

## Surface Characterization of Carbon Fibers as Anode Materials for Li Secondary Batteries

Tsutomu Takamura, Hidekazu Awano, Tetsuya Ura  
and Yasunari Ikezawa

*Department of Chemistry, College of Science, Rikkyo University  
Toshimaku, Tokyo 171, Japan  
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**Abstract:** Pitch-based mesophase carbon fibers prepared at different temperatures were heat-treated at temperatures lower than those of the preparation and the electrochemical Li doping/undoping characteristics were evaluated in relation to the data of IR, mass, etc.

Presence of surface hydroxyls were confirmed by FTIR for lower temperature sample which showed poor anode characteristics. Upon oxidative heating, removal of surface hydroxyls took place, resulting in a remarkable improvement of the electrode characteristics. At the same time, surface roughening took place, which was confirmed by SEM and double layer capacity measurements.

In situ mass spectra observed during the heat-treatments showed gas evolution of H<sub>2</sub>O, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and/or H<sub>2</sub> depending on the conditions. These data together with those of weight loss and conductivity provided us a valuable information in regard to the evaluation of the electrochemical characteristics.

**Keywords:** Carbon Fiber, Li Secondary Battery, Li Doping/Undoping FTIR, In situ Mass, Surface Characterization, SEM.

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## 1. Introduction

A number of studies on Li secondary batteries have so far been carried out for obtaining a carbon anode material having more improved characteristics of capacity, high charge/discharge current and cycleability[1-5]. Most of them, however, appear to be concentrated in the research of internal structures. The electrochemical reaction, however, takes place at the surface of the electrode, and hence, studies of the electrode surface should be stressed to be done more actively. We have studied on the surface for the purpose of obtaining more improved characteristics and could show the effectiveness of the surface modification[6-9].

Characterization on the basis of surface chemistry in relation to the electrode characteristics is of great importance since it affords us more effective way of the improvement[10-12].

Recently, carbon materials prepared at lower temperature have attracted attention because they have been found to have far larger doping capacity as compared to the ideal capacity of graphite(372mAh/g)[4],[10-14]. However, they have prevented the actual use for commercial batteries because of their poor cycleability. Characterization by use of analytical tools is of important for investigating what is the cause of the poor cycleability.

In an attempt to clarify the relation between the surface chemistry and the electrochemical characteristics we investigated FTIR and in situ mass spectra together with the meas-

urements of SEM, weight loss, conductivity and double layer capacity. We found all of the measured results together with those of electrochemical evaluation were very valuable for the elucidation of the electrode characteristics.

## 2. Experimental

**Materials:** Felt type( 3 mm thick) of carbon fibers( 10  $\mu\text{m}$  in average diameter) of mesophase pitch based one(Melbron) prepared at three temperatures of 1000°, 800° and 700°C were provided by Petoca, Inc. To remove the water adsorbed during the storage all the samples were heated at 150°C for 1 hour before use.

**FTIR measurements:** Sample of carbon fiber felt was fixed vertically in the sample compartment of a Nihon Bunko FTIR spectrometer(Model JIR 5500) and the surface IR signals were accumulated and fed into a computer. Difference spectrum was obtained if necessary.

**In situ mass analysis:** A quadrupole mass analyzer was mounted on the vacuum line operated with a molecular turbo-pump and the gases evolved from the vacuum furnace at a desired temperature were introduced into the analyzer.

**Electrochemical evaluation:** The evaluation was performed mainly by obtaining the cyclic voltammograms of the fiber sample which was sandwiched between two Ni mesh(50 mesh) whose hems were spot-welded at several points, and used as a test electrode. Nonaqueous electrolytes

of ethylene carbonate(EC)and propylene carbonate(PC) mixture(1:1) containing 1 molar  $\text{LiClO}_4$  and 1:1(vol) mixture of ethylene carbonate(EC) and diethyl carbonate(DEC) containing 1 molar  $\text{LiClO}_4$  were used.

