

# A key technology to improve the cyclic performances of carbonaceous materials for lithium secondary battery anodes

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## Abstract

Any carbonaceous material does not necessarily provide a favorable surface for a smooth electrochemical lithium doping/undoping reaction because the carbon surface is covered with a very thin inhibiting surface layer. Especially, carbonaceous materials prepared at lower temperatures exhibit very poor charge/discharge cycleability. Removing such a surface layer was found quite effective to provide very favorable electrode surfaces for the doping/undoping reaction. Simple heating of the pristine sample in vacuum was effective, but a more effective and versatile method was a mild oxidation treatment at a moderate temperature only for several minutes. Upon being treated with the mild oxidation, the cycleability as well as high rate capacity of carbonaceous materials were improved to a great extent. A trace amount of water contained in nonaqueous electrolyte was also found to deteriorate the electrochemical properties, which was ascribed to the formation of retarding surface film such as LiOH through the reduction reaction with lithium cation and water during charging. © 1997 Elsevier Science S.A.

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## 1. Introduction

A number of studies on carbonaceous materials have improved their capacity, charge/discharge current and cycleability [1–12]. Most of them were concentrated in exploring better interior structures. At present, natural graphite or artificial carbon having graphitic structure prepared at very high temperatures is believed to be the most promising material [2–8]. Graphite, however, has a limited maximum capacity of 372 mAh/g. Therefore, interest has been focused on carbons prepared at temperatures lower than 1000 °C, because they sometimes exhibit a strikingly higher capacity [9–23]. In spite of this advantage, irreversibility of the doping/undoping reaction have prevented the application of low-temperature carbons. Especially a pronounced irreversible reduction (charging) capacity during the first charge is undesirable.

On the other hand, as a new concept of anode capacity, Faradaic adsorption of lithium on the surface of carbon was proposed by us, which was estimated to be over 500 mAh/g

for an active carbon having specific surface area of 1000 m<sup>2</sup>/g. Such an electrochemical adsorption process was very sensitive to the surface state of the carbon.

The cause of the irreversibility has been investigated based on the solid/electrolyte interface (SEI) [29] in connection with the material/electrolyte compatibility. Aurbach and co-workers [24–26] have studied extensively the surface films formed during charge/discharge cycles, allowing us to understand the interface substantially. The initial surface state, however, seems to have not yet been explored.

Since the electrochemical reaction such as doping/undoping reaction takes place at the carbon/electrolyte interface, characterization of the surface of the initial state is very important. When the surface is under undesirable reaction conditions, no sufficient capacity or charge/discharge current is expected to be available, even if the internal structure is quite convenient to accommodate a large amount of lithium. We studied the characterization and improvement of the surface state of several carbons and demonstrated that almost all of the carbons can be improved in their capacity and high rate characteristics as well as cycleability by a surface treatment [31–35]. The surface treatment procedure is rather simple, only the removal of inhibiting entities on the surface is necessary. Mild oxidation of the surface at a moderate

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temperature was found quite effective among the treatments examined [32,33]. Peled and coworkers reexamined our procedure to disclose the effectiveness [30]. They extended the study to find the cause of the improvement.

In the present study the authors showed that one of the important origins of the charge/discharge irreversibility are surface inhibiting entities such as  $-OH$  and adsorbed water, and the removal of the surface inhibiting layer is a key technology to attain a remarkable improvement of the doping/undoping cycleability of carbonaceous materials.

In addition to the above surface effect, a trace amount of water in the electrolytic solution is shown to be the second deteriorating factor.

## 2. Experimental

In order to avoid undesirable factors interfering with the surface condition as well as the electronic conduction, fabrication of the electrode by binding the carbon sample powder with some binder was not adopted. We have so far recommended to use fiber samples [31–34] for the characterization as pointed out by Verbrugge and Koch [22].

