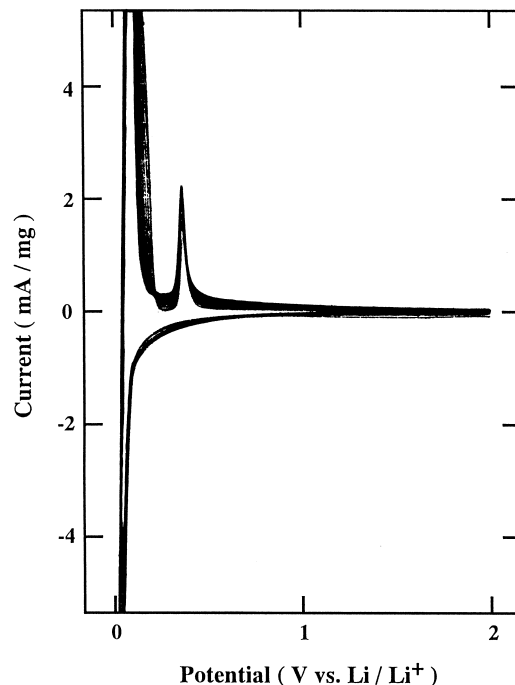


Fig. 6. CV curves in PC containing 1 M LiClO<sub>4</sub> of an active carbon fiber (Kuractive #2000) which was mildly oxidized followed by the deposition of a 500-Å thick Ag film. Potential sweep rate: 1 mV/s.

inactivation of the surface site which is quite sensitive to the environment. Since Peled pointed out the concept of SEI [15,16], it has been recognized to play an important

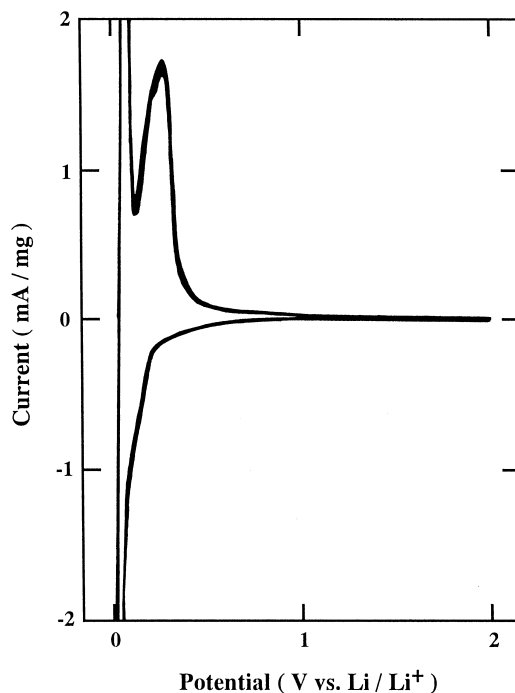


Fig. 7. CV curves in EC/DMC containing 1 M LiClO<sub>4</sub> of a highly graphitized carbon fiber felt prepared at 3100°C (Melblon 3100, pristine sample) which was deposited with a 400-Å thick Ag film. Potential sweep rate: 1 mV/s.

role for Li to be intercalated. Especially, for the surface process, SEI is considered the dominating factor. We attempted to control the SEI by covering the carbon surface with a metal film, where SEI formed on the metal surface is expected to have a different physical property. As the metal, Au and Ag were examined. An example is shown for the case of a Ag film deposition in Fig. 6, where a ca. 500-Å thick Ag film was deposited on to the surface of the active carbon which was used for obtaining Fig. 5. As seen in the figure, the stability of the FAd peak was obviously improved. A small anodic peak at 400 mV is attributed to the electrochemical releasing of Li from the Ag film. This was confirmed by measuring a CV curve with a Ag film deposited on a Ni plate which is considered to be inert for Li insertion. A challenge to obtain an amplified FAd capacity was performed with the most preferable surface treatment: mild oxidation followed by the deposition of a Ag film. By this procedure, the charge could be increased up to 240 mAh/g.

The second issue, namely, to minimize a very large initial irreversible charging capacity can also be achieved by modifying the surface. Covering with a Ag film was found quite effective for improving the graphitized carbon. Expecting to be given rise to a similar effect, we applied a Ag film on the active carbon fiber. The results was very successful as shown in Fig. 6 where the initial charging irreversible capacity is shown to be quite much reduced.

One may be concerned on the blocking effect of the covering metal film to prevent the insertion of Li into substrate carbon. We examined the effect of Ag film by using a graphitic carbon fiber whose entire surface was covered with a Ag film of 400 Å thick Ag film. The obtained CV's are shown in Fig. 7, where an emphasized anodic peak due to Li deintercalation is clearly seen indicating that the covering metal film has no retardation of Li intercalation.

#### 4. Conclusions

In order to facilitate the occurrence of FAd, we found that cleanliness of the surface and maintaining a good

electrical contact are the key factors. The capacity of FAd of Li on the carbon surface can be increased by mild oxidation. The gradual degeneration of the anodic peak during the repetition of cycles can be suppressed by evaporating Ag on to the carbon fiber surface.

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