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Short communication

Particle-size effect of carbon powders on the discharge capacity of lithium ion batteries

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Abstract

To improve the performance of the negative electrodes for lithium-ion batteries, a study has been made of the particle-size effect of carbon powder on discharge capacity and the optimum mixing ratio between large (average diameter: 25.8 μm) and small (average diameter: 4.2 μm) powder particle size has been found. The largest capacity is obtained when the large particle size fraction is about 70 wt.%. The smaller the particle size ratio, the larger the capacity, where the particle size ratio is the ratio of the average diameter of the smaller component to that of the larger one. These results indicate that discharge capacity is closely related to carbon powder packing, which is controlled by the mixing weight and particle-size ratios.

Keywords: Lithium secondary battery; Anode; Carbon powder; Capacity; Particle size effect

1. Introduction

Lithium-ion batteries are in great demand as high-energy-density power sources. To ensure long cycle life and safety, different types of carbon have been studied for the battery anode. Carbon and graphite intercalate lithium ions into their layered planar lattice structure electrochemically. Graphite anodes do not exhibit capacities exceeding 372 mA h g^{-1}, because graphite cannot electrochemically form a lithium composition exceeding LiC_6. Much effort has been exerted in overcoming this limitation. Disordered carbons prepared by heat-treating mesocarbon microbeads [1], polymers (polyacene, poly(*p*-phenylene), and poly(furfuryl alcohol)) [2–5], and carbon prepared by templating [6] have been proposed as anodes for lithium-ion batteries.

In this work, a study is made of the particle size effect of carbon materials on battery discharge capacity. It is found that optimum mixing and particle-size ratios exist between larger and smaller particle sizes and contribute to maximum discharge capacity. A similar effect of hydrogen storage alloy powder on the discharge capacity of nickel hydrogen batteries has been reported [7].

2. Experimental

The carbon used in this study was prepared by heat-treating coke at 3000°C. This carbon powder was separated into three particle sizes (Figs. 1 and 2) which had an average diameter of 25.8, 12.1 and 4.2 μm (Table 1), i.e., large, intermediate, and small. Working electrodes were fabricated using two different particle size fractions, changing their mixing ratios, and mixing the carbons with 5 wt.% binder consisting of 66% acetylene black, 33% polytetrafluoroethylene, and 1%

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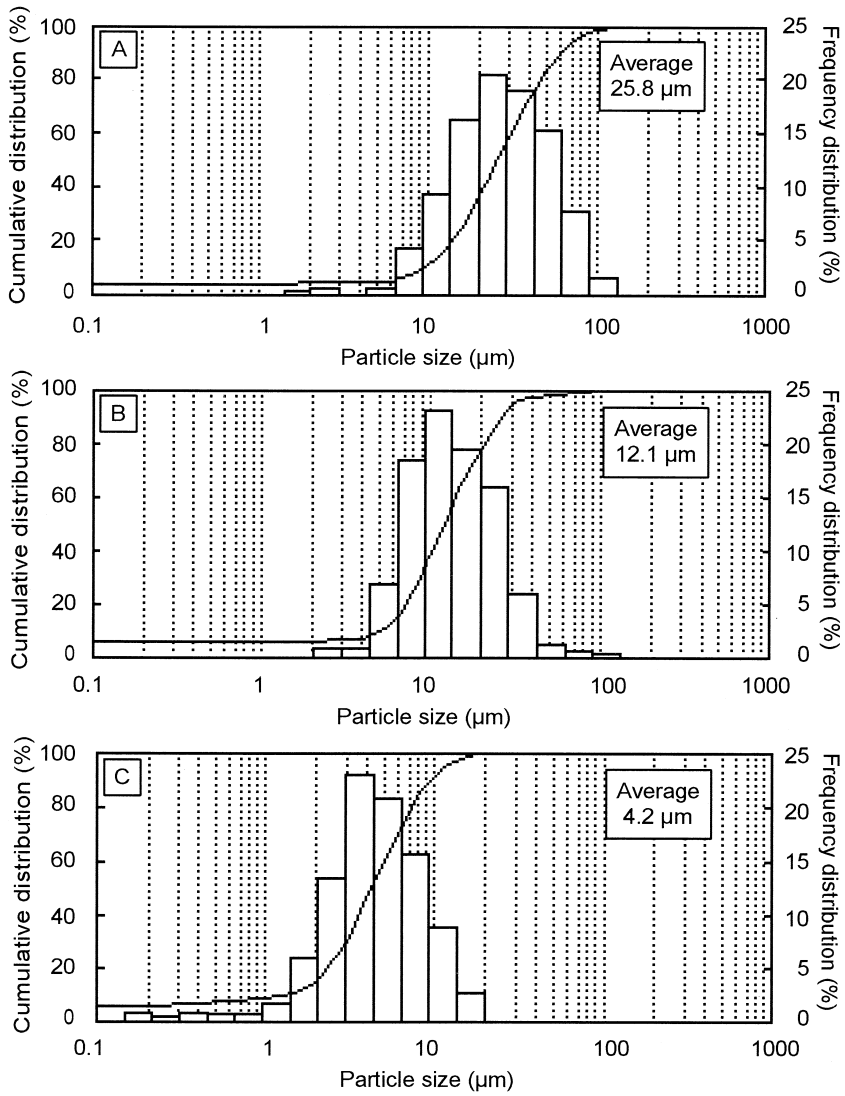