Carbon materials used consisted of fibers prepared and processed under various conditions. The first sample is felt-type fiber mat prepared from mesophase petroleum pitch by the melt blowing process. These Melblon fibers prepared by Petoca (Melblon) were tested at various temperatures. The second sample is a textile of active carbon fibers prepared from phenol resin (Kuraray, Kuractive #2500 and Kuractive #1500, with BET specific surface areas of 2500 and 1500  $m^2/g$ , respectively), and those prepared from poly(acrylonitrile) fibers (Tokai Carbon, FW 510 and FW 310 with specific BET surface areas of 1300 and 800  $m^2/g$ , respectively). The third one is paper-like carbon mat where the mesophase fiber was bound with epoxy resin to form non-

woven paper which was then pyrolyzed for heat decomposition. All the samples were heat-treated at 150 °C in vacuum for 1 h before use.

Carbon samples were cut into 1 cm  $\times$  1 cm pieces with an appropriate thickness and submitted to surface heat-treatment. After the treatment they were sandwiched between two sheets of 50 mesh nickel screen having a lead wire, and then, the two nickel sheets were spot-welded at many points of the edge.

The surface treatment was mainly done either by heating the fibers at a desired temperature in the infrared vacuum furnace under a pressure of  $10^{-6}$  torr or in an air atmosphere. In the latter atmosphere the sample was placed in a crucible and covered with a sufficient amount of acetylene-black powder, and heated.

Electrochemical characterization was performed mainly with cyclic voltammetry and constant current charge and discharge in an electrolyte of propylene carbonate (PC), a volumetric 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), or EC + PC (1:1) containing 1 M  $LiClO_4$  at room temperature. The electrolytic cell was of three-electrode type having a reference electrode of metallic lithium, which was kept in a glove box filled with dried argon.

## 3. Results and discussion

### 3.1. Low-temperature carbon

Pristine carbon fiber prepared from mesophase pitch at 700 °C gave rather poor cyclic characteristics in PC. The cyclic characteristics in EC + DMC shown in Fig. 1(a) were worse than with those in PC. Such a tendency in a different medium is similar with that of the graphite structure except that for the latter much better cycleability is recovered [27,28]. The

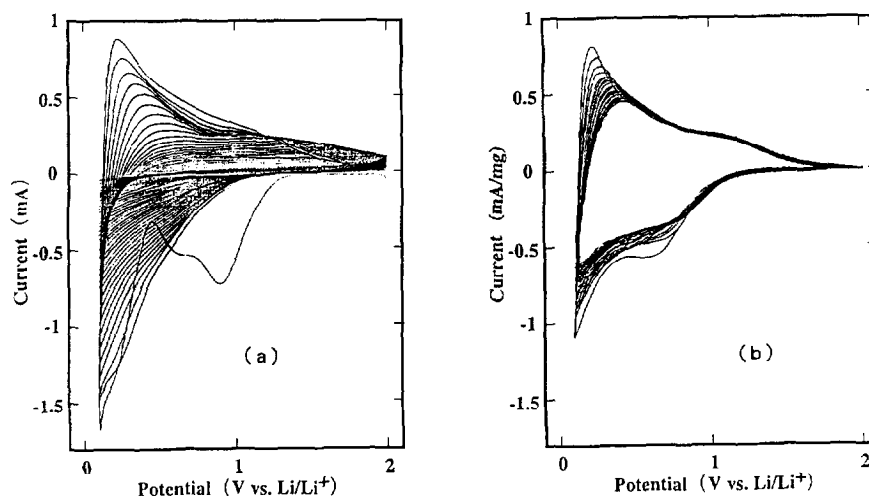


Fig. 1. Cyclic voltammograms of Melblon (prepared at 700 °C) in EC/DMC containing 1 M  $LiClO_4$  measured (a) before and (b) after heating in vacuum at 680 °C for 1 h and heated at 500 °C for 5 min with a sufficient amount of acetylene-black covering the sample surface. Sweep rate: 1 mV/s.

