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Stable charge/discharge of Li at a graphitized carbon fiber electrode in a pure PC electrolyte and the initial charging loss

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Abstract

Highly graphitized carbon is the most widely utilized anode material for Li-ion secondary batteries because of its high reversibility and reliability. However, it has so far been believed that well graphitized carbon material gives no stable Li charge/discharge performance in a pure propylene carbonate (PC)-based electrolyte, since PC decomposes vigorously at the surface of the graphite during the charging process. Surprisingly, we found that a single graphitized carbon fiber revealed a sufficiently stable performance in pure PC containing 1 M LiClO$_4$.

The initial irreversible charging capacity not only in PC but in an EC-based electrolyte was found strongly dependent on the conductivity homogeneity of the electrode. © 2001 Published by Elsevier Science B.V.

Keywords: Graphitized carbon anode; Li-ion secondary batteries; Propylene carbonate; Single carbon fiber; Prevention of PC decomposition

1. Introduction

The production amount of Li-ion secondary batteries is still increasing rapidly because of their superior performance in satisfying the strong demands of various portable electronic appliances. As the active material for the anode, highly graphitized carbons are most widely used because of its high reversibility and reliability. The electrolyte used for the graphitized carbon anode is in general based on ethylene carbonate (EC). Use of a large amount of propylene carbonate (PC) has been avoided, since PC decomposes without termination on the graphite surface during the charging process [1] and the decomposition is attributed to the cointercalation of PC molecule from the edge plane of the graphite, resulting in the exfoliation of the graphene layer [2].

However, PC is a very attractive solvent in view of providing a high conductivity electrolyte even at low temperature and the price is sufficiently low. It is, therefore, worthwhile to find out a condition where a graphitized carbon can be used in an electrolyte comprised of pure PC as the anode of Li-ion batteries. Many studies have so far

been conducted for suppressing the PC decomposition. Shu et al. proposed a method to use crown ether (12 crown 4) [3]. Aurbach et al. reported on the effective influence of carbon dioxide [4], and Besenhard and his coworkers showed that the decomposition was suppressed very efficiently by the addition of ethylene sulfite in the PC-based electrolyte [5]. In the absence of any additives, however, no paper appears to have been reported on the stable performance of a graphitized carbon in an electrolyte based on pure PC. Such a decomposition of PC has been found likely for the graphitized carbon fiber felt electrode. However, during the course of our experiment using a single fiber of graphitized carbon, we found by chance that PC did not decompose at the electrode even at sufficient negative potential. In the present paper, we would like to show the condition of stabilizing the graphite electrode against PC and to discuss the mechanism of the stabilization.

2. Experimental

2.1. Carbon materials

As the active materials for the anode, three types of mesophase pitch-based carbon fibers were used: (sample

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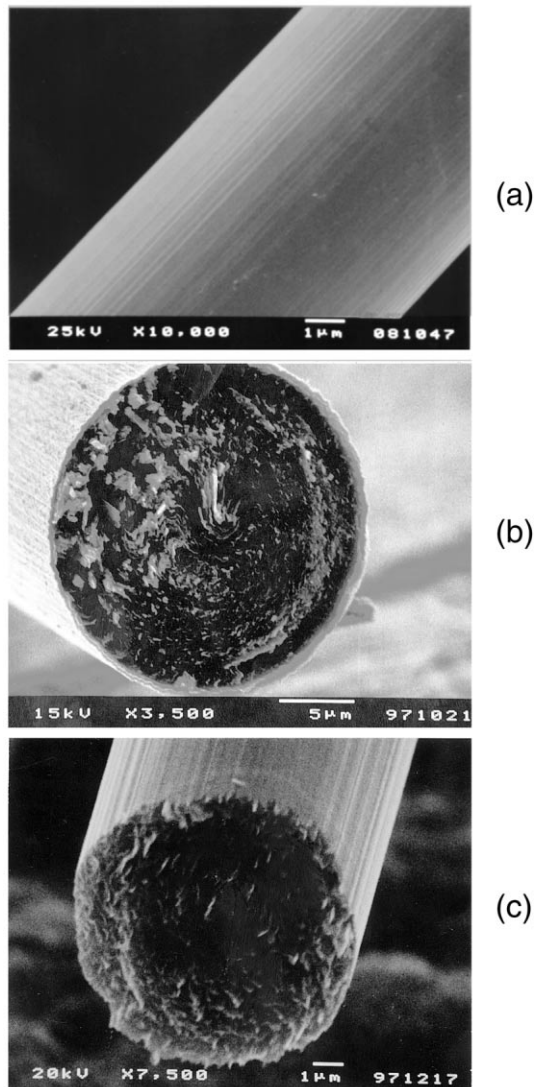*E-mail address*: keita_y@rc4.so-net.ne.jp (K. Yamaguchi).

