Effect of carbon additive on electrochemical performance of LiCoO$_2$ composite cathodes

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Abstract

LiCoO$_2$ composite electrodes are prepared with variation in the conducting agent and their cathodic performance is analyzed. Two carbon blacks (Super P and acetylene black) and one graphite (Lonza KS6) that differ in particle size and shape are employed as the conducting agents. The carbon blacks comprise nano-sized primary particles that are fused to give an aggregate. Lonza KS6 carries a flake-like shape with an average particle size of 6 μm, which is comparable with that of LiCoO$_2$ particles. The LiCoO$_2$ composite cathode containing Lonza KS6 exhibits better cycle performance than that of the cathode loaded with carbon black, presumably due to a more uniform dispersion of both the conducting agent and the LiCoO$_2$ active material. Better mixing in the slurry preparation step that is due to a similarity in the grain size of Lonza KS6 and LiCoO$_2$ may explain this feature. In composite cathodes containing the smaller-sized carbon blacks, however, the carbon particles agglomerate by themselves to become segregated from the LiCoO$_2$-rich region. The cathode capacity and cycle-life of a Lonza KS6 loaded electrode is improved further by adding smaller-sized carbon blacks as the conducting agents. It is expected that the smaller particles of carbon black fill the void spaces made by the larger-sized Lonza KS6 and LiCoO$_2$ grains. As a result, both the electrode conductivity and active surface-area of the LiCoO$_2$|carbon interface are enlarged. This leads to a decrease in the electrode polarization and a better utilization of the active material.
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1. Introduction

At present, transition metal oxides such as LiCoO$_2$ are utilized as the positive electrode (cathode) active material in lithium secondary batteries. Practically, cathode plates are fabricated by coating an electrode layer on a piece of metal foil or mesh that is used as the current-collector. The electrode layer is normally composed of an active material, a conducting agent, and a polymeric binder. Here, it is generally accepted that the role of the conducting agent is to enhance the electrode conductivity by filling the free spaces made by the grains of active material to form a continuous network until eventually the electrical conductivity approaches that of the conducting agent [1,2]. The other important role of the conducting agent is to absorb and retain electrolyte solution, which allows an intimate contact between Li$^+$ ions and the active material which, thereby, leads to better utilization of active material. Accordingly, a homogeneous dispersion of both conducting agent and active material throughout the interior of electrode layer

is a very important feature, among others, in practical lithium cells because the cell polarization and utilization of active material is determined by this feature [3–5].

The dispersion of electrode ingredients is controlled by several parameters such as particle size and shape, density, volume fraction of individual components, and inter-particle interaction forces. These parameters affect the mixing efficiency in the slurry preparation step and, consequently, the dispersion of electrode components in the composite electrode layer. On this basis, electrode ingredients such as active material, conducting agent and polymeric binder, as well as the mixing and coating method, should be deliberately selected to achieve a homogeneous dispersion [6].

The high electrical conductivity and chemical inertness of carbon blacks and graphite have led to their widespread use as conducting agents [1,2,7–10]. These carbonaceous materials differ in crystallinity, texture, morphology, particle size and purity, depending on their sources and manufacturing processes [11,12]. For example, many carbon blacks are composed of spherical primary particles that are fused into aggregates of various size and shape, whereas graphites have a plate or flake shape with a wide range of particle sizes. It is

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thus conceivable that electrode performance is strongly affected by the nature of carbon additives because the degree of dispersion is controlled by the physico-chemical properties of the carbons. Nevertheless, the role of the conducting agent in influencing electrode performance has not been fully assessed. Only a few reports have dealt with this issue in the area of secondary lithium batteries. For instance, Tarascon et al. [13] disclosed that the irreversible capacity strongly depends on the content of carbon black in the $LiMn_2O_4$ composite cathode. Jang and Oh [14] claimed that the use of carbon blacks of high surface-area increases the dissolution of manganese from $LiMn_2O_4$ composite cathodes. Finally, there are some studies which show that carbon black addition similarly affects the anodic performance of carbon composite electrodes [3,15].

