

Charge–discharge properties of a cathode prepared with ketjen black as the electro-conductive additive in lithium ion batteries

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Abstract

In order to investigate the influence of the dispersion state of electro-conductive additives on the properties of lithium ion batteries, we examined the charge–discharge properties of cathodes prepared with suspensions of ketjen black (KB) dispersed in an organic solvent with different particle sizes. Discharge capacity, durability and resistance to high-current discharge of the cathode prepared from a well-dispersed suspension was higher than those of the cathode prepared with ketjen black powder. Because ketjen black particles in the cathode prepared from a well-dispersed suspension formed a conductive dense-network uniformly, despite the low amount of additive, we concluded that an electro-conductive network made of ketjen black, which can transmit electrons smoothly from active materials to the collector, formed in the cathode when the cathode was prepared from a well-dispersed suspension.

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1. Introduction

Electro-conductive additives are generally employed in the preparation of the cathode of lithium ion batteries to compensate for the low conductivity of active materials such as LiCoO_2 , LiMn_2O_4 and LiNiO_2 and to allow these active materials to perform effectively [1–3]. Electro-conductive additives contribute to an increase in the capacity, the charge–discharge speed and the cycle life of lithium ion batteries. Conductive carbon particulates, such as acetylene black (AcB), ketjen black (KB) and graphite, are usually employed for this purpose [3–5]. The typical physical properties of these conductive particulates are shown in Table 1.

Carbon black is made up of particles fused together to form nodular aggregates. In most cases, their aggregates do not break up during dispersion and processing. Rather, the dispersion process consists of breaking up large agglomerates (consisting of a great number of these nodular aggregates compacted together). The dispersion process is considered complete when most of the larger agglomerates have been separated and wetted by the medium. Suspensions

of these particulates indicate conductivity attributed to the percolation mechanism [6] where the conductive network consists of particles that have graphite structures on the surfaces.

If these particulates are mixed with the active materials in an adequate medium, usually an organic solvent, the particulates form a conductive network residing in the void among active materials and interconnect through the particle-to-particle points of contact. The interconnection must fully spread from the surface of the active material to that of a current collector. Therefore, the conductive additives must be fine enough to fit in the void among active material beds.

However, it is very difficult to make these carbon particulates disperse homogeneously into other substances because they easily flocculate due to their large surface area and high oil adsorption, especially when the particulates must be dispersed in highly dense suspensions of active materials. If the conductive particulates are heterogeneously dispersed in the cathode, not only the performance of the battery might deteriorate, but also affect production speed, yield and battery safety [7,8].

In this study, we attempted to control the dispersion state of conductive additives by adding a pre-dispersed suspension of conductive particulates during the preparation of the cathode. Compared to the cathode prepared by adding the

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Table 1
Typical analytical properties of conductive carbon particles

Properties	KB	AcB	Graphite
DBP oil absorption (cm ³ /100 g)	360	212	–
Average size of primary particles (nm)	311	410	1754
Specific surface area (m ² /g)	800	76	31
Volatile matter content (%)	0.5	0.4	0.6
pH	9.0	7.7	7.5
Ash content (%)	0.1	0.05	7.3

powder of conductive particulates, it can be suggested that a pre-dispersed suspension consisting of smaller agglomerates enables the conductive network to be developed uniformly in the void among active materials. Thus, we prepared various cathodes by mixing the active materials with the powder of KB, AcB, graphite and a suspension of KB dispersed into *n*-methyl-2-pyrrolidone (NMP) with/without a dispersing agent. Using these cathodes, we investigated the effects of different conductive additives, amount of the additive and dispersion state of the additive on the charge–discharge properties.

2. Experimental

The active materials employed during the preparation of the electrodes were LiCoO₂ (Cellseed C-5, particle size: 5 μm) for the cathodes and Li-foil for the anodes. As electro-conductive additives, powders of ketjen black (EC-300J), acetylene black (Denka Black) and graphite (KS-6) were used. Poly(vinylidene fluoride) (PVDF, KF polymer 1100) was used as the binder. The current collector was Al-foil for the cathodes and Ni-foil for the anodes. A glass fiber filter was used as a separator.

Pre-dispersed suspensions of KB were prepared by slowly adding the required amount of dry powder of KB to NMP with/without a dispersing agent that was a derivative of vinyl pyrrolidone. Then, they were pulverized by a three-rolled mill. We obtained two types of KB suspensions, D0 and D1, with and without the dispersing agent, respectively. The average particle size of these suspensions (*d*₅₀) was 0.3 μm for D0 suspension and 3.0 μm for the D1 suspension.