Fig. 1. SEM photographs of graphitized single carbon fiber samples (all Petoca Ltd. made): (a): Melblon 3100 picked out from the integrated fiberfelt; (b): Carbonic 3110; (c): NF 415-3.4.
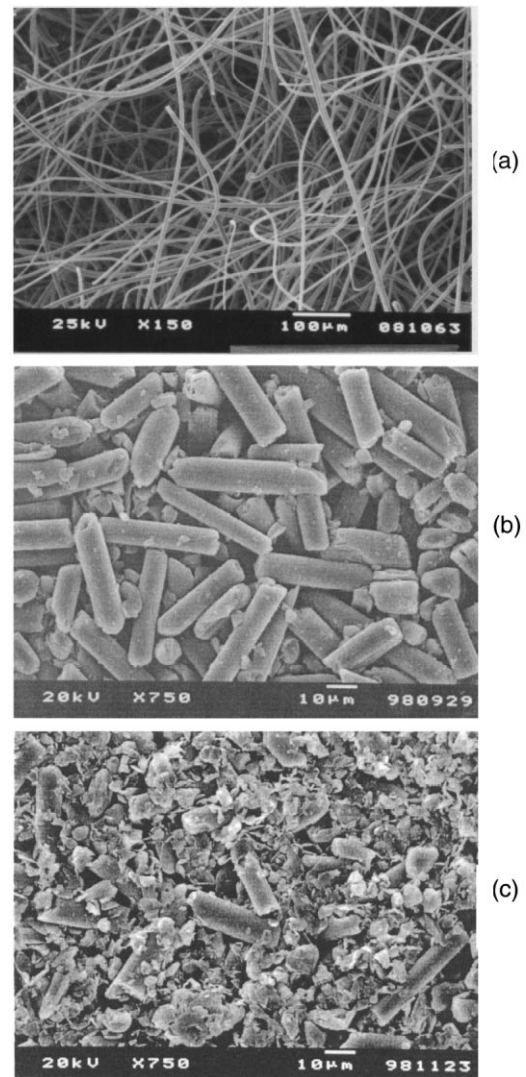

Fig. 2. SEM photographs of the graphitized integrated active materials of the fabricated electrodes: (a) a sheet of integrated fiber felt of Melblon 3100; (b) coated electrode comprised of short cut Melblon 3100; (c) same as (b) but loaded with 10 wt.% of graphite powder of Timcal SFG 6.

(a): Melblon 3100, $\varnothing = 7\,\mu m$, prepared at $3100°C$; sample (b): Carbonic 3110, $\varnothing = 30\,\mu m$, prepared at $3110°C$; sample (c): NF415-3.4, $\varnothing = 10\,\mu m$, prepared at $3110°C$, all of which are Petoca Ltd. made). The SEM pictures of these materials are shown in Fig. 1(a)–(c), respectively. For the measurement using a single fiber, one fiber was picked out from the integrated fiber felt. Monofilament type single fibers of Carbonic (sample (b)), and NF415-3.4 (sample (c)) were used as obtained. An integrated fiber felt of Melblon 3100 (prepared at $3100°C$) and powder of milled Melblon 3100 fiber was used for examining the performance of the integrated type of electrodes. The feature of these materials are shown as SEM photos in Fig. 2. Prior to the measurements, all the samples were heated at $250°C$ in vacuum for 2 h for removing the adsorbed water and other contaminants.