The prime concern of the work reported here is to examine the dispersion of electrode ingredients as a function of carbon additives. To this end, three different carbon additives that differ in size and shape have been selected and loaded in $LiCoO_2$ cathodes, either separately or as binary mixtures. The electrode conductivity, utilization of $LiCoO_2$ active material and cycle-life have been correlated with the extent of dispersion. Finally, the usefulness of binary carbon additives is discussed based on the dispersion of the electrode ingredients.

2. Experimental

2.1. Materials

As the conducting agent, a single or binary mixture (1:1 weight ratio) of Lonza KS6 (Lonza), Super P (MMM Co.) and acetylene black (Chevron Phillips Chem. Co.) was employed. $LiCoO_2$ (Nippon Chem. Co.) and poly(vinylidene fluoride) (PVdF) ($M_w = 187,000$, Solvay) was used as the cathode material and polymeric binder, respectively. For the preparation of composite cathodes, $LiCoO_2$ and conducting agent (8:1 weight ratio if not specified) were mixed in a pestle and dried at 120 °C overnight. Then, the binder solution of poly(vinylidene fluoride)/N-methyl pyrrolidone (NMP) was added to the mixture and homogenized to obtain a slurry mixture. The resulting slurry was spread on to an aluminum foil (20 μm in thickness) with a coater and then dried to evaporate NMP at 120 °C. The composite electrodes were roll-pressed in order to enhance the inter-particle contact and to ensure a better adhesion to the current-collector. The electrode thickness was controlled to be about 70 μm and the binder content was fixed at 10 wt.%.

2.2. Instrumentation

A transmission electron microscope (TEM) and a scanning electron microscope (SEM) were used to examine the powder morphology of carbon additives and to analyze the extent of dispersion in the composite cathodes. The electrical conductivity of composite cathodes was measured by means of the van der Pauw method [16]. Only the half-cell characteristics were analyzed in a beaker-type, three-electrode cell in which lithium foil (Cyprus Co.) was used as the counter and the reference electrodes. The electrolyte was 1.0 M $LiBF_4$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 volume ratio) (Tomiyama Co.). Galvanostatic charge–discharge cycling was conducted with a WBC-3000 battery cycler (Xeno Co.). All electrochemical measurements were carried out in a glove-box filled with argon.

3. Results and discussion

3.1. Cathodic performance according to carbon additives

TEM or SEM images of carbon additives that were used for the conducting agent are shown in Fig. 1. In order to compare the size of the conducting agent and the cathode active material, an SEM image of $LiCoO_2$ is presented in Fig. 1(d). Both Super P and acetylene black are composed of nano-sized primary particles that are fused to form an aggregate. The size of the primary particles is larger, however, in acetylene black. Lonza KS6, an artificial graphite, has a flake-like shape with an average particle size of 6 μm, which is comparable with that of $LiCoO_2$ particles.

The discharge capacity profiles of $LiCoO_2$ cathodes are shown in Fig. 2 as a function of cycle number, where a different conducting agent is loaded in each composite cathode. Based on the cycleability shown in Fig. 2, the composite cathodes can be broadly classified into two groups. The first group, in which Lonza KS6 is loaded by itself or as a binary mixture with the smaller-sized Super P, shows better cycleability than the second group, in which the smaller-sized carbons (Super P or acetylene black) are loaded by themselves or as binary mixtures. A composite cathode containing a mixture of Lonza KS6 and acetylene black also exhibited similar cycleability to that of the first group, and is thus omitted in the interests of clarity. A rather significant decay in capacity was also observed with the composite cathode containing acetylene black alone. The results shown in Fig. 2 illustrate that only those cathodes containing the larger-sized Lonza KS6 exhibit an acceptable cycleability. Moreover, the addition of smaller-sized carbon blacks to the larger-sized Lonza KS6 as a binary mixture further enhances the discharge capacity and cycleability of $LiCoO_2$ cathodes.

