

# Charge/discharge efficiency improvement by the incorporation of conductive carbons in the carbon anode of Li-ion batteries

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## Abstract

Influence of the conductive additive loading on the anode performance of Li-ion battery was investigated for the coated anode where graphitized mesophase carbon fiber (MCF) was used as an active material, and loaded with natural graphite (NG), acetylene black (AB) or Ketjen black (KB).

Incorporation of the conductive additive was quite effective to improve not only the cycle life, but also the rate of the electrochemical reaction. In addition, we found that the initial irreversible charging capacity (IICC) of MCF was suppressed to a great extent. The effectiveness was dependent on the kind of material loaded. On the other hand, making a homogeneous slurry for coating was found to be a key factor for the performance improvement. The most preferable choice of the preparation condition gave rise to a dramatic improvement. In contrast to these advantages, the carbon blacks showed a large IICC inherent to the materials which is an issue to be solved for actual use. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Conductive carbon additives; Carbon anode; Li-ion batteries; Cyclability; Initial irreversible charging capacity

## 1. Introduction

A number of studies have so far been performed for providing a high performance carbonaceous material for the anode of Li-ion batteries [1]. The electrochemical reactions involving Li transfer and exchange of electron, however, proceed at the electrode/electrolyte interface, and accordingly, the surface condition of the electroactive material particle and also the electric linkage of each particle to the current collector are the key factors [2]. Coating with a thin metal film over the surface of the graphitized carbon fiber has been proved to enhance the rate of the electrochemical reaction [3], and measurement

with a single fiber deposited with a silver film showed that the rate was as high as over 10 times [4] of that of the simply heat-treated sample. This is in consistent with the results obtained by Ogumi [5,6] et al. for natural graphite (NG).

Once the active material surface is modified, the next step for enhancing the reaction rate is to provide a good pathway for the electron transfer. Ahn et al. [7] reported that loading of stainless steel fibers in the MCMB anode enhanced the reaction rate.

Graphitized mesophase carbon fiber (MCF) is a good electron conductor with a cable-like structure like that used by Ahn et al. [7]. Therefore, it appears unnecessary to use an additional conductor. In a preliminary experiment, however, we found that the loading of some conductors gave rise to a remarkable improvement of the cyclability [8], which requires a more systematic examination for obtaining the most favorable condition. In the present paper, we will demonstrate the improvement of the electrode charac-

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teristics of a coated anode where MCF are mixed with a varied amount of NG, acetylene black (AB) or Ketjen black (KB).

## 2. Experimental

As an anode active material, milled carbon fiber of Melblon 3100 (Petoca made, well graphitized) was used. The active material powder was dried by heating at 250°C for 2 h in vacuum.

The electro-conductive materials used were pulverized NG (JSP, mean diameter, 3  $\mu\text{m}$ ), AB and KB. The conductive materials were used without further treatment.

The test electrode was fabricated by coating a slurry mix on a 15- $\mu\text{m}$ -thick pure copper sheet with a doctor blade, dried in a hot dry air, and pressed with a roll. The slurry mix was prepared by mixing a dry mix comprised of active material powder and conductive additive powder with the binder solution of *n*-methylpyrrolidone and polyvinylidene fluoride (PVDF). Two different mixing ways were adopted: manual mixing in an agate mortar and mixing with a rotating blade. The shape of the mixer blade, the rotating speed and the slurry mix formation ratio were important factors for obtaining a homogeneous slurry. For the dry mix with a higher amount of the additive, a larger amount of the binder solution was required for