2.2. Fabrication of the test electrodes

A felt type test electrode (Fig. 2(a)) was fabricated by sandwiching a $1\,cm \times 1\,cm$ square felt with a thickness of 1 mm between two sheets of Ni expanded metal of larger size and the rims were spot-welded at several points to maintain a good electrical contact.

A coated electrode which was fabricated by coating the slurry prepared by dispersing a mixture of 93 wt.% of the fiber particles and 7% of polyvinylidene fluoride in n-methyl pyrrolidone on a 15 μm thick copper foil, drying and pressing (Fig. 2(b)). A conductive additive of natural graphite powder of mean diameter of 5 μm was mixed in the slurry if necessary (Fig. 2(c)). A 1.4 mm diameter disk was punched out from the coated sheet and sandwiched with two sheets of Ni expanded metal whose rims were then spot-welded at

several points and offered to the electrochemical measurements.

Single fiber electrode was fabricated by fixing a 15 mm long straight sample fiber and was fixed on one end of 0.5 mm diameter Ni wire with a conductive carbon-paste, which was mounted vertically on a PTFE made lead holder having an electrical contact terminal.

2.3. Electrochemical cell

A tip of the sample fiber was positioned vertically at the center of a cylindrical Pyrex glass cell (35 mm outer diameter, two-electrode system), and partially immersed with 5 mm depth in the electrolyte. A pure metallic Li foil (Mitsui Metal Co.) was used as the counter electrode. It was not necessary to use the three-electrode system in this experiment, since the current was at most 10 μA which is low enough to ignore the resistance polarization in this electrolyte. In the case of an integrated fiber felt or coated test electrode, the fabricated electrode was immersed vertically in the electrolyte contained in a cylindrical Pyrex glass cell with three-electrode system.

Two kinds of electrolyte were examined: one is a 1:1 (v/v) mixture of EC and dimethyl carbonate (DMC) containing 1 M $LiClO_4$ (Tomiyama Chemicals, the contaminant water being less than 15 ppm) and the other, pure PC containing 1 M $LiClO_4$ (Tomiyama Chemicals, the contaminant water being less than 20 ppm). The pure metallic Li foils (Mitsui Metal Co.) were used as reference and counter electrodes.

2.4. Electrochemical measurement

Electrochemical measurement was conducted mainly with a linear sweep cyclic voltammetry (CV) with a sweep rate of 1 mV/s. The CVs were recorded repeatedly with 20 cycles with a Hokuto-Denko HA-151 Potentio-galvanostat. The first scan was started at 2.0 V versus Li/Li^+ toward negative potential direction. All the measurements were performed in a glove box filled with a flowing dry argon gas at room temperature. SEM photographs were obtained with a JEOL JSM 5200 Scanning Electron Microscope.

3. Results and discussion

3.1. Comparison of CVs obtained in EC-based electrolyte

It is well known that highly graphitized carbon materials are in general utilized as the anode active material in an EC-based electrolyte with a high stability. At the first charging process (negative polarization), however, a capacity loss is recognized with a limited size. The charging loss, the initial irreversible charging capacity, has been attributed to the reductive decomposition of the electrolyte whose decomposed products are considered to form a passivation layer on

the carbon surface, resulting in preventing the further decomposition of the electrolyte. In constant, whenever PC is used as the electrolyte, it decomposes vigorously with an endless manner. Such an unlimited decomposition has been ascribed to the solvent cointercalation causing a spontaneous exfoliation of the graphene layer [1,2]. This proposed mechanism appears to imply that the PC decomposition is an inevitable phenomenon different from that observed with an EC-based electrolyte. But we would like to propose that the PC decomposition can be regarded to be grouped in the same category of the initial charging loss taking place in the EC-based electrolyte. The experimental evidence will be shown to correlate the decomposition to the origin of the common initial charging loss in the EC-based electrolyte.

