

Recent trends in carbon negative electrode materials

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Abstract

The use of graphite-type materials as the negative electrodes for rechargeable lithium batteries is increasing. For graphite-type materials, we proposed the intercalation mechanism taking into account the influence of crystallite size and stacking of the graphitic layers. We found graphite-type materials with a reversible capacity of 430 mAh g^{-1} over a theoretical limit capacity of 372 mAh g^{-1} . This higher capacity is due to cavities existing in carbon that are capable of storing lithium ions. © 1997 Elsevier Science S.A.

Keywords: Carbon; Electrode materials; Negative electrodes; Rechargeable lithium batteries

1. Introduction

Studies on carbon negative electrodes for rechargeable lithium batteries have been extended quite rapidly in recent years. The market of rechargeable lithium batteries is increasing more and more to reach about twenty billion yen per year in Japan. Hence, some companies related to the battery material still enter into the market even now. As carbon negative electrode materials, hard carbon (non-graphitizable carbon), graphite or graphitized soft carbon (graphitizable carbon) are used in practical rechargeable lithium batteries at present. Moreover, some charge/discharge reaction mechanisms have been proposed for carbonized materials having higher capacities than 372 mAh g^{-1} corresponding to the composition of LiC_6 . We have also studied the charge/discharge characteristics of mesocarbon microbeads (MCMB) [1,2].

In the present paper, we discuss the characteristics of both the graphite-type and the hard carbon-type materials as promising carbon materials.

2. Comparative investigation of present carbons

Graphite-type and hard carbon-type materials represent carbon materials generally used in the negative electrodes of rechargeable lithium batteries. Hereafter we mainly discuss the difference between the characteristics of graphite-type and those of the hard carbon-type materials.

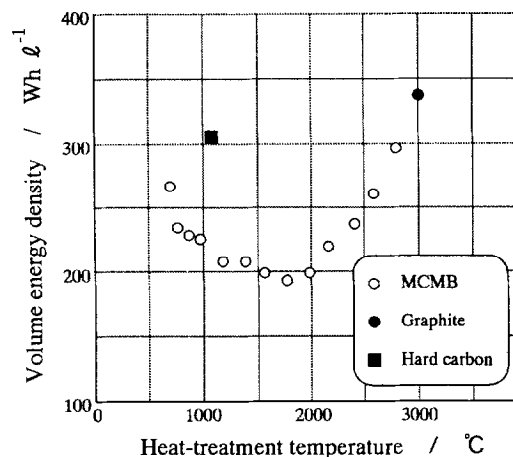


Fig. 1. Relationship between heat-treatment temperature of MCMB and the volume energy density.

Fig. 1 shows the relationship between the heat-treatment temperature (HTT) of MCMBs and the volume energy density roughly calculated by taking into account their rechargeable capacities, coulombic efficiencies and densities. Furthermore, in comparison with data of MCMBs, those of a hard carbon-type material and typical natural graphite are also shown in Fig. 1. The natural graphite is plotted as a HTT of 3000 °C for convenience. It obviously indicates that the volume energy densities of graphite-type materials become higher than those of hard carbon-type materials and even high capacity-type materials heat-treated below 1000 °C.

On the other hand, the irreversible capacities of graphite-type materials are less than those of hard carbon-type ones. In terms of rate capability, graphite-type materials seem to

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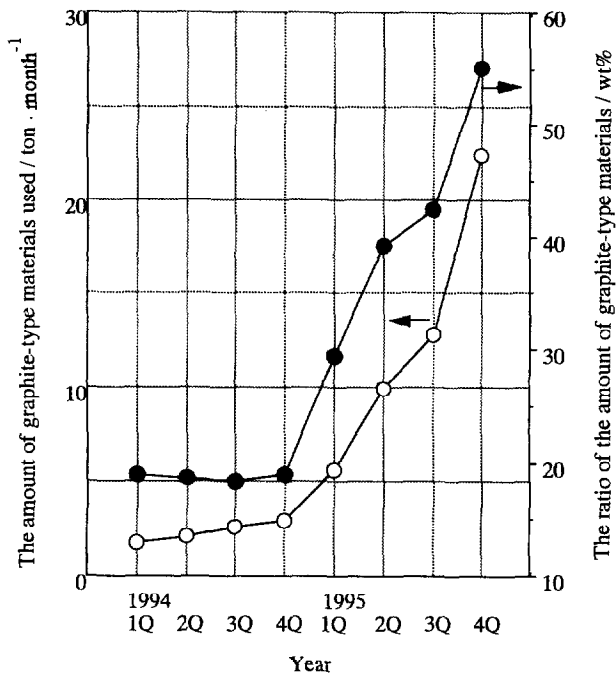


Fig. 2. The change in the amount of graphite-type materials used as negative electrodes for rechargeable lithium batteries in recent years: (○) the amount of graphite-type materials used, and (●) the ratio of the amount of graphite-type materials.

have an advantage over hard carbon-type ones. Moreover, from the view point of the risk that lithium metal might deposit in the charge, graphite-type materials have the charge/discharge potential range over around 90 mV versus Li/Li^+ and are considered to be safer than hard carbon-type ones as the negative electrodes for practical batteries. To make matters worse, we have found that the reversible capacities of hard carbon-type materials tend to decrease when they are exposed to humid air for a few days.

As a result, the ratio of graphite-type materials used as negative electrodes for rechargeable lithium batteries is increasing, as shown in Fig. 2 (from Nomura Research Institute, Japan).

3. Reaction mechanisms

3.1. Intercalation mechanism

The intercalation mechanism has been well known since 1955. However, we found the relationship between the composition of stage 1 graphite intercalation compounds with lithium (Li-GICs) and the crystallite sizes of the pristine graphite taking into account the in-plane structure and stacking sequence [3]. Namely, the intercalation mechanism of the influence of small crystallite sizes was proposed.