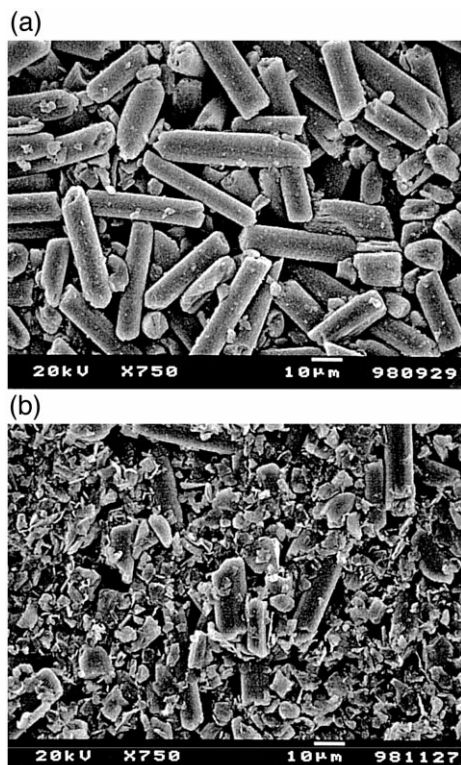


Fig. 1. SEM images of a coated electrode of MCF without (a) and with (b) 15% loaded natural graphite powder (mean size: 3  $\mu\text{m}$ ).

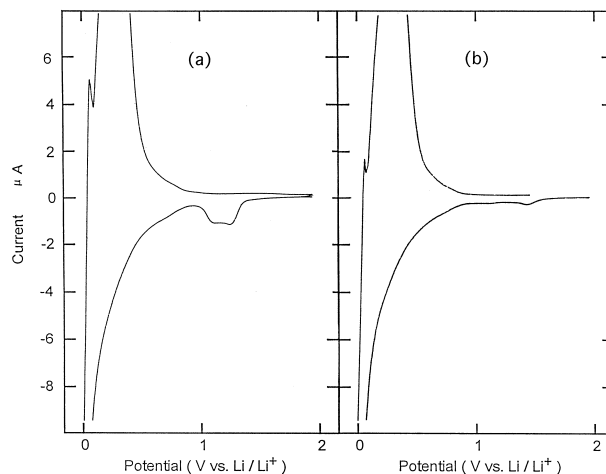


Fig. 2. CVs of coated electrode of MCF without (a) and with (b) 15% loaded natural graphite powder (mean size: 3  $\mu\text{m}$ ). CVs were obtained in EC/DMC (1:1, by volume) containing 1 M  $\text{LiClO}_4$  with a potential sweep rate of 1 mV/s.

obtaining a homogeneous slurry, especially in the case of KB. The amount of the conductive additive was varied from 1% to 10% to the active material by weight.

The electrochemical evaluation was performed with a Hokuto-denko Potentiostat/galvanostat Type HA-151 by which cyclic voltammograms (CV) were obtained in a beaker-type three-electrode cell. A constant current charge/discharge test was also performed with a coin type cell. All the measurements were conducted in a glove box

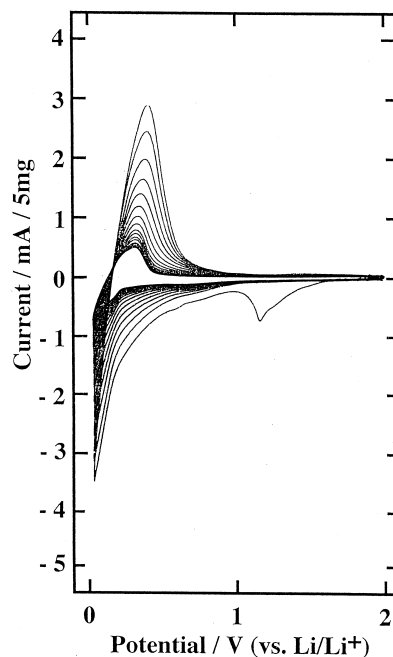


Fig. 3. Repeated CVs of a coated electrode of MCF measured in EC/DMC (1:1, by volume) containing 1 M  $\text{LiClO}_4$  with a potential sweep rate of 1 mV/s. The electrode was fabricated with a slurry prepared manually.

filled with a dried argon stream at room temperature. The electrolyte was EC/DMC 1:1 mixture containing 1 M  $\text{LiClO}_4$ .