Provided that the same active material is used, the amount of the specific initial charging loss is supposed to be the same irrespective of the difference in the fabrication process of the electrode since the charging loss is originated from the interface between the active material surface and the electrolyte. For the purpose of confirming this supposition we compared the amount of the charging loss among the three electrodes fabricated with different procedures but using the same material. The results are shown as CVs in Fig. 3(a)–(c), which correspond to the electrodes fabricated with sandwiched felt, coated milled fiber and a single fiber, respectively. As seen in Fig. 3 not only the initial irreversible capacity (seen as a single curve expanding downside) but the cycleability differ strongly depending on the difference of the fabrication procedure although the same source of the active material was used. In order to examine what factor is influencing the size of the irreversible capacity, we fabricated a coated electrode loaded with 10 wt.% of flake graphite power (Timcal SFG 6). If we compare the SEM photograph of Fig. 2(b) and (c) the voids among the coated
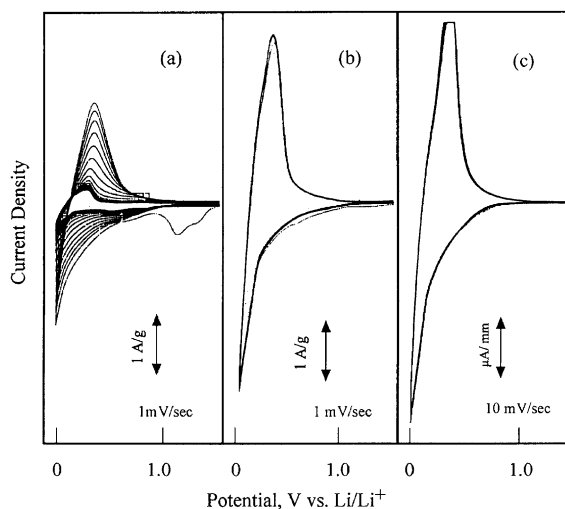

Fig. 3. Cyclic voltammograms (in EC/DMC containing 1 M $LiClO_4$) of the electrodes having the same source of graphitized carbon fiber (Melblon 3100) but the electrode fabrication is different: (a) milled fiber coated on a copper foil; (b) integrated fiber felt sandwiched between Ni expanded metal sheets; (c) single carbon fiber.
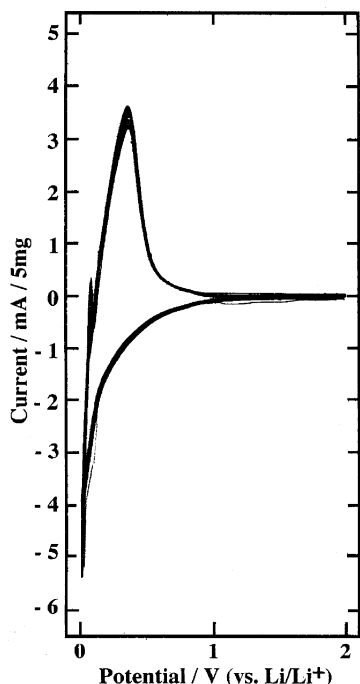
Fig. 4. Cyclic voltammogram of a coated electrode of graphitized carbon fiber (Melblon 3100) loaded with 10% of graphite flake (Timcal SFG 6) in EC/DMC containing 1 M LiClO$_4$ with a potential sweep rate of 1 mV/s.

fiber particles on the unloaded electrode are almost filled on the loaded electrode with the loaded flake, suggesting that the electrical contact among the particles is much improved.

The obtained CV with the flake loaded electrode gave rise to an extremely reduced initial irreversible capacity accompanied with the remarkable improvement of the cycleability as shown in Fig. 4. The main difference of the physical properties between the two electrodes in the absence and presence of the electro-conductive graphite flake assist to improve the electrical conductivity throughout the whole area of the electrode. Among the different electrodes examined the single fiber electrode is believed to be the most homogeneous in the electrical conductivity distribution and accordingly, is expected to give the most reduced current due to the initial charging loss. The obtained result shown in Fig. 3(c) agrees with this expectation.

