

Effects of the macroscopic structure of carbon black on its behaviour as the anode in a lithium secondary cell

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Abstract

The anodic behaviour of various carbon black (CB) samples prepared by the oil furnace method has been investigated in 1 M LiPF₆ solution in ethylene carbonate–1,2-dimethoxyethane 50/50 (by volume). These CB samples had different macroscopic structures, though their microscopic parameters such as d_{002} and L_c remained constant substantially. The irreversible capacity at the initial reduction stage increased almost linearly with the BET surface area. The reversible capacity, on the other hand, showed no correlation with the BET area and was large for a highly aggregated coarse CB sample. The neck position connecting two primary CB particles was considered to be mainly active for the electrochemical insertion/extraction of lithium including effective electrolyte penetration on to the carbon surface.

Keywords: Secondary lithium cells; Carbon black; Anodes

1. Introduction

The application of a carbon material for the negative electrode of the so-called lithium-ion battery has been investigated intensively in recent years [1–5], where the reversible insertion/extraction of lithium into/from a carbon matrix occurs upon charge/discharge instead of the deposition/dissolution of metallic lithium. The dendritic growth of lithium on charging can be avoided and hence the use of carbon anodes can be expected to prolong the cycle life of a cell and to improve its reliable safety.

On the other hand, the use of a carbon anode may lower the specific energy of a cell because of a higher reversible potential and of the limited amount of lithium accommodation in a carbon matrix. These two factors affecting the specific energy can vary with the kind of carbon materials. So far, a variety of carbon materials such as natural graphite [6], cokes [3], carbon fibres [7], non-graphitizable carbon [8], pyrolytic carbon [9], etc., have been investigated. Especially, natural graphite was reported by Dahn et al. [4] to have a theoretical capacity of 372 mAh/g (LiC₆), whereas a larger capacity than this value has been pointed out recently for certain poor crystalline carbons [10–14].

In the previous study [15], there were found out irreversible processes of a carbon black (CB) anode in a propylene carbonate–1,2-dimethoxyethane (PC–DME) solution only on the first cyclic voltammetry (CV) sweep in addition to two reversible processes: the first one at about 0.2 V was due to lithium insertion/extraction into/from a CB matrix and the second at about 0.9 V might be a faster reaction on the CB surface. As for the irreversible capacity, the gas evolution dangerous for a sealed battery was confirmed to be negligible (~1%) compared with the formation of a surface film on CB [15]. The analytical results for this surface film by both transmission electron microscope (TEM) and electron spectroscopy for chemical analysis (ESCA), furthermore, have been reported in Ref. [16].

The present paper describes the effects of the macroscopic structure of CB on its anode characteristics in a lithium secondary cell.

2. Experimental

Nine different CB samples were examined in this work. They were prepared by incomplete combustion of hydrocarbons (oil furnace method) and then heated at 1200 °C in an argon atmosphere. The CB sheets

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(~0.25 mm in thickness) were obtained by hot-pressing the mixture of 90 wt.% CB with 10 wt.% poly(tetrafluoroethylene) (PTFE) binder. The sample electrodes were prepared by pressing these sheets on to a nickel foil current collector and then dried at 200 °C under vacuum.

A usual three-electrode beaker cell was constructed in an argon atmosphere. The counter electrode was a lithium foil with a large surface area and the reference electrode was a lithium chip. The electrolyte was 1 M LiPF_6 solution in EC(ethylene carbonate)–DME (50/50 (by volume)). The charge/discharge cycling was carried out galvanostatically at a rate of 0.2Li/6C h or by CV at 0.05 mV/sec between 2.0 and 0.0 V.

The macroscopic structure of CB was characterized by an average particle diameter determined by TEM observation, the specific surface area by nitrogen adsorption BET method, and the absorbed amount of dibutylphthalate (DBP) [17]. The DBP results showed the agglomerate of primary CB particles.

3. Results and discussion

3.1. Characterization of primary CB particles

Fig. 1 shows the TEM view of typical CB samples. The average diameter of primary particles is in the range from 25 to 66 nm. The absorption of DBP by

100 g of CB, on the other hand, is in the range from 68 to 160 ml. From the macroscopic view point, there are four types of CB, namely: (i) poorly aggregated fine particles; (ii) highly aggregated fine particles; (iii) poorly aggregated coarse particles, and (iv) highly aggregated coarse particles.