SEM images of the fabricated electrode were taken with a JEOL Scanning Electron Microscope Type JSM 5200 S.E.

### 3. Results and discussion

#### 3.1. Initial irreversible charging capacity (IICC)

The IICC can be attributed to the electrochemical reduction decomposition of the electrolyte in contact with the active material surface [9], and appears to be unable to be suppressed unless the surface of the active material is modified. We compared the CVs of the test electrode with and without the conductive additive of NG flakes. The results obtained with an electrode containing only the active material (Fig. 1(a)) are shown in Fig. 2(a), where we see distinct two peaks at around 1.2 and 1.3 V vs.  $\text{Li/Li}^+$  which appear only at the first reduction scan. In contrast, when we loaded graphite flakes, for example 15% (Fig. 1(b)), the IICC was reduced remarkably as shown in Fig. 2(b) even though the same active material was used. Similar results were also obtained with the other additives. Such an effect can be attributed to the attainment of homogeneous distribution of high conductivity all over the electrode surface. In contrast, if the conductivity distribution is heterogeneous, and such an electrode is once polarized, the topological potential in the electrode is supposed to be different here and there due to the different ohmic drop depending on the conductivity, causing different elec-

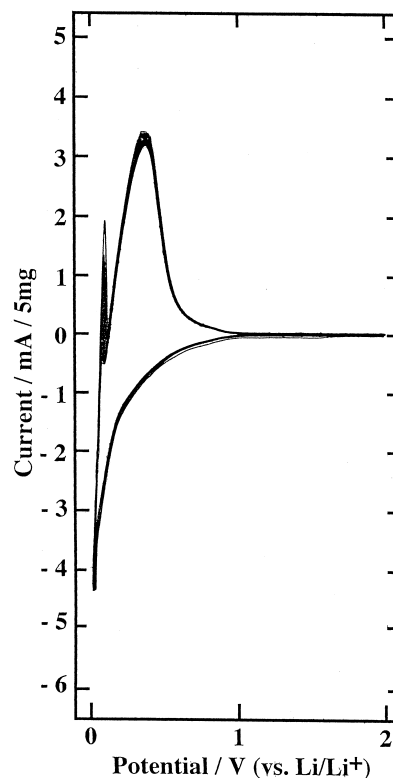


Fig. 5. Repeated CVs of a coated electrode of MCF (without conductive additives) measured in EC/DMC (1:1, by volume) containing 1 M  $\text{LiClO}_4$  with a potential sweep rate of 1 mV/s. The electrode was fabricated with a slurry prepared by using a mechanical mixer.

trochemical reactions to occur and resulting in a formation of a complicated SEI which is supposed to be more or less