We found that the cycleability has a parallel relationship with the reversibility of the initial charging. As shown in Figs. 3–6 whenever the sample gives a minimized initial charging loss the cycleability of the electrode is quite favorable. This can be elucidated based on the structure of the passive layer on the carbon surface (SEI). The reduction decomposition of the electrolyte is supposed to be not so simple since the initially generated entities will successively be reduced to generate daughter entities and so on, and the conformation of the surface passive layer is considered to be consisting in the derivative of such generated entities. Compactness and the uniformity of the passive layer formed on the surface are considered to control the size of the initial irreversible capacity. During the polarization,
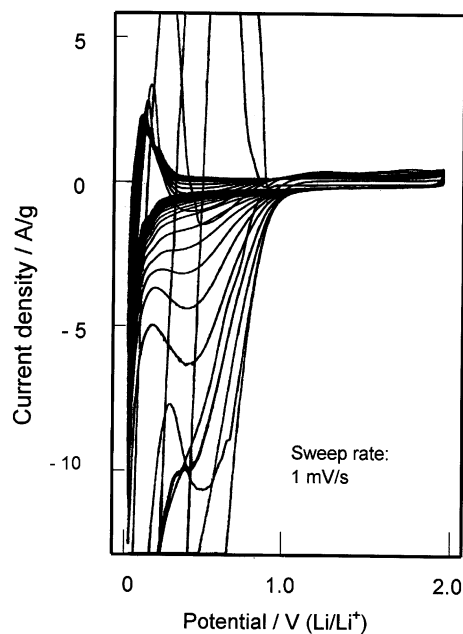

Fig. 5. Cyclic voltammogram of graphitized fiber felt electrode (Melblon 3100) in PC containing 1 M LiClO$_4$.

if the electrical contact among the carbon particles differs from place to place, the polarization potential is expected to be different from place to place depending on the different Ohmic drop, resulting in the formation of inhomogeneous and complicated surface film. This is not favorable for the satisfactory retardation of the irreversible charging reaction, but the homogeneous distribution of the electrical conductivity is believed to form a favorable compact passivation layer to prevent the excess charge loss.
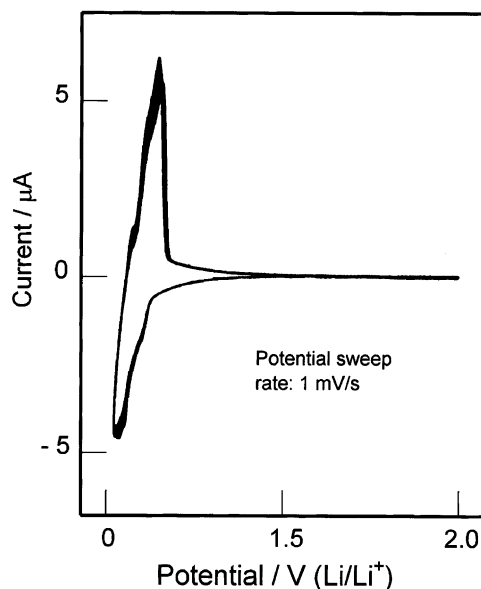

Fig. 6. Cyclic voltammogram of a single fiber electrode of Melblon 3100 in PC containing 1 M LiClO$_4$.

3.2. CVs obtained in PC electrolyte

As in the case of graphite a graphitized fiber felt electrode (Melblon 3100) showed a vigorous decomposition of PC as shown in Fig. 5. The decomposition of PC starts about at 0.7 V during the potential scan towards negative potential side with huge irregular reduction peaks due to PC decomposition accompanied with gas evolution. A part of the reduction products was oxidized in the reverse potential sweep and gave also huge oxidation current peaks.

A single fiber was picked out from the Melblon felt and offered to the same measurements (in PC). The results are shown in Fig. 6. It was surprising that very stable repeated CVs (20 cycles) without any indication of PC decomposition were obtained even if the same source of the material was used. The cycleability was very good as well. The CVs can be compared with those obtained with a single graphite fiber electrode (NF 415-3.4) in a 1:1 (v/v) mixture of EC and dimethyl carbonate (DMC) containing 1 M $LiClO_4$ (Fig. 7). The CVs are very similar to each other being difficult to distinguish the difference. The reason why the stable CVs could be obtained in PC is discussed in the next section.