### 3. Results and Discussion

#### Cyclic voltammograms(cv)

Cyclic voltammograms of  $1000^\circ\text{C}$  pristine sample obtained in EC/PC electrolyte are shown in Fig.1. The cv contains two broad cathodic current peaks at around 0.5 V and near 0 V, and these are considered to be paired with the anodic peaks of 0.2 V and 0.6 V, respectively. Both of the peaks are well attributed to the doping and undoping of Li in the carbon matrix, implying two types of doping mechanism are present.

As seen in the figure, the current tended to

be reduced after many repetitions of the cathodic and anodic cycles, indicating an unfavorable cycleability.

An irreversible cathodic current is seen on the cv of the first cathodic scan. Presence of such kind of unfavorable irreversible current has been pointed out by some authors[10-14] and studies to remove the irreversibility has been attempted[15], but no satisfactory method appears to have been proposed until now. This may be because of the lack of an useful information on the surface chemistry of carbon.

Of the unfavorable cycleability two causes are possibly considered: The one is due to the instability of the internal structure of carbon against doping and undoping of Li. The other is the instability of the carbon surface due to the presence of some reacting surface entities.

For the purpose of removing the unfavorable surface entities we heated the pristine sample in a mild oxidative atmosphere at  $700^\circ\text{C}$

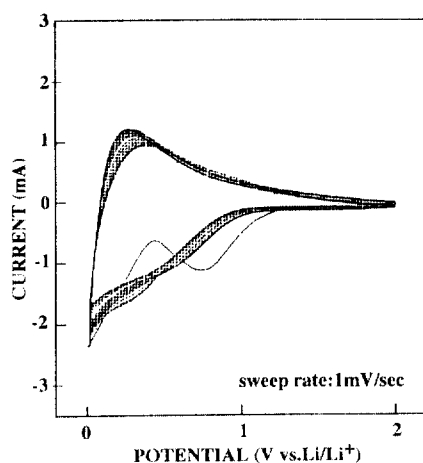


Fig.1 Cyclic voltammograms of pitch-based CF prepared at  $1000^\circ\text{C}$  in EC+PC containing 1M  $\text{LiClO}_4$ . (pristine sample)

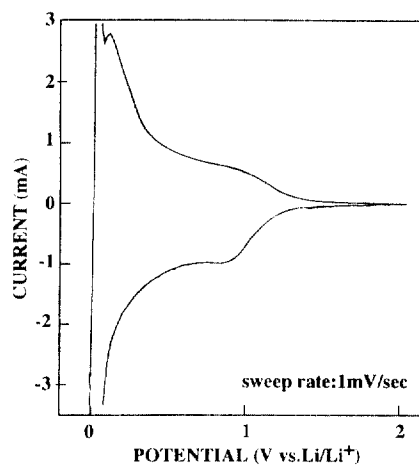


Fig.2 Cyclic voltammograms of pitch-based CF prepared at  $1000^\circ\text{C}$  in EC+PC containing 1M  $\text{LiClO}_4$ . The sample was heat-treated at  $700^\circ\text{C}$  for 5minutes covered with acetylene black

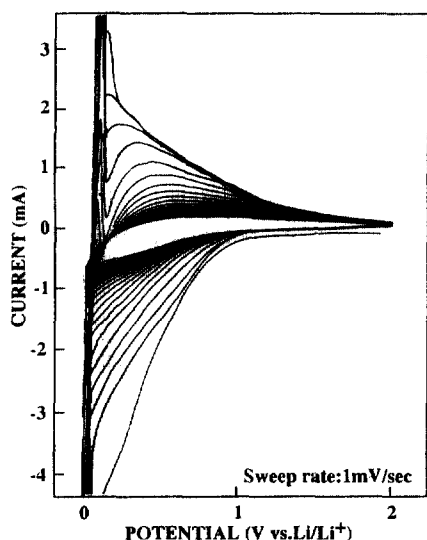


Fig.3 Cyclic voltammograms of pitch-based CF prepared at 800°C in EC+DMC containing 1M LiClO<sub>4</sub>. (pristine sample)