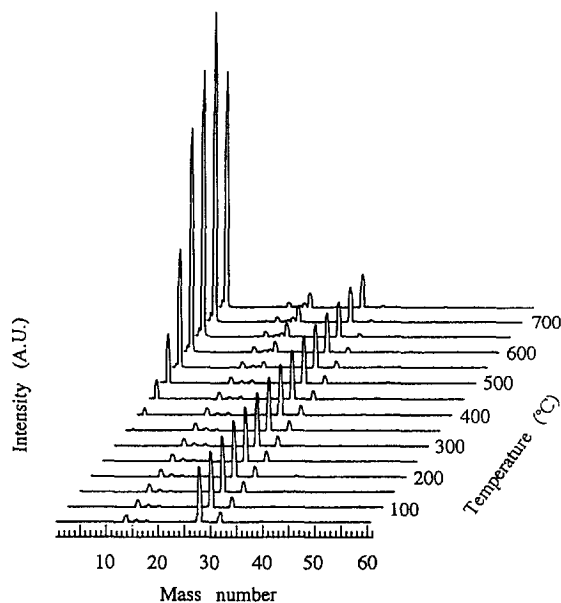


Fig. 2. In situ mass spectra of gases liberated from Melblon (prepared at 700 °C) during the step-wise heating in a vacuum line.

solvent dependent stability has been explained by the intrinsic properties of the reactivity between the material and the solvent. A series of heat-treatment examinations, however, disclosed that the poor reversibility could be improved by removal of the unfavorable surface-retarding layer.

The 700 °C sample was not stable during heat-treatment, i.e., when it was heated at 700 °C, it changed gradually into a more carbon-rich structure by releasing water, ethylene, CO, H<sub>2</sub>, etc., which was proved by in situ mass analysis, (see Fig. 2). This implies that a simple heat treatment cannot be applied to the 700 °C sample for the purpose of removing surface inhibiting layer. Hence, we applied a mild oxidation treatment at a sufficiently lower temperature. The 700 °C sample was placed in a crucible and covered with a sufficient amount of acetylene-black powder and heated at a temperature of 500 °C for several minutes. Mild oxidation proceeded during the heating as shown also by Peled et al. [30]. Short time heating at a temperature lower than 200 °C is considered not to cause a change in the interior structure. The oxidation is expected to proceed preferably on the surface, the surface layer being taken off. The cyclic voltammogram obtained after the mild oxidation procedure is shown in Fig. 1 (b). The cycleability was improved after the treatment. This is one example of the prove of our conception.

The second example is on the 1000 °C sample whose cycleability and high rate capability was remarkably improved by the same procedure. The pristine sample gave poor cyclic voltammetry on repeating cycle (Fig. 3(a)), but the characteristics were improved upon mild oxidation at 500 °C only for 5 min (Fig. 3(b)). In a preceding paper we showed similar effects with a simple heating in vacuum [32,33]. But in the latter case it was necessary to heat the sample at 980 °C. The present evidence demonstrates the effectiveness of mild oxidation.

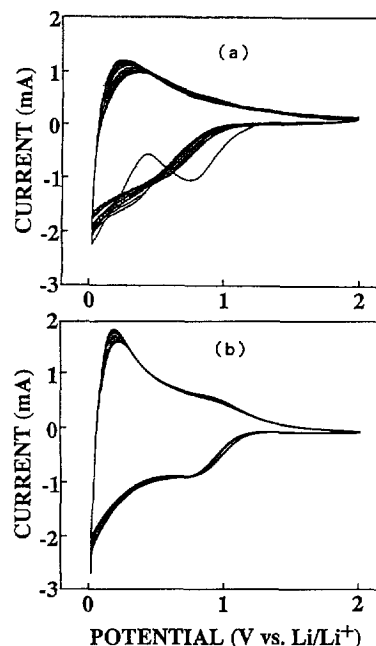


Fig. 3. Cyclic voltammograms of Melblon (prepared at 1000 °C) in EC/PC containing LiClO<sub>4</sub> measured (a) before and (b) after the heat-treatment at 700 °C with a sufficient amount of acetylene-black covering the sample surface for 5 min. Sweep rate: 1 mV/s.