3.3. Effect of the protecting-skin-layer

The sample fibers used in this experiment (Melblon 3100 and NF 415-3.4) have a protecting-skin-layer (PSL) which was formed during the manufacturing process (see Fig. 1). One may ascribe the stability to the presence of PSL of Melblon. If this is true, a fiber having a thicker protecting layer is expected to reveal more stable CV curves. Carbonic is also a graphitized carbon fiber, but having a thick PSL as shown in Fig. 1(b). We, then, examined with a Carbonic
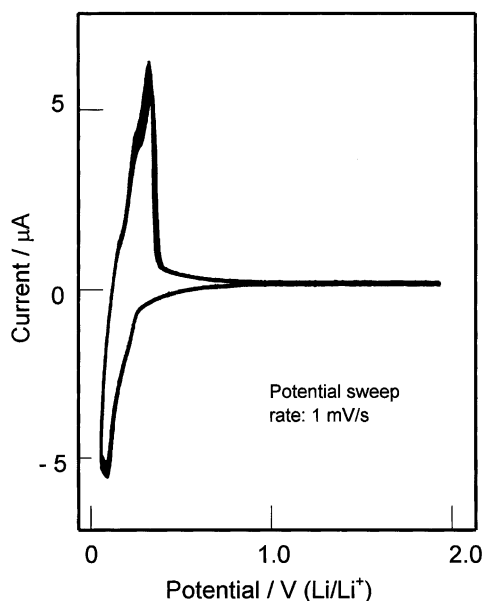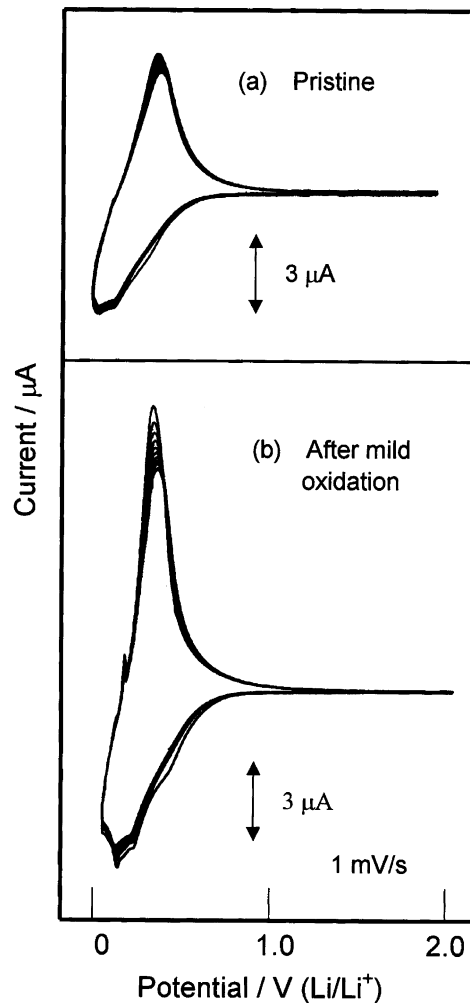

Fig. 8. Cyclic voltammogram of a single carbon fiber having thick protective skin (Carbonic) in PC containing 1 M $LiClO_4$. The CVs were obtained before and after the mild oxidation treatment.

single fiber. The results are shown in Fig. 8(a), where we see very stable CV showing no indication of initial decomposition. This appears to prove the above presumption based on PSL. Removal of the surface layer of PSL, therefore, is supposed to cause the CV to be unstable. We performed thinning of the surface skin by mild oxidation [5–8], which is very effective to erase the surface by burning off, whereby the surface contaminants can be removed. The results are shown in Fig. 8(b) which has no indication of the initial irreversible charging current due to the PC decomposition and the peak current is rather enhanced though the cycleability is a little deteriorated. Now, we have verified that the removal a surface part of PSL has no effect to cause the PC decomposition. We could examine the stability of PC also with NF415-3.4 whose PSL is thinner than that of Carbonic (Fig. 1(c)). From these results, we see the removal of PSL has no effect on the stability in PC.