Fig. 1. Carbon powder particle size distribution. Average diameter: (A) 25.8 μm; (B) 12.1 μm; (C) 4.2 μm.

surface-active substance. A mixture of about 0.03 g was pressed onto a nickel mesh collector at a pressure of 3.76 ton cm^{-2} to make a 1.33 cm^2 tablet, and discharge capacities were tested. Charge–discharge cycling tests of samples were conducted using a three-electrode cell in a 1-M $LiClO_4$ ethylene carbonate/diethyl carbonate (EC/DEC) mixed solvent (1:1 by volume) (Mitsubishi Chemical) at 30°C. The reference and counter electrodes were lithium foil. Charge–discharge curves were obtained at a current density of 0.1 mA cm^{-2} between 0 and 1.5 V vs. Li/Li^+ using a charge–discharge unit (Hokuto Denko, 6 ch, 10 V1A) and a Y–T recorder (Yokogawa Electric, μ R180. Model 4176) or a charge–discharge unit (Toyo System, TYS-30TUOO) with a personal computer and charge–discharge control software. The electrical resistance of the disc electrode was measured in an ambient atmosphere at room temperature (22–23°C) by means of a four-point probe technique with a Yokogawa 4328A Hewlett Packard Milliohmmeter.

3. Results and discussion

Charge–discharge cycle life was evaluated by combining two different sizes of carbon powder and changing their mixing ratios. The maximum capacity was obtained when the large-size powder was about 70 wt.%, i.e., the weight ratio of the large to small powder was 7:3 (Fig. 3). The observation that the capacities for three different cycle numbers (third, fifth, 10th) are nearly equal illustrates that cyclability is good over this extent of cycling. The irreversible capacity loss on the first cycle was 263.5 mA h g^{-1} and the charge–discharge current efficiency was 49.8% for the carbon electrode made from the large particle fraction of 70 wt.% powder. The capacity loss greatly decreased as the charge–discharge cycling test