When we consider the spheres of radius, r , the specific surface area, A , is given by $3/(\rho r)$, where ρ is the density of a particle. The relationship between the specific surface area and the representative radius of primary particles is shown in Fig. 2 for all CB samples used. As seen in this Figure, A is almost proportional to $1/r$ excepting only one sample of (Z). This sample (Z), which has been obtained under extreme preparation conditions, has a rough and porous surface in contrast to the other samples.

3.2. Effects of specific surface area on the irreversible capacity

Typical CV data for type (a)–(d) CB samples are compared in Fig. 3. Every voltammogram ensures a good cycleability and reversibility of these CB anodes except for the first cycle, where an irreversible cathodic current peak appears at about 0.65 V. Strictly, there is another irreversible cathodic peak at a higher potential region for type (a) samples. On the basis of irreversible capacity proportional to the specific surface area of petroleum coke, Fong et al. [3] concluded that the

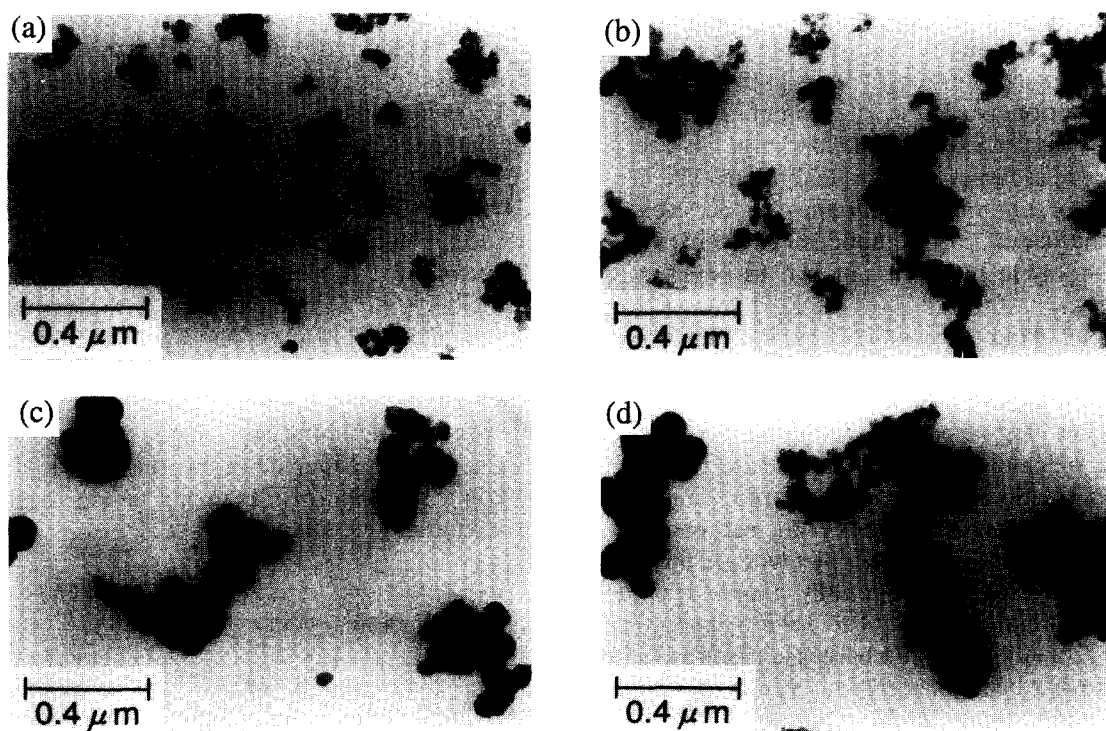


Fig. 1. Transmission electron microscope photographs of typical carbon black samples: (a) poorly aggregated fine particles; (b) highly aggregated fine particles; (c) poorly aggregated coarse particles, and (d) highly aggregated coarse particles.

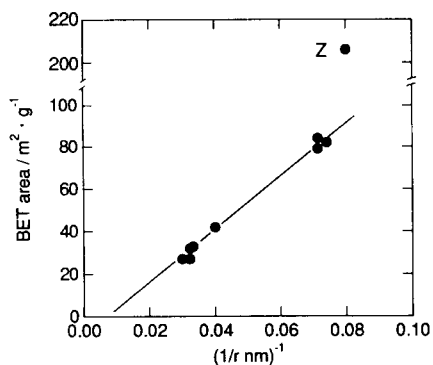


Fig. 2. BET surface area by nitrogen adsorption vs. inverse of representative radii of primary particles for all carbon black samples.