In order to identify the favorable role of binary carbon mixtures, the electrode conductivity and first discharge capacity were compared between the composite cathodes. As seen in Fig. 3, composite cathodes containing the binary carbon mixture, in which the Lonza KS6 content amounts to 30–70 wt.%, outperform those loaded with a single carbon in respect of electrode conductivity and first discharge capacity. Also apparent in Fig. 3 is that there is a close relation between the electrode conductivity and initial discharge capacity of
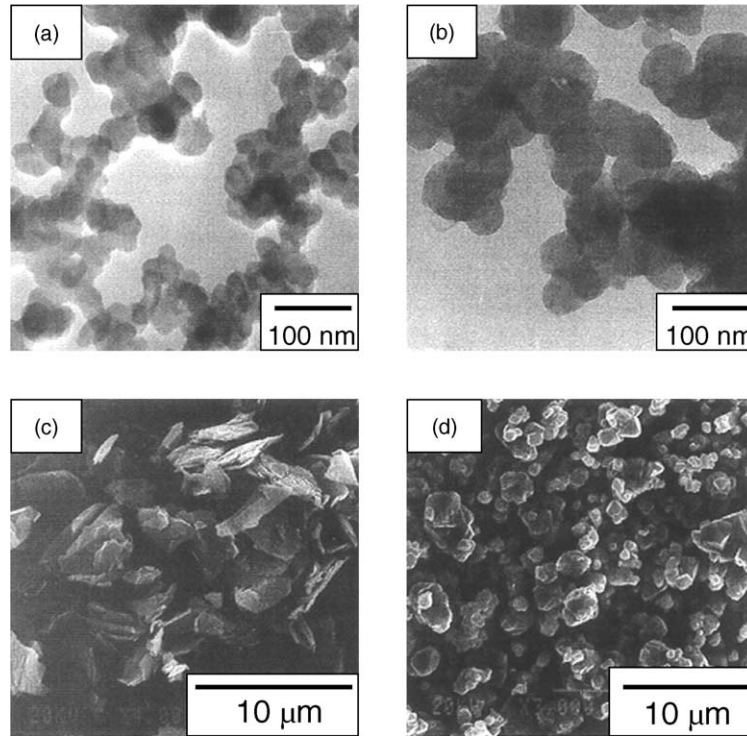
Fig. 1. TEM images of carbon blacks and SEM images of Lonza KS6 and LiCoO$_2$ active material: (a) Super P; (b) acetylene black; (c) Lonza KS6; and (d) LiCoO$_2$. Note that, carbon blacks are nano-sized, while Lonza KS6 is micron-sized like LiCoO$_2$ active material.
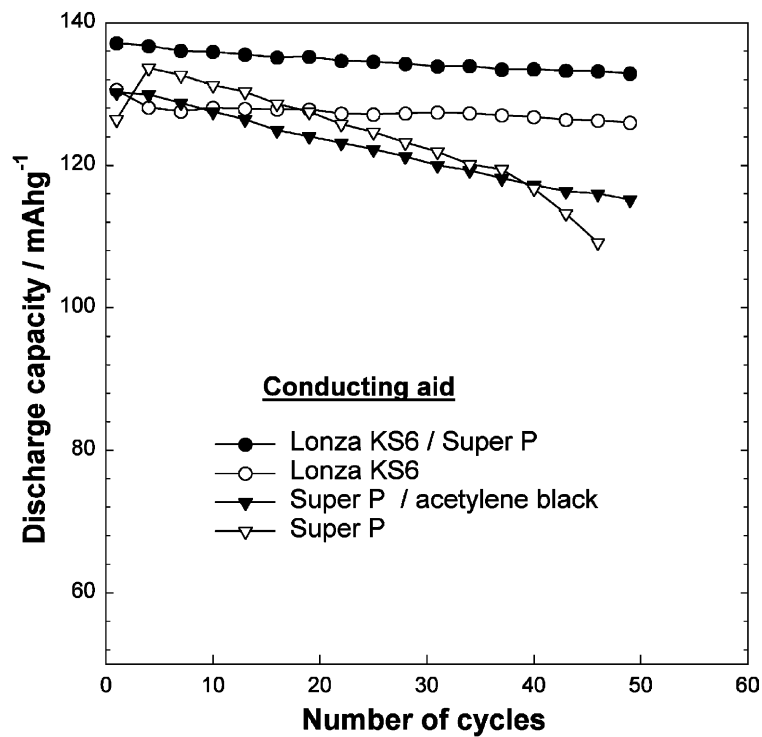