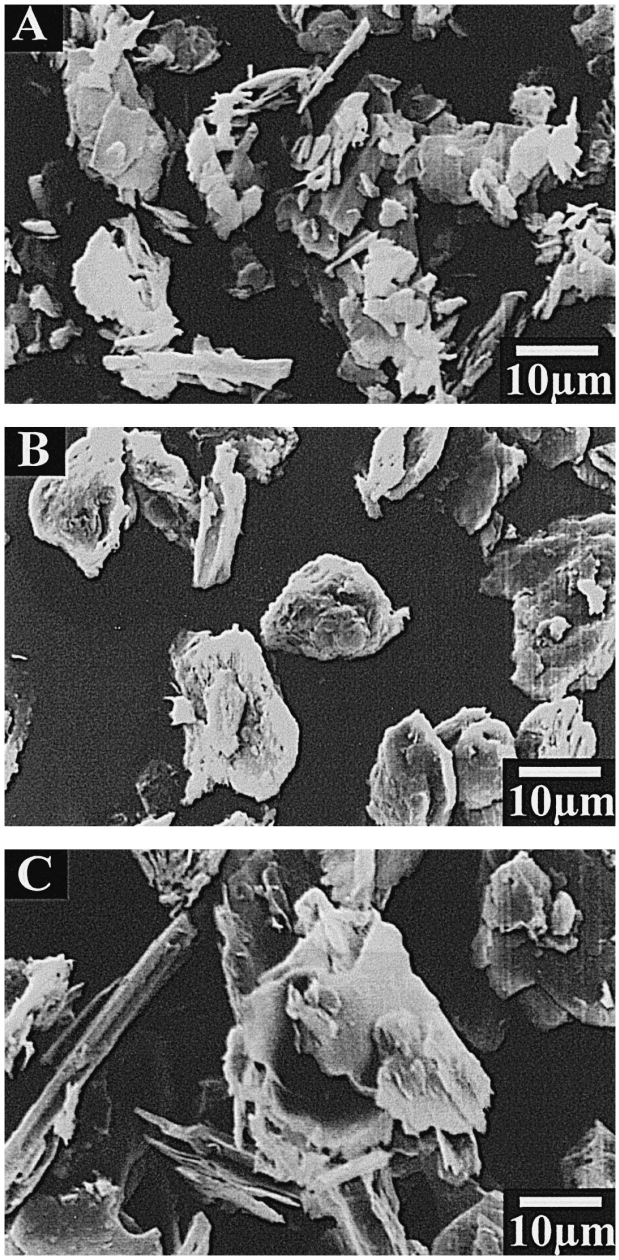

Fig. 2. Electron micrographs of carbon separated into three particle sizes. Average diameter: (A) 25.8 μm; (B) 12.1 μm; (C) 4.2 μm.

progressed, and charge–discharge current efficiency was kept at about 96–97% from the fourth cycle onwards, regardless of the large particle fraction. In different combinations, i.e., intermediate and small or large powders, the maximum capacity was obtained at about 70 wt.% of the larger powders, although the variation in capacity was not very great (Figs. 4 and 5). By plotting the maximum capacity obtained from Figs. 3–5 vs. the particle size ratio, we found that the smaller the particle

Table 1
Characteristics of carbon separated into three particle size fractions

	Small-size particle	Middle-size particle	Large-size particle
Average particle size [μm]	4.20	12.11	25.81
X-ray diffraction			
$d_{(002)}$ [Å]	3.368	3.367	3.365
$Lc_{(002)}$ [Å]	368	368	371
BET surface area ($m^2\ g^{-1}$)	5.7	3.1	2.3

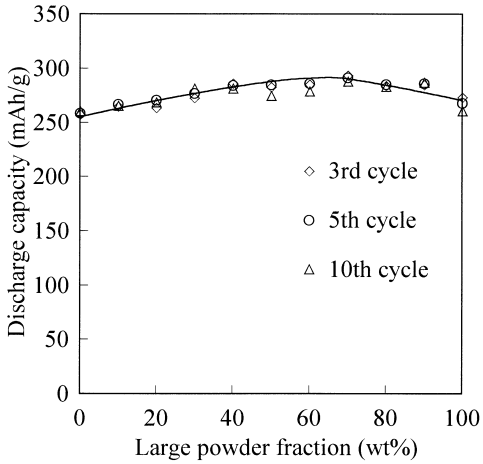

Fig. 3. Discharge capacity at 0.1 mA cm^{-2} in 1 M $LiClO_4$ /EC + DEC vs. fraction of large powder using powders with diameters of 25.8 and 4.2 μm.

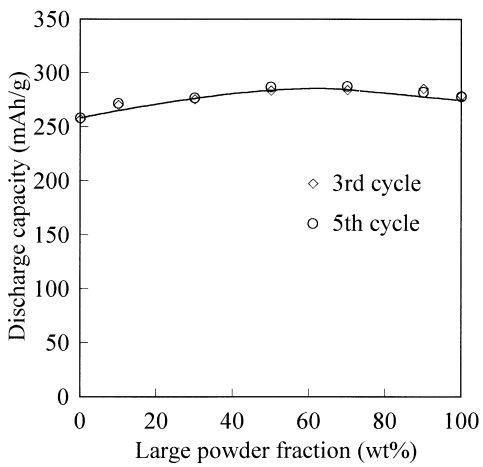

Fig. 4. Discharge capacity at 0.1 mA cm^{-2} in 1 M $LiClO_4$ /EC + DEC vs. fraction of large powder using powders with diameters of 12.1 and 4.2 μm.

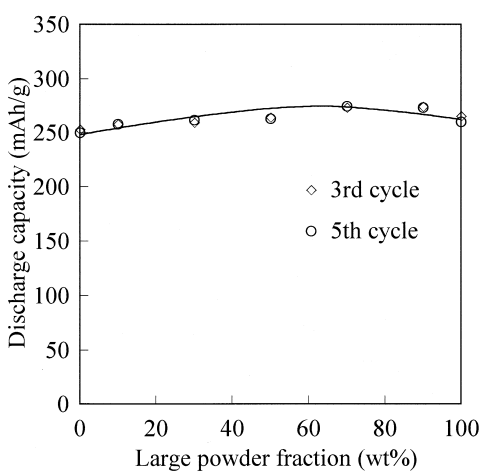

Fig. 5. Discharge capacity at 0.1 mA cm^{-2} in 1 M $LiClO_4$ /EC + DEC vs. fraction of large powder using powders with diameters of 25.8 and 12.1 μm.