### 3.2. High-temperature carbon

The mild oxidation is also effective to high-temperature carbon whose surface is recognized to be much stable compared with low-temperature carbon. Fourier-transform infrared analyses (FT-IR) on graphite structure samples prepared at 3100 °C gave no indication of the presence of surface -OH and adsorbed water, even after standing in air for a long time. In this case, simple heating alone at any temperature in vacuum gave rise to no improvement in charge/discharge properties of the pristine sample. When, however, it was heated at 700 °C with a sufficient amount of acetylene-black covering on the surface, the current-voltage (CV) curve gave an obviously enlarged sharp current peak both on the reduction and the oxidation branches. In addition, the cycleability was improved as well. The situation is compared in Fig. 4(a) and (b).

The change in CV curve during the heating was dependent on the heating time; first, the peak height was increased with time to reach a maximum value, and then it decreased accompanied with poor cycleability. This is due to the deterioration of the fiber by an excess of oxidation. The optimum treatment time was about 5 min under the present heating conditions. A possible explanation of such a current enhancement and cycleability improvement by mild oxidation is as follows. The cylindrical fiber surface is almost covered with a skin whose chemical composition is essentially different from the retarding film on the low-temperature carbon. As being recognized on the high magnification scanning electron microscopy (SEM) picture [37], the skin consists of graphite plane

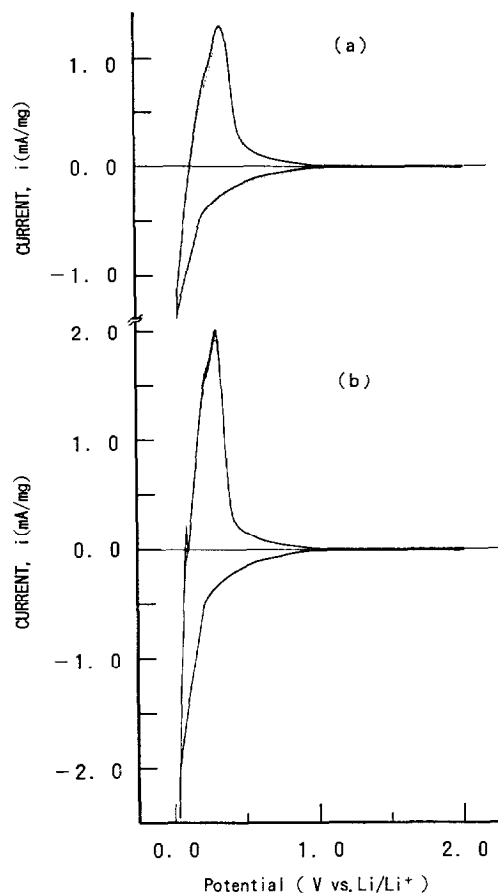


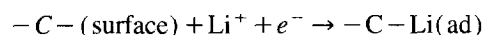
Fig. 4. Cyclic voltammograms of highly oriented Melblon (prepared at 3100 °C) in EC/DMC containing 1 M LiClO<sub>4</sub> measured (a) before and (b) after the heat-treatment at 700 °C for 3 min with a sufficient amount of acetylene-black covering the sample surface. Sweep rate: 1 mV/s.

covering entirely in parallel with the cylindrical surface of the fiber. The presence of the skin will cause the retardation of the smooth electrochemical reaction since the lithium ion

is expected to penetrate with difficulties across the graphite plane. Mild oxidation is considered effective to remove gradually the graphite skin. Complete removal of the skin will cause the collapse of the cylindrical structure of the fiber, resulting in deterioration of the performance.