Fig. 2. Discharge capacity profiles of composite cathodes. Conducting agent is indicated in the inset. Composite cathodes are composed of LiCoO$_2$, conducting agent, and PVdF binder (8:1:1 weight ratio). The electrolyte is 1.0 M LiBF$_4$ in EC:DEC (1:1 volume ratio) mixture. Cycling is performed at a current density of C/2. Note that, composite cathodes can be classified into two groups based on cycleability: one group is noted with circles, while the other with triangles.
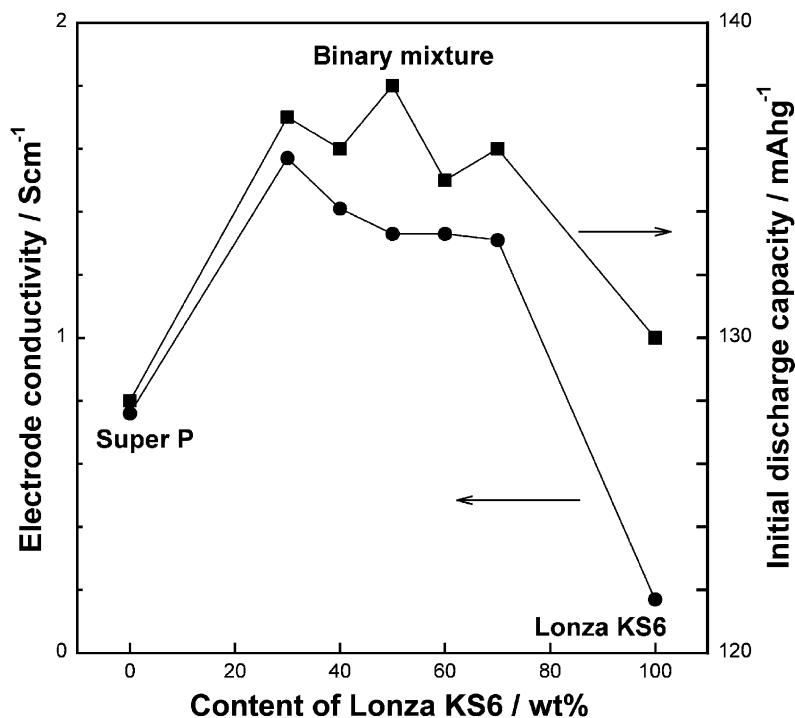
Fig. 3. Electrode conductivity and initial discharge capacity of composite cathodes. Weight fraction of Lonza KS6 in binary mixture of Lonza KS6 and Super P is indicated on horizontal axis. There is a parallel relation between electrode conductivity and first discharge capacity of composite cathodes.