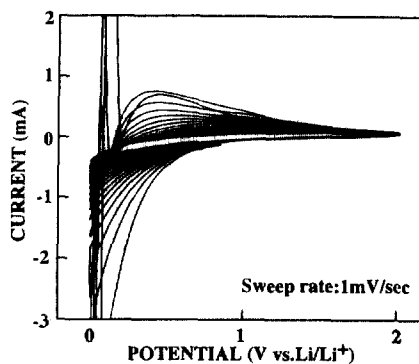


Fig.4 Cyclic voltammograms of pitch-based CF prepared at 700°C in EC+DMC containing 1M LiClO<sub>4</sub>. (pristine sample)

which is far lower than the preparation temperature of 1000°C and no change in the internal structure is expected to take place. The results are shown in Fig. 2, where we see a remarkable improvement not only in cycleability but in the doping capacity (current increase). Also, the initial irreversible cathodic current disappeared on cv completely. Such kind of remarkable improvement in the electrochemical characteristics can be attributed to the refinement of the surface and not the internal structure as will be explained later.

Of the 800°C and 700°C samples, the poor reversibility of cv was quite much pronounced as seen in Figs. 3 and 4. In the case of such lower temperature prepared samples, not only the surface unfavorable entities but the instability of the internal structure are considered to participate in the poor electrochemical characteristics as explained later.

When heated in an oxidative atmosphere at

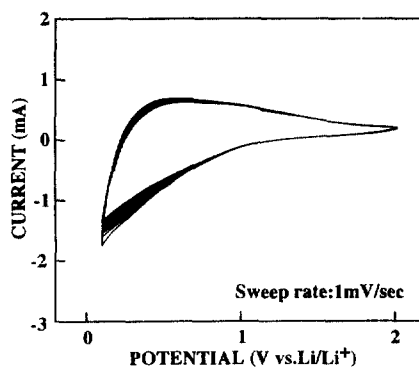


Fig.5 Cyclic voltammograms of pitch-based CF prepared at 700°C in EC+DMC containing 1M LiClO<sub>4</sub>. The sample was heat-treated at 500°C for 5 minutes covered with acetylene black.

500°C for a few minutes, the low temperature sample was improved in the reversibility as shown in Fig. 5. The capacity (current increase), however, was not attained by this treatment.

On the other hand when it was heated in vacuo at 690°C for 1 hour, then the partially

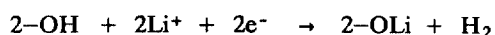
oxidized sample gave a cv of highly improved pattern which shows high doping/undoping current and improved cycleability.

### FTIR spectra

Presence of surface hydroxyls was fairly confirmed by taking the IR spectra of carbon fiber samples. As seen in Fig. 6, a strong broad absorption peak is recognized at around  $3400\text{ cm}^{-1}$  which can reasonably be ascribed to the  $-\text{OH}$  stretching vibration of hydrogen bonded hydroxyls most of which is considered to be on the surface. Since the diameter of each fiber is around  $10\text{ }\mu\text{m}$  and the skin depth of infrared light is around  $1\text{--}3\text{ }\mu\text{m}$ , a part of infrared information of internal structure of the carbon is possibly involved in the obtained spectra.

In order to ascertain that the surface  $-\text{OH}$  could be eliminated by the oxidative heat-treatment, we obtained the difference FTIR spectrum by subtracting the spectrum of heat-treated

sample from that before the treatment, which is shown in Fig. 7, where we can see a strong broad band at around  $3400\text{ cm}^{-1}$ . This is indicative of the decreased amount of surface  $-\text{OH}$  after the heat-treatment. Hence, a remarkable improve in the electrochemical characteristics shown in Fig. 2 is well understood by the removal of surface  $-\text{OH}$  which is reactive with formed Li through the cathodic reaction like



The surface  $-\text{OLi}$  thus formed is considered to be electrically insulative, hence, it retards the successive electrochemical reaction to proceed.