On the other hand, the relationship between the volume fraction of the graphitic structure (P_1) of MCMBs and their charge/discharge characteristics has been examined, and it was found that the capacity ranging from 0 to 0.25 V versus Li/Li^+ was proportional to the P_1 of the MCMBs [4]. It

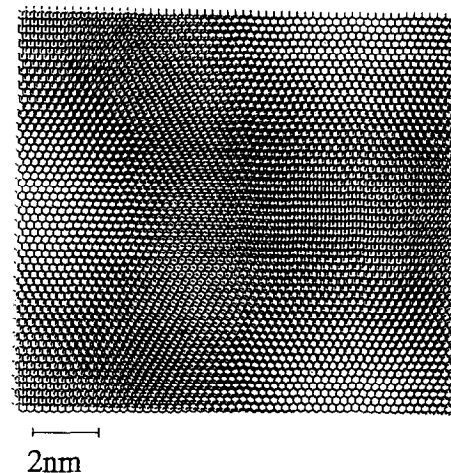


Fig. 3. Simulation for the turbostratic structure where upper carbon plane is twisted by 1.14° against lower plane.

indicates that the lithium storage mechanism in this potential range corresponds to the lithium-intercalation reaction into the graphitic layers with the *AB* or *ABC* stacking. That is, the intercalation mechanism considering the influence of stackings of graphitic layers was proposed.

As the result of these considerations, it was found that the composition of the Li-GIC can be expressed by the following equation as a function of the crystallite sizes (L_a and L_c) and the lattice constants (a_0 and c_0) of pristine graphite [5]

$$\frac{C}{\text{Li}} = 6 \left(1 + \frac{c_0}{2L_c} \right) \left\{ \frac{(L_a + a_0)^2}{P_1 L_a^2 + a_0^2/3} \right\} \quad (1)$$

where a_0 is equal to 0.246 nm.

Furthermore, the projected probability function (PPF) for the first nearest neighbor carbon layer plane was calculated for the MCMB [6]. It was found that the degree of rotational misorientation can be estimated from the displacement of the two peak tops on the PPF pattern, and that the angle of misorientation decreases with increasing the HTT of MCMB. As shown in Fig. 3, the simulation of the turbostratic nature of layer stacking based on the angle of misorientation showed the moiré pattern formed by a pair of the nearest layer planes.

3.2. Cavity mechanism

We investigated on a charge/discharge reaction mechanism for higher capacity MCMBs heat-treated below 1000 °C. Although all the higher capacity can be considered to be due to intercalation mechanism as a formation of LiC_2 [8,9], it is hard to accept the mechanism with such a high packing density of lithium ions. In addition, the GICs having the composition of LiC_2 has never been synthesized with the exception of a preparation under high pressure. We considered that the higher capacity should not only be explained by the intercalation mechanism.

Accordingly, we concluded that the cavities existing in MCMBs are capable of storing lithium ions to give high capacity. We estimated the cavity amount by assuming a

simple model of a crystallite, and derived the following equation expressing the total cavity amount in carbon in a unit volume (cavity index, CI) [7]

$$CI = 1 - \frac{D}{D^i} \times \frac{c_0}{c_0^i} \times \left(\frac{a_0}{a_0^i}\right)^2 \times \frac{L_c}{L_c + c_0/2} \times \left(\frac{L_a}{L_a + a_0}\right)^2 \quad (2)$$

where D and the superscript, i denote the density and the values for ideal graphite, respectively. On the basis of the derived equation, we found a good relationship between CI values of MCMBs and their reversible capacities. As a result, we proposed a new cavity mechanism for the charge/discharge reaction of high capacity MCMB. The cavity mechanism can be applied to graphite-type materials as mentioned below, being different from the so-called hydrogen mechanism [10].

4. Promising carbon

As a recent trend for carbon negative electrode materials, almost all battery manufacturers have selected graphite-type materials except one major company. In fact, graphitized MCMBs produced at Osaka Gas have been ordered by many battery manufacturers.

However, there is a theoretical limit capacity of 372 mAh g^{-1} as the major weakness of graphite-type materials. Regarding this point, we obtained an attractive result for one of the graphite-type materials that we had investigated. Fig. 4 shows its discharge (which means de-intercalation) curve, indicating a considerably large capacity of 430 mAh g^{-1} over the limit capacity. We now consider that this higher capacity is also due to cavity mechanism described above. It suggests that we can still enlarge the capacity of graphite-type materials as well as that of hard carbon-type ones.

Judging from these circumstances, a demand of graphite-type materials as the negative electrode materials for rechargeable lithium batteries will increase.

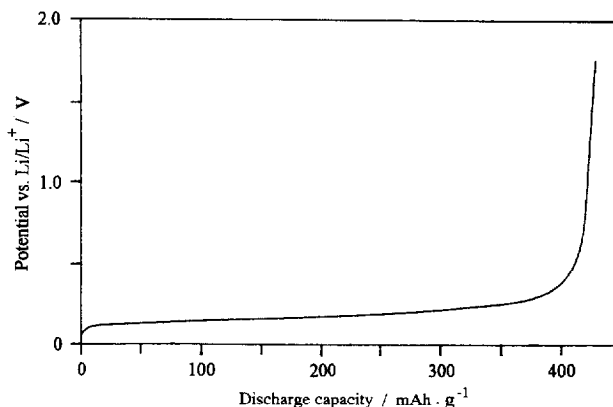


Fig. 4. The typical discharge curve of the graphite-type material having a capacity over the theoretical value.

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