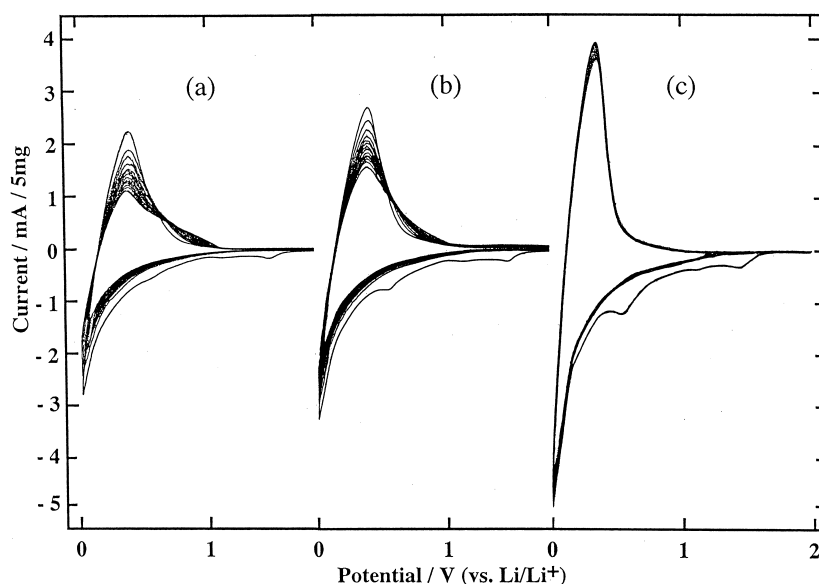


Fig. 4. Repeated CVs of a coated electrode of MCF with loaded AB. CVs were measured in EC/DMC (1:1, by volume) containing 1 M  $\text{LiClO}_4$  with a potential sweep rate of 1 mV/s. Weight percent of loaded AB: (a) 2.5%, (b) 5%, (c) 10%.

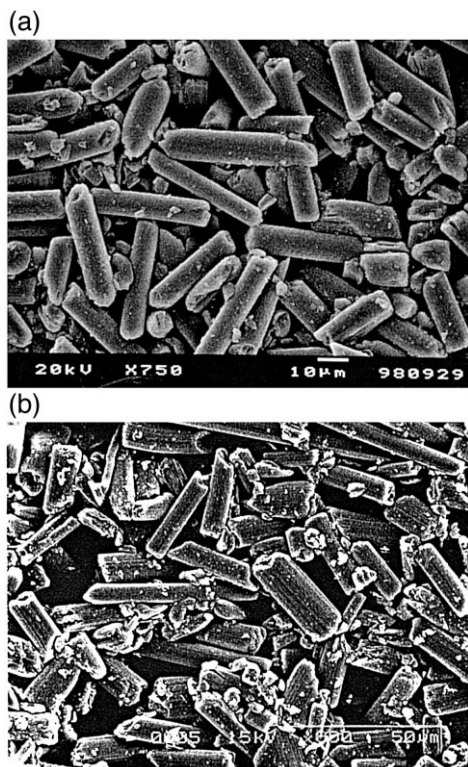


Fig. 6. SEM images of coated electrodes with no conductive additives fabricated with (a) a slurry prepared manually, and (b) that prepared by using a mechanical mixer.

porous and requires a large amount of charge until completion of the layer.

On the other hand, if the electrode is sufficiently homogeneous in its electric contact all over the surface, the reduction reaction of the electrolyte is expected to be monotonous, giving rise to a simple SEI which is supposed to be compact and thin enough to require only a small quantity of charge for the completion of the layer. Such a tendency will be seen also in the following section.

### 3.2. Cyclability

Single component electrode in the absence of the conductive additives showed poor cyclability. Fig. 3 gives such an example, where the height of the anodic CV peak linked to the intercalation of Li from the active material is shown to be successively diminished. A reduction current peak group appearing on the curve of negatively forward scan in the potential range 1 to 1.5 V can be attributed to the irreversible reduction of the electrolyte as pointed out in the preceding section (IICC).

The CV curves obtained with the electrode having different amounts of loaded AB are shown in Fig. 4, where the slurry was prepared by mixing in agate mortar manually. As shown in these figures, the successive diminution of the peak height is significantly retarded with the in-

crease of the amount of loading, accompanying with the successive suppression of the current peak related to IICC.

A similar improvement effect was also observed with KB loading. However, because of the presence of internal void in this carbon black particle, an appreciable amount of the binder solution was absorbed into the void causing a difficulty in the manual preparation of a good homogeneous slurry.

### 3.3. Effect of homogeneous mixing

The difficulty of the manual preparation of homogeneous slurry with KB could be removed by a mechanical mixing where a mixer with an appropriate shape of the blade was used. Of course, the most suitable mixing ratio involving the solvent, the binder and the carbon black was examined, respectively, according to the loading amount.