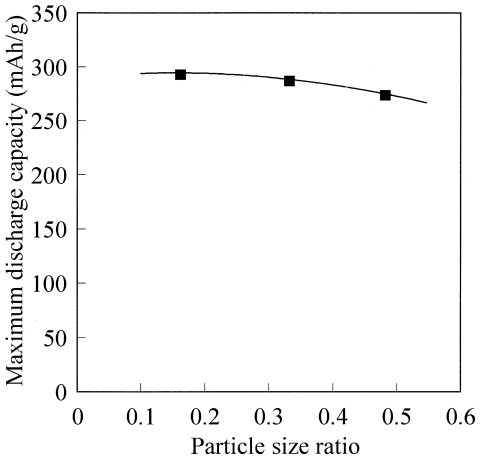

Fig. 6. Maximum discharge capacity vs. particle size ratio.

size ratio, the larger the capacity (Fig. 6). In Fig. 6, the particle size ratio is defined as the ratio of the average diameter of the smaller component to that of the larger one.

The fact that the maximum capacity was obtained at about 70 wt.% of the larger powders and the larger capacity was obtained at a smaller particle size ratio seem reasonable in light of the results of Furnas [8]. He studied packing in beds of iron ore, coke, lead shot, and limestone to determine the laws of gas flow in a blast furnace and generalized the results to show how porosity varied in a bed made up of varying proportions of two components with different particle sizes. Thus, better packing can be achieved when the sizes differ widely than when the sizes are nearly the same, i.e., the smaller the particle size ratio, the higher the packing, when two different sizes of particles are mixed. Furnas also pointed out that the two components each have an individual porosity of 40%; in practice, close-graded particles pack with a porosity of 40–50% regardless of the particle size [8,9]. The highest packing occurs at $\geq$ 65% of the large fraction at any given particle size ratio and moves to slightly higher percentages of large particles as the particle size ratio decreases [8,9]. If the particle size ratio is 0.2, the minimum porosity, i.e., the largest packing, is obtained at about 70 vol.% of the large particle size fraction [9], which coincides with the condition for largest discharge capacity found in our work (Fig. 3). Our data is, however, based on weight percent (Figs. 3–5), because it is difficult to prepare the disc electrode by fixing the volume percent. Thus, our results cannot be compared directly with those in the literature [8,9]. However, if the density of the mixed carbon powder does not vary markedly with the mixing-weight ratio, it may be possible to explain our results in terms of Furnas' findings and to conclude that changes in discharge capacity (Figs. 3–5) are closely associated with the packing of carbon powder, which is controlled by the particle size ratio and the mixing-weight ratio of large-to-small particle size components. To quantitatively verify packing conditions, the density of an anode tablet was measured after changing the mixing ratio (Fig. 7). The fact that the highest density is obtained at about 70 wt.% of the large powder fraction indicates that the highest packing occurs at this mixing ratio.

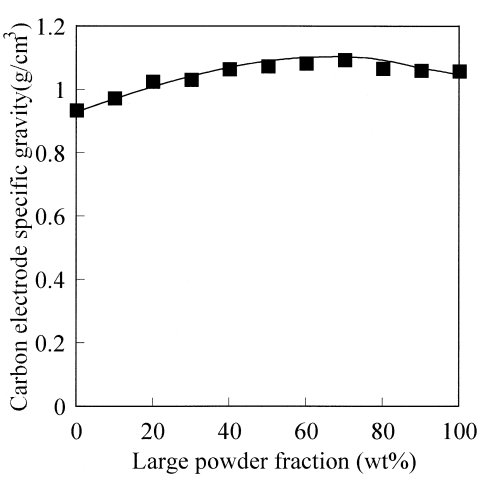

Fig. 7. Density of carbon disc electrode obtained at 3.76 ton cm^{-2} vs. fraction of large powder using powders with diameters of 25.8 and 4.2 μm.