the composite cathodes. It is thus tentatively assumed that the favorable feature provided by the binary carbon mixture comes from a conductivity enhancement in these electrodes. To confirm this, the extent of cathode polarization was compared between the cathodes containing different conducting agents. The galvanostatic discharging voltage profiles of some composite cathodes are given in Fig. 4. It is seen that the cathode polarization is minimal in the cathode
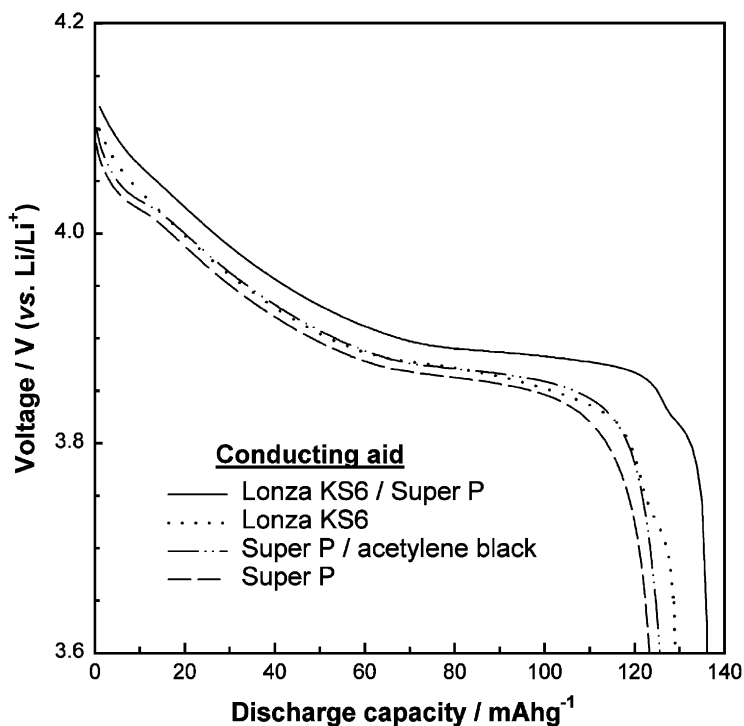

Fig. 4. First discharge voltage profiles that compare cathode polarization and discharge capacity between composite cathodes. Experimental conditions are same as for Fig. 2.
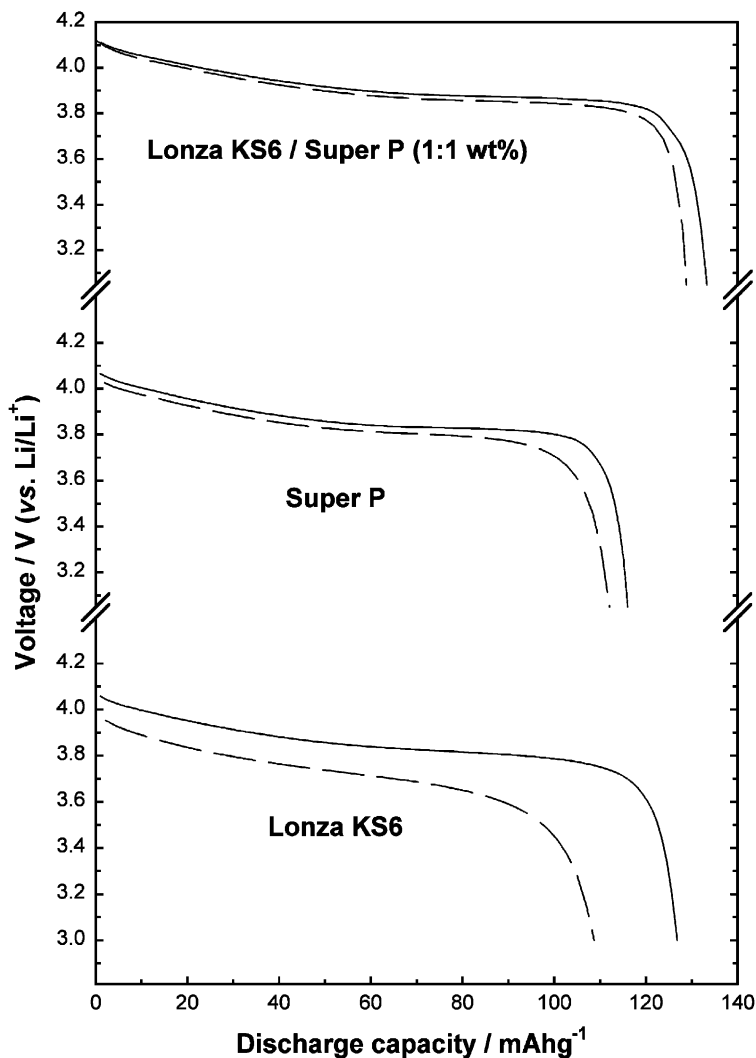
Fig. 5. First discharge voltage profiles traced at two current densities: solid lines at $C/2$; and dashed lines at $1C$. Conducting agent is indicated in inset. Other experimental conditions same as for Fig. 2. Note, Lonza KS6 loaded cathode shows most serious cathode polarization.