Surprisingly, the CV obtained with a well-mixed slurry without any conductive additives gave a very stable deintercalation peak, as shown in Fig. 5. At the same time, the IICC peak was suppressed as well. When we compare the SEM images between the two electrode fabricated with a hand-made slurry and the mixer-made one (Fig. 6(a) and (b)), presence of a considerable amount of tiny particles,

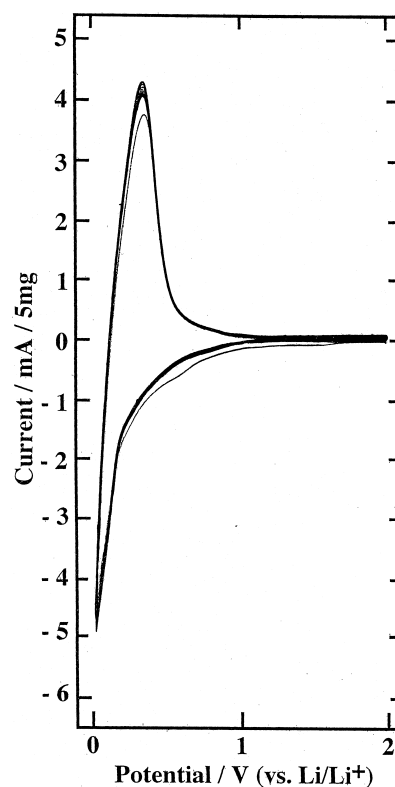


Fig. 7. Repeated CVs of a coated electrode of MCF with 5% loaded AB, the electrode being fabricated with a slurry prepared with a mechanical mixer. CVs were measured in EC/DMC (1:1, by volume) containing 1 M  $\text{LiClO}_4$  with a potential sweep rate of 1 mV/s.

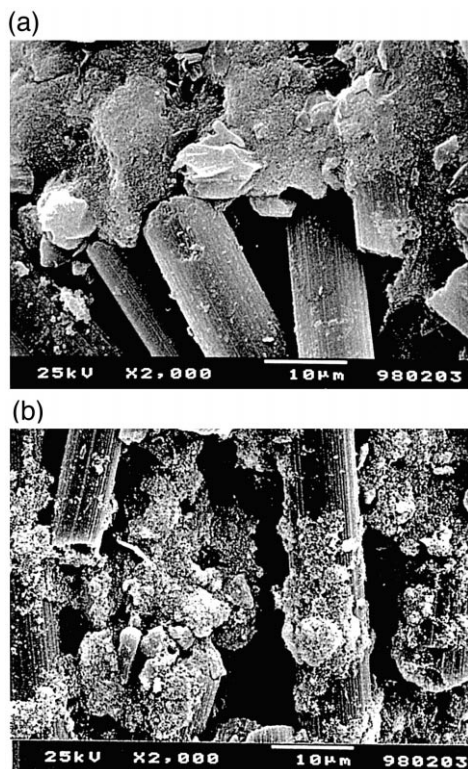


Fig. 8. SEM images of coated electrode of MCF loaded with 5% AB. (a) Fabricated with a slurry prepared manually; (b) fabricated with a slurry prepared with a mechanical mixer.

which is supposed to be formed by crushing of the active fiber material during the mixing, can be seen on the surface of the electrode fabricated with a mixer-made slurry. The particles are supposed to behave just like a loaded conductive additive. Furthermore, we can demonstrate the effect of the homogeneous mixing. The results given in Fig. 7 which was obtained with a mechanical mixer-made slurry loaded with 5% of AB exhibit a surpassing CVs as compared with those obtained with a manual-made slurry loaded with the same amount of AB (Fig. 4(b)). Homogeneously mixed AB can be seen in SEM shown in Fig. 8(b) in comparison with that obtained with the manual mixing (Fig. 8(a)). Fig. 9 shows CV of the electrode loaded 5% KB with a much improved performance. These results indicate that obtaining a homogeneous slurry is a key factor for the fabrication of a high performance electrode. It was difficult to detect in SEM images the difference in binder situation between the two electrodes fabricated with a hand-made slurry and a mixer-made one. Homogeneity of the layer of the binder covering over the surface of the active material surface is supposed to influence the performance improvement.