Active materials and conductive additives, the powders of carbon particulates or the KB suspensions, were dispersed in NMP solution of PVDF. Then, the slurry of the electrode was coated onto Al-foil and subsequently dried at 120 °C. Dried electrodes were compacted by constant pressure. Typical mass loading of the electrodes corresponded to an electrode capacity of ca. 3.0 mAh/cm². The electrodes were tested using a lithium metal anode in a half cell configuration type cell. Electrolyte was 1 M LiClO₄ in PC solution throughout the experiments. Charge–discharge properties were measured employing a battery tester (SM-8, Hokuto Denko Co.) at a constant current rate of 0.1C to 4.3 V for the charge process and 0.5C to 3.1 V for the discharge process.

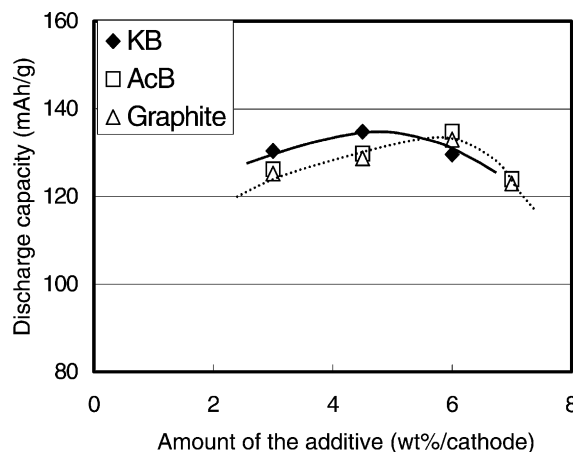


Fig. 1. Effects of the amount of the electro-conductive additive on discharge capacity at the second cycle. The cathodes were prepared by adding the additives as powder.

3. Results and discussion

3.1. Effect of the conductive additive on charge and discharge

Fig. 1 shows the discharge capacity of cathodes prepared using different conductive additives as a function of the amount of the additive. The discharge capacity of each cathode increased to a maximum as the amount of additive was increased and decreased with further increases in additive content. These critical amounts of the additive that indicate maximum capacity were similar to the optimal amount of additives reported earlier [2,9]. The increase observed when the low amount of conductive additives were added could be attributed to enhanced transmission of electrons from the LiCoO₂ surface to the collector. However, beyond a critical amount of the additive, we could not prepare a homogeneous electrode because the viscosity of the electrode slurry became extremely high. Thus, it can be suggested that heterogeneity of the electrode causes a decrease of the discharge capacity.

Among these conductive additives, the cathode prepared with KB had a higher capacity at lower amounts of the additive. It is known that KB suspension indicates higher conductivity than that of AcB or graphite at the same loading, although the volume resistivity in pressed powder is nearly equal. This behavior can be explained because there is a large number of primary particles per unit volume for the KB suspension because the pore volume of KB is larger than that of other particulates.

The cycle characteristics of the cathodes prepared with the previously mentioned conductive additives are shown in Fig. 2. The cathodes were prepared using the optimal amount of each additive (AcB and graphite: 6.0 wt.%, KB: 4.5 wt.%). The cycle behavior was almost the same although the amount of the additive differed. This means that for the cathode prepared with KB, the conductive network

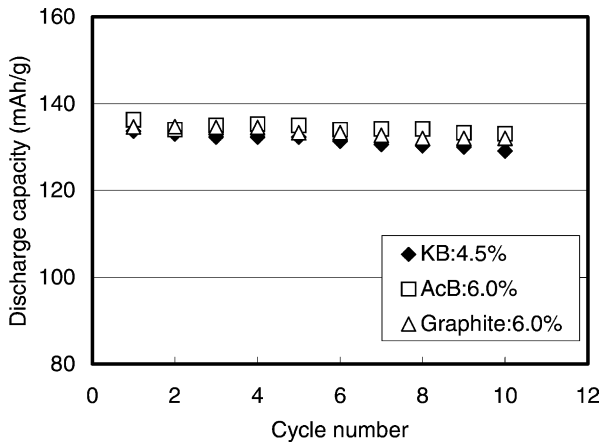


Fig. 2. Comparison of cathode cycle behavior. The additive was the optimal amount as indicated.

was well-developed even though the amount of the additive was smaller. Therefore, the efficiency of the cathode in the lithium ion battery is subject to the degree of conductive network consisting of the carbon particulates.

3.2. Effect of dispersed state of KB on charge–discharge property

To disperse aggregated KB into a viscous medium is difficult, as mentioned earlier. It can be considered that the cathode prepared by adding KB powder is not dispersed enough for full electrode utilization. Thus, we attempted to control the dispersion state of KB in a cathode by suspending KB in NMP.