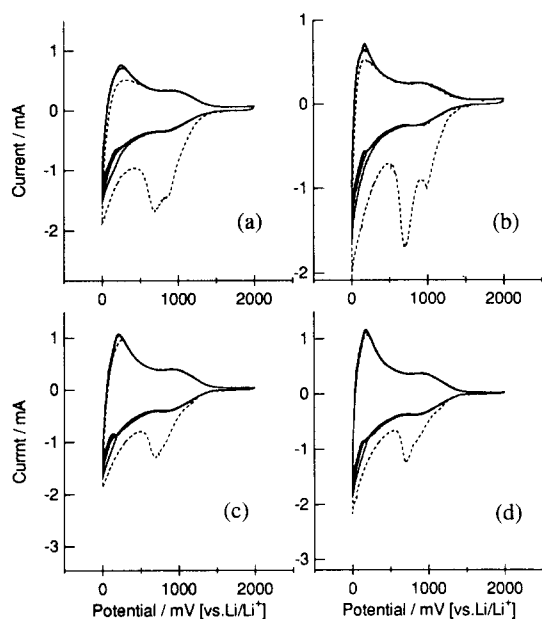


Fig. 3. Cyclic voltammograms of typical carbon black samples at 0.05 mV/sec: (·····) 1st cycle, and (—) 2nd–5th cycles. (a) poorly aggregated fine particles; (b) highly aggregated fine particles; (c) poorly aggregated coarse particles, and (d) highly aggregated coarse particles.

irreversible reaction is due to a surface film formation. In order to determine the irreversible capacity by galvanostatic experiments as they conducted, the reversible and irreversible processes should take place independently from each other at different potential regions, which is not the case for the present CB anodes.

Hence, the irreversible capacity in this work is estimated from the difference in the CV cathodic charge between the first and second cycles (Q'_{CV}), or from the difference between the first galvanostatic reduction charge and the succeeding galvanostatic oxidation charge (Q'_{GS}). The correlation between the obtained irreversible capacities and the BET surface area A is shown in Fig. 4. Although Q'_{GS} is considerably larger than Q'_{CV} , probably due to the incomplete extraction of inserted lithium under galvanostatic conditions, both

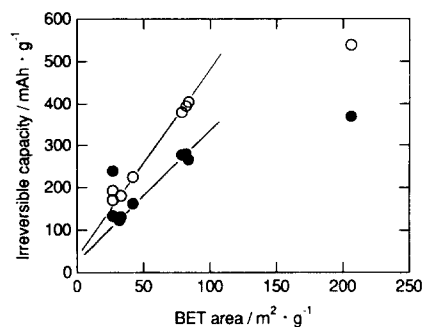


Fig. 4. Irreversible capacity at the initial reduction stage at about 0.65 V vs. BET area: (●) cyclic voltammetric data, and (○) galvanostatic data.

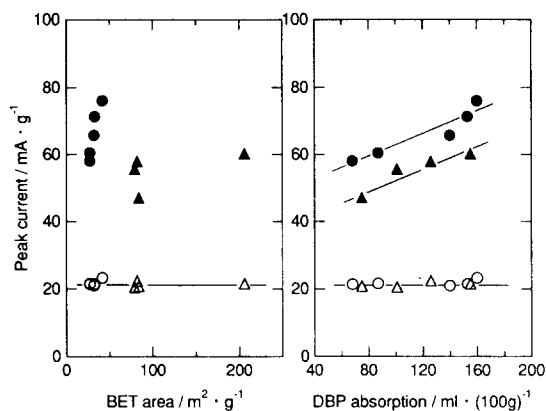


Fig. 5. Changes in anodic peak current at (●, ▲) 0.2 V and (○, △) 0.9 V with (a) BET surface area and (b) the amount of DBP absorption. (○, ●) fine primary particles, and (△, ▲) coarse primary particles.

of these irreversible capacities increase almost linearly with A , where the only sample (Z) again gives exceptional data. These results show that a CB having the smaller specific surface area is the more favourable anode material on the basis of initial irreversible capacity data.