containing a binary mixture of Lonza KS6 and Super P. The extent of cathode polarization is further compared in Fig. 5, where the discharging voltage profiles of three cathodes are presented at two different current densities. The cathode containing a binary mixture of Lonza KS6 and Super P exhibits only a slight increase in polarization when the current density is doubled from the $C/2$ to the $1C$ rate thereby, and, delivers a comparable discharge capacity at the two current densities. The most serious cathode polarization is observed with the Lonza KS6 containing cathode. The discharge capacity at $1C$ amounts to only 83% of that measured at $C/2$ due to the polarization.

The results presented so far strongly indicate that electrode conductivity plays an important role in affecting cathode performance. The use of a binary carbon mixture as a conducting agent is thus desirable. There appears, however, a contradictory result to this generality in the cause of cathodes loaded with a single carbon additive. That is, the cathode containing Lonza KS6 alone shows a

better cycleability (Fig. 2) and a larger initial capacity even if its conductivity is lower than that of the Super P loaded electrode (Fig. 3). Therefore, other factors in addition to electrode conductivity should be considered to provide a general explanation. As described in the Section 3.2, the dispersion of electrode ingredients is a more important factor in affecting the overall electrode performance. This can also account for the difference in the electrode conductivity, such that the previous discussion on the conductivity-dependent electrode performance is still valid.

3.2. Dispersion of electrode ingredients according to carbon additive

SEM images of composite cathodes that are fabricated with different conducting agents are shown in Fig. 6. When the smaller-sized carbon blacks are used, the carbon and $LiCoO_2$ particles are segregated to give a poorer uniformity in dispersion (Fig. 6(a) and (c)). A more uniform dispersion
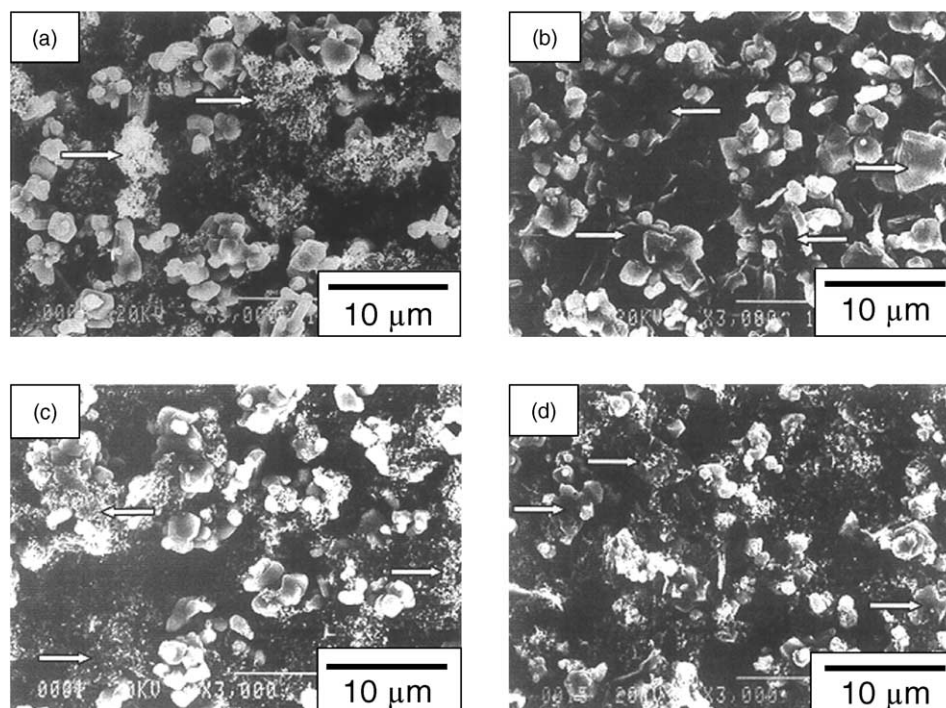
Fig. 6. SEM pictures of composite cathodes loaded with different conducting agents: (a) Super P; (b) Lonza KS6; (c) binary mixture of Super P and acetylene black (1:1 weight ratio); and (d) binary mixture of Lonza KS6 and Super P (1:1 weight ratio). Arrows locate carbon additives.