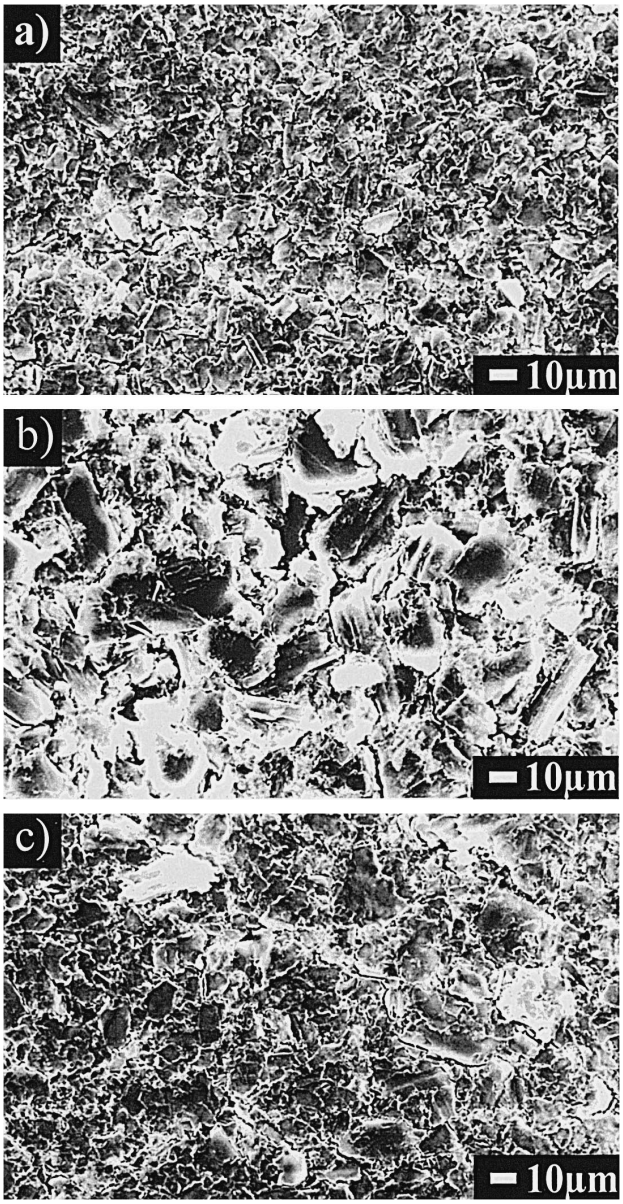

Fig. 8. Electron micrographs of disc electrode surface: (a) 4.2 μm diameter powder, (b) 25.8 μm diameter powder, (c) 70 wt.% large powder and 30 wt.% small powder.

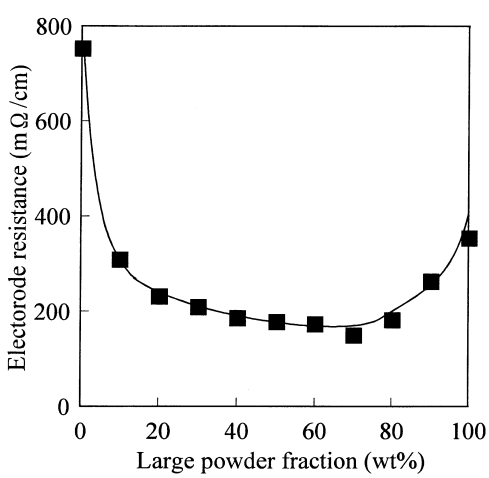

Fig. 9. Change in electrical resistance of an electrode made from different mixing weight ratios using powders with diameters of 25.8 and 4.2 μm.

The electron micrographs shown in Fig. 8 appear to support the above result. The sample which consists of 70 wt.% large carbon powders and 30 wt.% small carbon powders appears to be in the most-condensed state (Fig. 8c). Thus, the discharge capacity is found to depend on the carbon powder packing, and the densest packing of the carbon powder disc electrode yields the largest discharge capacity. This is believed to increase the contact area between the carbon particles which improves the electrical network system, and enhances the use of the carbon powder. This was confirmed by measuring the electrical resistance of the electrode made from carbon powders of different mixing weight ratios, as seen in Fig. 9. Clearly, the electrode resistance is the smallest for the large particle fraction of 70 wt.%. Although our results were obtained with a carbon disc electrode, it should also hold true for a coated carbon electrode using a binder such as polyvinylidene fluoride. Also, the present results may be applicable to cathodes which use powdered materials such as MnO_2 and $LiCoO_2$.

4. Conclusions

Using coke carbon, the particle-size effect of carbon powder on the discharge capacity of a lithium secondary battery has been studied. As the particle size ratio is decreased, the discharge capacity is increased, and a large-particle fraction of 70 wt.% yielded the highest discharge capacity.

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