### 3.4. Current peak height

As pointed out by Ahn et al. [7], the use of conductive additives was also helpful for enhancing the electrochemi-

cal reaction rate. This was confirmed by our study: the anodic peak height in Fig. 4(c) is noticeably enhanced as compared with that in Fig. 3. Also, homogenization of slurry is shown to be effective, as seen in Fig. 5, whose CV shows higher anodic peak height as compared with that in Fig. 3. The highest enhancement was achieved in the case of 5% loading of KB, the CV being shown in Fig. 9. In spite of an excellent improving effect, KB has a serious issue to be solved, i.e., to minimize the large ICC inherent to KB, which is clearly seen in Figs. 9 and 10 in the potential range 0.2 to 0.8 V. The constant current charge/discharge curves in Fig. 10 are those obtained for the first charging (insertion) and the successive discharging. More than three potential plateaus on the charging curve are more enhanced with the increase of KB content, and accordingly, attributed to the ICC of KB. On the other hand, there is no distinctive difference among the discharge curves obtained with different KB contents, which can be elucidated by assuming that the reduced entities formed during the charging are stable and cannot be oxidized.

### 3.5. Cyclability under constant current rate

Cyclability test was made with a 0.3-C rated constant current charge/discharge for the electrodes containing AB,

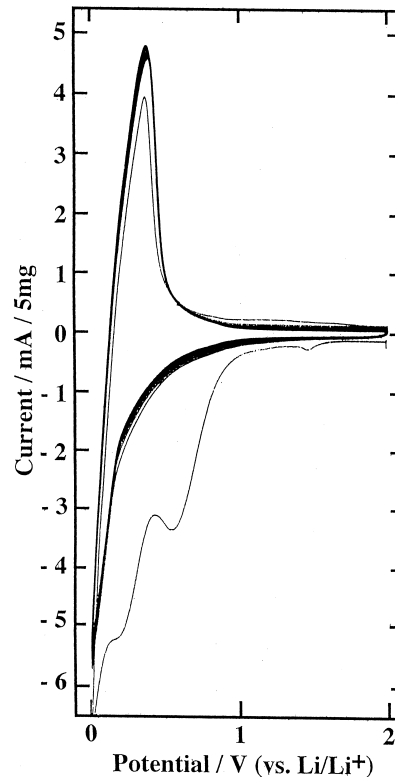


Fig. 9. Repeated CVs of a coated electrode of MCF with 5% loaded KB, the electrode being fabricated with a slurry prepared with a mechanical mixer. CVs were measured in EC/DMC (1:1, by volume) containing 1 M LiClO<sub>4</sub> with a potential sweep rate of 1 mV/s.