### 3.3. Active carbon fibers and new type lithium-storing mechanism

Active carbon fiber exhibited a very broad CV diagram with irreversibility as shown in Fig. 5(c). The broad CV curve is attributed to the charging/discharging of the electrical double layer as well as Faradaic adsorption of lithium on the carbon surface. When we heated the sample over several hundreds degrees Celsius, a new sharp peak appeared at nearly 0 V. An example is shown in Fig. 5(b) for the sample heated at 1400 °C in vacuum. It is expected that the higher the heating temperature, the cleaner is the surface of the carbon. Cleaned surface is considered to give sites for adsorbing lithium atoms through the following surface reaction



which is as the so-called 'under potential deposition' (UPD) on the surface of metals [38]. The origin of this sharp peak is ascribed to the above UPD reaction. The sharp peak could be reproduced very easily when we heated the active carbon sample covered with acetylene-black at 700 °C for several minutes as shown in Fig. 5(b). Here again the mild oxidation is shown to be very effective to remove the surface contamination.

### 3.4. Effect of water in the electrolyte

The sharp UPD peak, however, was not reversible but decreasing upon repeating the CV cycles as shown in Fig. 5. The behaviour was found to be dependent on the CV scan

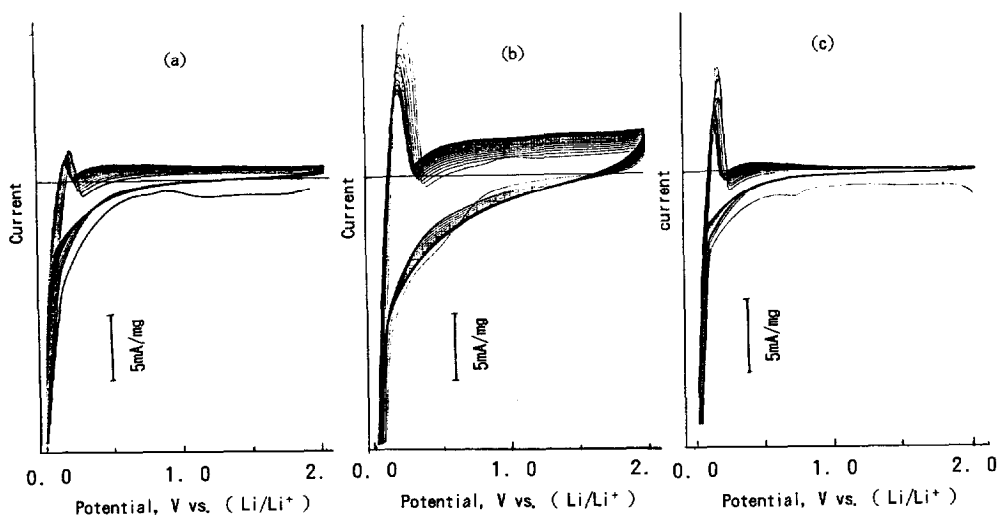


Fig. 5. Cyclic voltammograms of active carbon fiber of Kuractive #2500 with and without heat-treatment: (a) pristine sample; (b) heat-treated at 700 °C for 3 min with a sufficient amount of acetylene-black covering the sample surface, and (c) heated at 1400 °C for 5 min under a pressure of 10<sup>-5</sup> torr. Sweep rate: 1 mV/s.

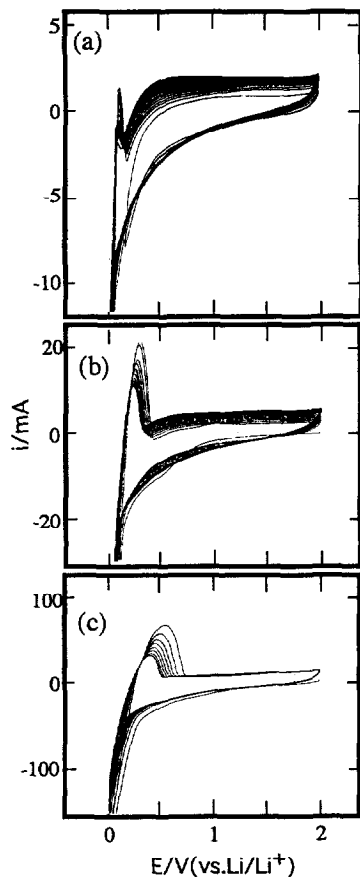


Fig. 6. Cyclic voltammograms of active carbon fiber of Kuractive #2500 in EC/PC containing 1 M  $\text{LiClO}_4$  measured after the heat-treatment under a pressure of  $10^{-5}$  torr at  $1400^\circ\text{C}$  for 5 min. Sweep rate (mV/s): (a) 1; (b) 10, and (c) 100.