As pointed out earlier[16], the electrochemical reduction reaction of solvent may be possible to occur also in the present case, and the surface  $-\text{OH}$  is considered to be involved in the reaction.

Therefore, we can conclude that the origin

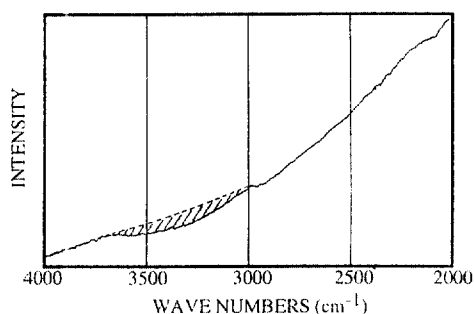


Fig.6  
IR refraction-absorption spectrum of  
mesophase carbon fiber prepared at  $1000^\circ\text{C}$

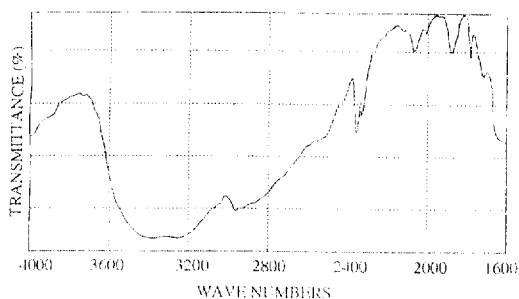
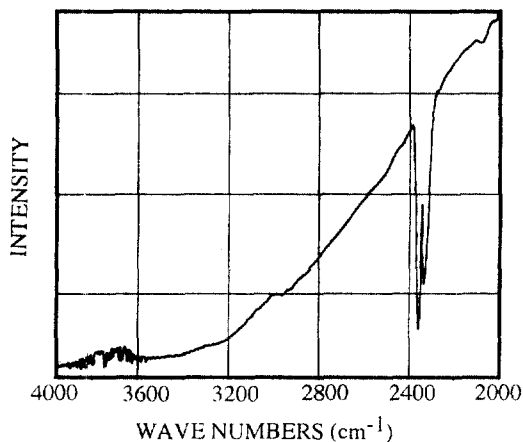


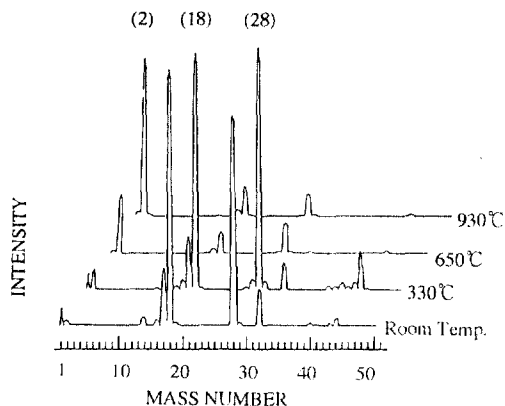
Fig.7  
Difference IR spectrum obtained by subtracting the spectrum  
of the sample heated with acetylene black from that of pristine  
 $1000^\circ\text{C}$  sample



**Fig.8** IR spectrum of pitch-based CF prepared at 700°C (pristine sample)

of the retardation of electrochemical doping/undoping of Li is the surface retarding layers like surface hydroxyls, and the removal of them from the carbon surface results in a favorable reversibility of the electrochemical reactions.

Pristine fiber samples prepared at 700°C or 800°C gave FTIR spectra shown in Fig. 8, where two broad bands can be seen at 3400  $\text{cm}^{-1}$  and 2950  $\text{cm}^{-1}$ . The former is indicative of the presence of hydrogen bonded hydroxyl group, and the latter can be ascribed to  $\nu_{\text{C-H}}$  of some alkane or alkene group which may be present as the incomplete pyrolysis residues of petroleum pitch. This assignment is reasonable because the pyrolysis during the preparation proceeded at low temperature with a restricted time. After heating the sample at 500°C for long time under the reduced pressure of  $10^{-6}$  Torr, the measured weight loss was about 20% and the FTIR spectrum showed a remarkable decrease in absorbance of both the bands.