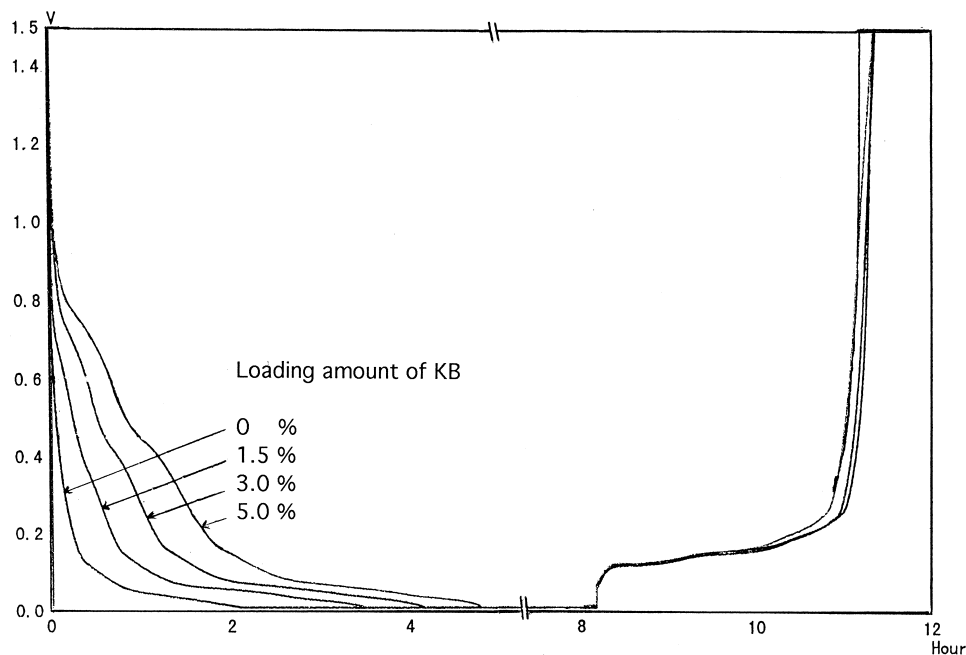


Fig. 10. Constant current first cycle charge/discharge curves of the coated electrodes of MCF loaded with varied amounts of KB. The electrode was fabricated with a slurry prepared with a mechanical mixer. The potential–charge curves were measured in EC/DMC (1:1, by volume) containing 1 M  $\text{LiClO}_4$  with a discharge rate of 0.3 C.

KB, and no additive. The test results are shown in Fig. 11. As is seen in the figure, a capacity as high as over 300 mA h/g could be retained with only 1.5% KB loaded, which is in contrast to the non-loaded electrode which retained only 243 mA h/g at 10th cycle.

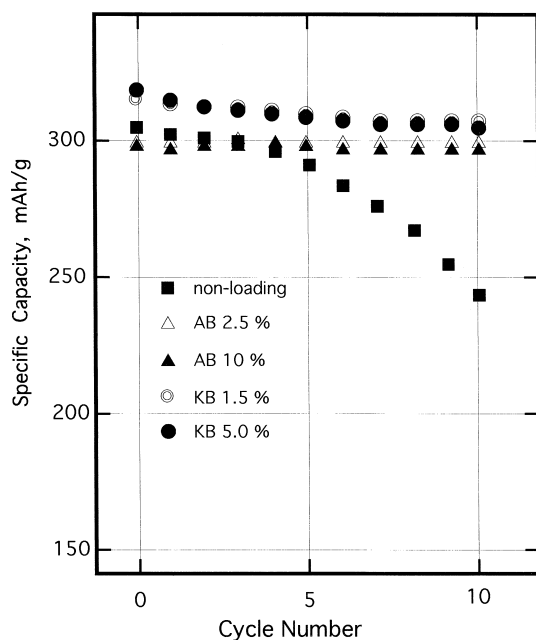


Fig. 11. Capacity change during the constant current cycle test for the electrodes loaded without and with varied amounts of AB and KB. The potential–charge curves were measured in EC/DMC (1:1, by volume) containing 1 M  $\text{LiClO}_4$  with a discharge rate of 0.3 C.

It is natural to presume that the incorporation of conductive additives in the electrode will reduce the discharging capacity/total weight of the loaded material since the electrode contains more inactive additives. Opposing to the presumption the anode capacity/total weight of the coated materials (not based on the active material weight) was, in fact, increased in spite of the reduced amount of the active material loading as seen in Fig. 11. This can be attributed to an increase in the utilization efficiency of active material being assisted by the conductive additive.

#### 4. Conclusions

Dispersion of electro-conductive carbon in the coated anode has been proved to be a key factor for obtaining a reliable anode of Li-ion secondary battery for high rate use. Improvement of the anode performance due to the conductive carbon loading includes: (1) remarkable increase of the cyclability; (2) suppression of the IICC to a great extent; (3) increasing of the charge/discharge rate; and (4) increased utilization efficiency for withdrawing the charged capacity.

Homogenization of slurry mix was found to be a key factor for obtaining a high performance anode irrespective of the presence of the conductive additives.

We can conclude that for obtaining a high performance anode, the fabrication procedure is also quite important in addition to exploring a new material.

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