The particle size distributions of D0 and D1 suspensions are shown in Fig. 3. In this figure, the size distribution of the suspension prepared without pulverization is also shown as a reference. It can be seen that the particle size of KB was reduced by the pulverization treatment and the addition of

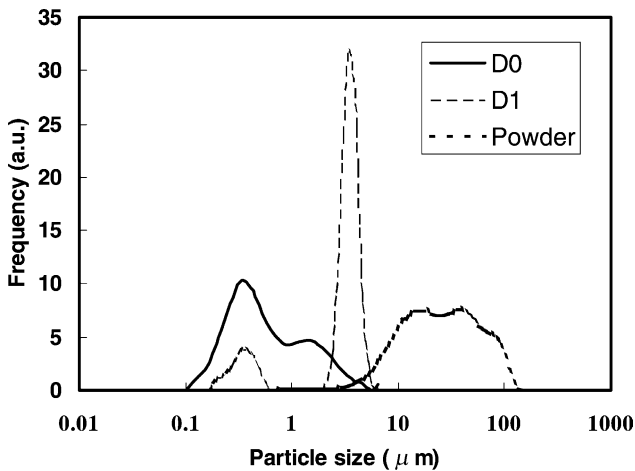


Fig. 3. Particle size distributions of D0 and D1 suspensions and the suspension without pulverization.

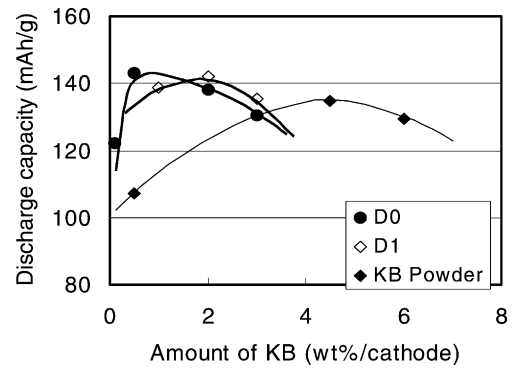


Fig. 4. Effects of the amount of the electro-conductive additive with pre-dispersed suspension on discharge capacity at the second cycle.

the dispersing agent. Thus, we could obtain a well-dispersed suspension made of sub-micron particles of KB.

Fig. 4 shows the discharge capacity of the cathodes prepared with these KB suspensions as a function of the amount of the additive in dry base. The effect of the additive content in the cathodes prepared with pre-dispersed KB suspensions on the discharge capacity was similar to that observed in the cathode prepared with KB powder. That is, the amount of the additive was critical to achieve maximum capacity. However, the optimum amount of additive for the cathode prepared with the D0 suspension was reduced drastically. In the optimum content, the cathode prepared with the D0 suspension exhibited about a 10% increase in discharge capacity, while the amount of the additive was less than 1/10 compared to the cathode with KB powder.

The cycle behavior for the cathodes prepared with pre-dispersed suspensions was also examined. Fig. 5 shows the results for the cathodes prepared with the optimal amount of the additive (D0 suspension: 0.5 wt.%, D1 suspension: 2.0 wt.%). The durability performance was kept constant, while the additive content was extremely low.

To verify that this enhancement was attributed to the dispersed structure of KB particles in the cathode, we examined the dispersion state of KB in the cathode directly under a scanning electron microscope (Fig. 6). In contrast to

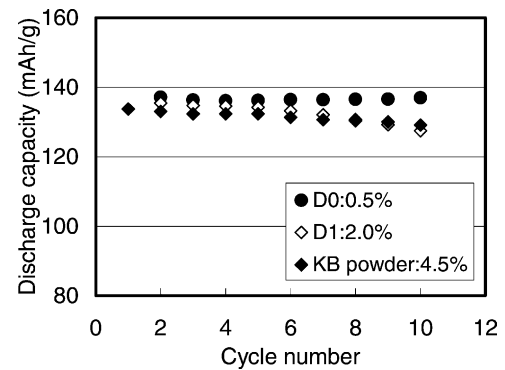


Fig. 5. Cycle behavior of the cathodes with pre-dispersed suspension. The optimal amount of each additive was indicated.