rate. The higher the scan rate, the slower diminishing rate, as shown in Fig. 6. This suggests that the cause of the peak diminishing is not on the surface but in the bulk solution. The water content in the solution was found to affect the diminishing rate [36]. Water in the bulk diffuses to the surface where lithium atoms have been adsorbed. When the water molecule comes in contact with the adsorbed lithium, it readily reacts with lithium to form  $\text{LiOH}$  on the surface. The active sites for UPD thus become deactivated by the poisoning effect of water in the bulk.

### 3.5. Carbon fiber paper

Carbon papers prepared by the process of nonwoven cloth are available for various kinds of application, but those prepared for the application in lithium-ion batteries is rather rare since the binder covering almost the whole surface of the fiber is less active during the electrochemical reaction. The starting materials used as the binder are epoxy, poly(vinyl chloride), poly(vinyl alcohol), and phenolic resins, etc., all of them can be carbonized by pyrolysis. The surface of the pyrolyzed binder tends to be covered with inert film formed from gases and/or tar-like substances generated from materials during the pyrolysis process.

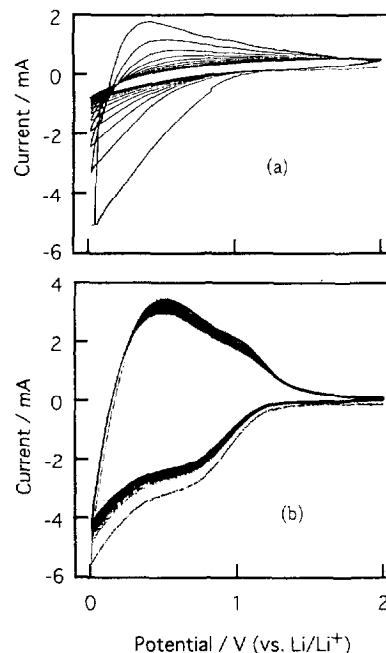


Fig. 7. Cyclic voltammograms of C/C composite carbon paper prepared with a matrix of carbonaceous pitch based mesophase fiber prepared at  $1200^\circ\text{C}$  and an epoxy binder which was pyrolyzed at  $1000^\circ\text{C}$  after hardening. The CVs were measured in EC/DMC containing 1 M  $\text{LiClO}_4$ : (a) pristine sample; (b) heat-treated at  $500^\circ\text{C}$  for 1 min with a sufficient amount of acetylene-black covering the sample surface. Sweep rate: 1 mV/s.

The CV diagram of the pristine carbon paper shows in general a hopeless feature with its very poor cycleability and very limited current as shown in Fig. 7(a). Once submitted to a mild oxidation treatment, the feature changed favourably as shown in Fig. 7(b). Since the temperature of the mild oxidation treatment is lower than that of the preparation temperature of the fiber matrix, the structural change of the matrix can be ignored during the treatment. Only a probable change is the removal of the surface inhibiting layer or contaminants. This example strongly supports the effectiveness of the mild oxidation.

## 4. Conclusions

Even carbon materials having very high capability of accepting doped lithium atoms are shown to lose the accepting ability when the carbon surface is covered with some inhibiting layers such as  $-\text{OH}$ , adsorbed water, or  $\text{LiOH}$  formed through the reaction with surface lithium and water in the bulk solution.

It has been proved that the removal of the inhibiting and/or contaminating entities from the carbon surface as well as from the electrolyte is the key technology to improve the reversibility as well as capacity during high current doping/undoping reactions. In the screening test of high performance carbon materials, we suggest that the surface cleaning as well as removing water from bulk electrolyte should be performed in advance.

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