These results imply that the existence of a surface protecting-skin-layer is not the cause of the stabilization against the PC decomposition.
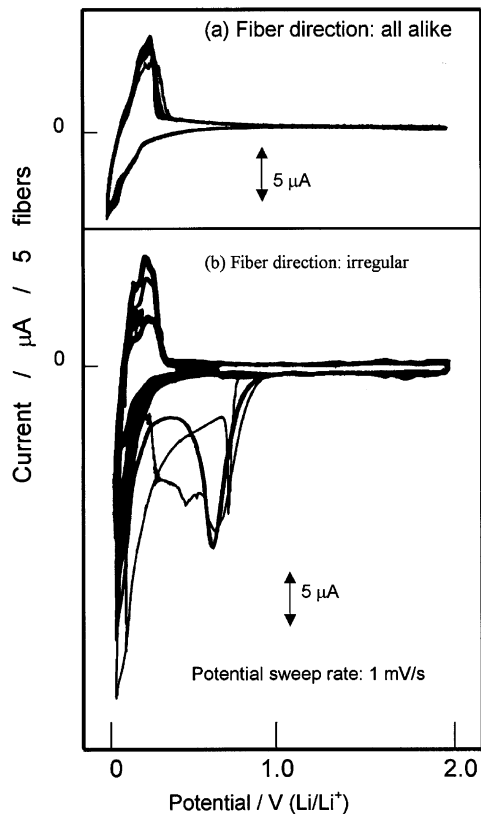

Fig. 7. Cyclic voltammogram of a graphitized single carbon fiber (NF415-3.4) in EC/DMC (1:1) containing 1 M $LiClO_4$.

0 4 nm r
0 4 nm r

0 4 nm r

Fig. 9. Cyclic voltammogram (in PC containing 1 M LiClO$_4$) of five Melblon 3100 fibers bundled together: (a) all fibers have the same direction; (b) the direction of each fiber is irregular.

3.4. Homogeneity of the electric conductivity

Difference between a single fiber and an integrated fiber felt is not in the material but may be in the difference in the aggregation. In the aggregated electrode the electrical contact between each fiber is supposed to be different from place to place which will cause an inhomogeneity in the conductivity distribution. Upon polarization of such an electrode, the topological potential is not the same as that at the different position as already discussed in Section 3.1.

We examined this assumption by using a fiber bundle electrode where five Melblon fibers with the same length were bundled by pasting together with carbon paste and fixed to the Ni current collector. Two types of the bundle electrode were examined: the one had fibers having a uniform direction, and the other, the direction of each fiber was irregular. The CVs obtained with these electrodes are shown in Fig. 9. The electrode having a uniform fiber direction revealed stable CVs with good cycle life and no decomposition current (Fig. 9(a)), while a bundle electrode having an irregular fiber direction gave unstable CVs having

irregular very large reduction currents due to PC decomposition (Fig. 9(b)). Summarizing the results, PC can be definitely stable even at the graphitized carbon as far as the electrical conductivity is kept homogeneous throughout the whole electrode. If on the electrode there is an inhomogeneous potential distribution, various kinds of reduction will occur place by place at the same time. As a result, an inhomogeneous SEI is formed, which is considered to be not tight and compact.

4. Conclusions

One of the major cause of the initial irreversible charging capacity (charging loss) can be attributed to the inhomogeneity of the electrical distribution over the electrode. Loading of the conductive additive on the coated electrode is quite effective to realize suppressed initial charging loss and good cycleability.

By using a single graphitized carbon fiber we have been able to show no reductive decomposition of PC electrolyte even at the graphitized electrode. This may induce a discussion on the mechanism of PC decomposition at the graphite electrode.

The uniformity of the electrical conductivity distribution is supposed to play an important role for preventing the initial charging loss and PC decomposition.

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