**Fig.9** Mass analysis results of 1000°C Mesophase carbon fiber Heat-treated from 25°C to 930°C in *vacuo*.

These results indicate that 700°C and 800°C samples are in the metastable state and tend to decompose gradually even at the heating temperature lower than the preparation temperature. During the decomposition the samples were transformed into a carbon rich matrix by releasing several gases of hydrogen containing molecules. This was clearly proved by the *in situ* mass analysis together with the conductivity measurements.

#### In situ mass analysis

At first the 1000°C sample was heated at 930°C in the mass analysis vacuum line and the gases released during the heating were analysed. Even though the weight loss during the heating was too low to be measured, evolution of  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}_2$ , then  $\text{H}_2$  were detected.

In Fig. 9 an example of mass spectra is shown, which was obtained during the stepwise heating from room temperature. Mass numbers

of 2, 16, 18, 28, 32 and 44 are the main constituent, from which evolution of gases indicated above is inferred. Evolution of  $H_2$  at the latest stage indicates that the pyrolysis of hydrocarbon residue is still proceeding even in the  $1000^\circ C$  sample.

Release of several gases was more pronounced in the low temperature sample of  $700^\circ C$  or  $800^\circ C$  even with heating at low temperature of  $500^\circ C$  *in vacuo*. Time dependence of mass signals during the pyrolysis at constant temperature was examined for these samples. An example is shown in Fig. 10, where a large amount of gases is shown to be evolved for long time. The weight loss measured after 1 hour heating for  $700^\circ C$  sample was up to 23% all of which was attributed to the gases released from the sample matrix.

The electric conductivity of the carbon matrix is expected to increase during the pyrolysis since the amount of residual hydrocarbon is decreased with the results of increase in the carbon content in the matrix. Measured conductivity showed a dramatical increase with

the increase of heating temperature.

Combining these results indicated above, we conclude that carbon fiber prepared at lower temperature tends to be decomposed to release hydrogen containing gases even at the temperature far lower than that of preparation. As a result of the enrichment of carbon content, and the reduced amount of hydrocarbon residue, the electric conductivity is increased dramatically. All of these are considered to assist to increase the reversibility of the Li doping/undoping electrochemical reactions.

After the mild oxidative heat-treatment, the reversibility of the electrochemical Li doping/undoping process was quite much improved as shown in Figs. 2 to 6. A part of the cause of the improvement can be ascribed to the enlargement of the surface area. This could be recognized by comparing the SEM pictures of the sample fibers before after the heat-treatment. This was pointed out also by Peled[15].

#### 4. Conclusions

Electrochemical reversibility of Li doping/undoping reaction of pitch based carbon fiber was found quite much improved if the surface retarding layer such as surface hydroxyls are removed away by heat-treatment *in vacuo* or in mild oxidative atmosphere. The low temperature prepared carbon fibers were found to be metastable and tend to be decomposed into more carbon rich matrix by releasing hydrogen containing compound gases even at the temperature far below the preparation temperature. As a

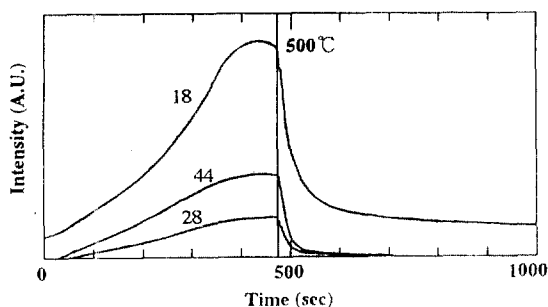


Fig.10 Time sequence of *in situ* mass peak height for several gases released from  $700^\circ C$  carbon fiber heated at about  $500^\circ C$ .

result, the fibers gave rise to an improved characteristics in electrochemical reaction.

All the mechanisms stated above were the results analyzed with the analytical characterization with FTIR, *in situ* mass, and so on.

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