3.3. Effects of agglomerate and the reversible capacity

The heights of the anodic current peaks at about 0.2 and 0.9 V during the third CV cycle are plotted against the BET surface area (Fig. 5(a)) and the amount of DBP absorption (Fig. 5(b)), which has been a standardized procedure in ASTM (American Society for Testing and Materials) [18] to evaluate the void space among closely packed CB particles, that is, the extent of agglomerate. The peak current at 0.9 V depends neither on the BET area nor on the DBP absorption and is constant for all kinds of CB tested. The peak current at 0.2 V, on the other hand, is larger for coarse CB particles than for fine CB particles and tends to increase with the extent of agglomerate as seen in Fig. 5(b), whereas it has no correlation with the BET area as in Fig. 5(a).

Since the peak current at about 0.2 V has been revealed previously [15] to correspond to the insertion/extraction of lithium into/from a CB matrix under diffusion control in the solid phase, fine CB particles having the larger contact area with the electrolyte and a shorter diffusion path is expected to give a larger capacity per unit weight of carbon. The obtained data in Fig. 5(a) suggest that we should take into account a certain factor other than the BET area, to which the irreversible capacity is almost proportional, in order to consider the reversible insertion/extraction processes of lithium.

The agglomerate of CB particles in a sample electrode may be different from that of the as-prepared oil furnace powder, because the CB agglomerates can be deformed under shearing or compressive stress [17]. The so-called 24M4DBP test, where the above DBP experiments are carried out after compressing at 24 000 psi (165.5 Mpa) four times, has been adopted to evaluate the mechanical destruction of the agglomerate from Δ DBP defined as the difference in the DBP absorption amounts between 24M4DBP and normal tests.

The correlation between the anodic peak current at 0.2 V and thus determined Δ DBP, which is the larger for the more highly aggregated sample and for the larger radius of primary particles, becomes now clear in Fig. 6. From these results, the insertion/extraction of lithium is considered to take place partially at the limited site of CB surface, where the aggregated structure has been destroyed mechanically in the preceding procedures. Two connecting primary CB particles by agglomerate are considered to have parallel graphitic planes to each other at the point of contact [19], though a primary particle itself has the concentrically spherical lamellar structure unfavourable for lithium diffusion [20,21]. But the main reversible reaction is considered to be controlled by the neck position connecting two primary CB particles where the amount of DBP is almost absorbed. Because even the poorly aggregated

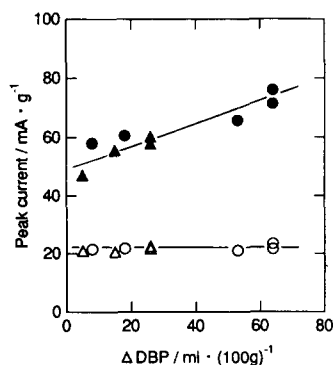


Fig. 6. Analogous plots to those in Fig. 5(b) after taking into account of the mechanical deformation of the carbon black agglomerate during the preparation of a sample sheet, see Section 3.3.

fine particles, whose Δ DBP is very small (5.3 ml/100 g), has decent amount of reversible capacity.

The anodic peak current at 0.9 V dependent neither on the amount of DBP absorption nor on Δ DBP, on the other hand, has already been shown to disappear when CB is highly crystallized and to be a charge-transfer controlled fast reaction [15]. Further details for this peak shall be discussed in the following paper.

To summarize the above results, coarse CB primary particles after aggregated extensively are suitable for the negative electrode material for a lithium secondary cell, where the neck position of connecting two primary CB particles in the agglomerate probably leads to be the electrochemically active CB surface for lithium insertion and hence to a large charge capacity. Furthermore, coarse CB primary particles give a small irreversible capacity for an undesired reaction per unit carbon weight owing to the small specific area.

4. Conclusions

The effects of macroscopic structure of CB materials on their anode characteristics in a lithium secondary cell have been revealed as follows:

(1) The irreversible capacity for the initial reduction at about 0.65 V is almost proportional to the BET specific area of CB samples.

(2) The reversible capacity as estimated from the anodic peak current at about 0.2 V on cyclic voltammograms, which corresponds to the insertion/extraction of lithium, is large for a CB consisting of coarse primary particles and having a well-aggregated structure. This reversible reaction is considered to proceed mainly at the neck position connecting two primary CB particles in the agglomerate. Another anodic peak current at a higher potential of 0.9 V, on the other hand, is independent of the BET area and of the amount of DBP absorption.

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