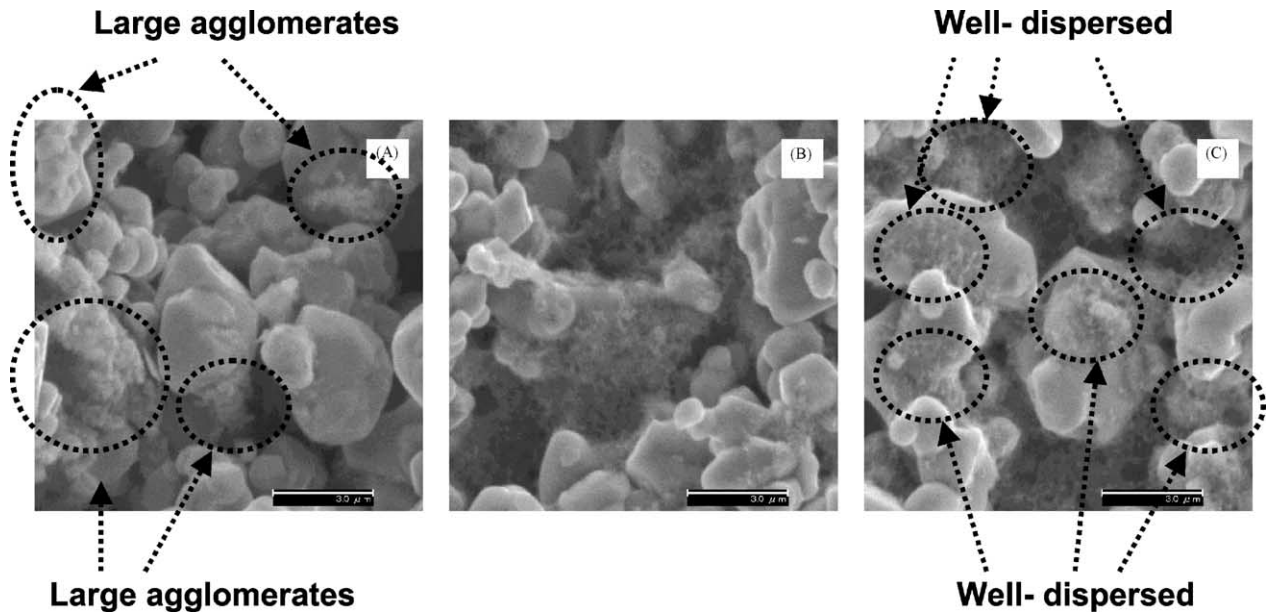


Fig. 6. Scanning electron micrographs of cathodes containing KB: (A) cathode with KB added as powder; (B) cathode containing D1 suspension; (C) cathode containing D0 suspension. The cobweb-like structures of KB can be observed in the cathodes of (B) and (C).

the cathode prepared with KB powder where there seemed to exist large agglomerates of KB particles, the KB particles in the cathodes prepared with the D0 suspension formed cobweb-like structures in the void among the active materials. We found that the dispersibility of KB particles increased in the cathode prepared with the pre-dispersed suspension. Consequently, it can be considered that the improvement of the properties of the cathodes prepared with lower amounts of additives was due to the conductive dense-network developed uniformly in the cathode, which can transmit electrons smoothly from the LiCoO_2 surface to the collector.

Fig. 7 shows the influence of the current rate in the discharge process on the discharge profile of the cathodes prepared with pre-dispersed suspensions. The discharge profiles of these cathodes were almost the same at the current

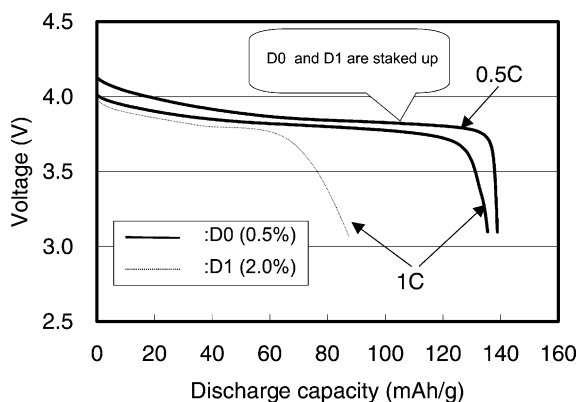


Fig. 7. Change in discharge curves of the cathodes to which D0 or D1 paste was added for different current rates.

rate of $0.5C$. However, at a higher current rate, the difference in discharge capacity became remarkable. The discharge speed of the cathode prepared with the D0 suspension, which is well-dispersed, is about 1.5 times as compared to the D1 suspension, despite the use of $1/4$ the amount of additive compared to D1 when the discharge rate is high ($1C$). This fact suggests a reduction of internal resistance in the cathode. It can be concluded that the reduction of internal resistance in the cathode occurs because of the conductive dense-network consisting of well-dispersed particles in the cathode.

4. Conclusions

Electro-conductive additives in the cathode contribute to increase the performance of lithium ion batteries. In order to investigate the influence of the dispersion state of electro-conductive additives on the properties of lithium ion batteries, we studied the charge–discharge properties of cathodes prepared with various carbon particulates in various dispersion states. By adding a pre-dispersed suspension during the preparation of the cathode slurry, a conductive dense-network consisting of well-dispersed particles in the void between the active material particles formed in the cathode. The amount of the additive required was extremely low. This cathode showed high capacity, good durability and resistance to high-current discharge.

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