of both carbon and $LiCoO_2$ particles can be achieved by using Lonza KS6 alone or as a binary mixture of Lonza KS6/Super P (Fig. 6(b) and (d)). The difference in dispersion may be explained in terms of the mixing efficiency at the slurry preparation step. It is a common practice that the mixing efficiency is better when the two components have a comparable particle size. A more homogeneous mixing is thus expected in the Lonza KS6/$LiCoO_2$ system because of their similar size. The substantial difference in size between the carbon blacks and $LiCoO_2$ grains may not allow uniform mixing in the slurry. The density of the electrode components may be another criterion in determining the mixing efficiency in the slurry preparation step. The density of $LiCoO_2$ (4.9 g cm^{-3}) is so much different from that of carbon blacks (1.8 g cm^{-3}) that two components cannot be mixed homogeneously. It is likely that the heavier $LiCoO_2$ particles settle down, while the lighter carbon black tends to float in the mixing step. This segregation may be alleviated when Lonza KS6 is used because it is slightly denser (2.2 g cm^{-3}).

From now on the conductivity-dependent cathode performance, as well as the contradiction encountered with the single carbon system will be accounted for by the dispersion of electrode ingredients. First of all, in the cathode containing the binary mixture of Lonza KS6 and Super P, the larger-sized Lonza KS6 is well dispersed with $LiCoO_2$, while the smaller-sized carbon blacks fill the gaps made by the larger-sized carbon and $LiCoO_2$ grains. If this is the case, then the electric conduction network will be well developed along with an enlargement in the surface-area

of the carbon|$LiCoO_2$ interface. The former feature allows a higher electrode conductivity and less significant cathode polarization (Figs. 3 and 5). An improved utilization of active material is achieved due to the latter feature (Fig. 2).

The difference in cycleability between the two groups of cathodes (Fig. 2) may also be rationalized based on the dispersion of electrode components. If the carbon additives are not uniformly dispersed, which is pertinent to the second group, the active materials are not evenly utilized and they also experience an unequal topological potential. Then, some of active materials are overcharged–overdischarged, which eventually degrades their activity to leads to gradual fade in capacity. The first group of cathodes is rather free from this undesirable feature due to a more uniform dispersion.

The contradictory results observed with the single carbon system, which cannot be rationalized on the basis of electrode conductivity, can be explained along the same lines. The better cycleability of the Lonza KS6 loaded cathode seems to be due to a more uniform dispersion of the active materials and carbon additives than in the Super P loaded counterpart (Fig. 2). The poorer conductivity of this cathode may, however, be ascribed to an ill-formed conductive network between the Lonza KS6 particles (Figs. 3 and 5). For electrical conduction in the present composite cathodes, the number of contact points between the more conductive carbon grains is more crucial than those made by the less conductive $LiCoO_2$. In the present work, even if the amount of conducting agent is the same in terms of the weight fraction (10 wt.%) for each composite electrode, the volumetric fraction of Lonza KS6 is smaller than that of the

carbon blacks because it is denser. Moreover, the number of contact points between Lonza KS6 particles is expected to be much smaller because these particles are larger in size. A poorer conductivity is thus expected in this cathode.

Finally the poorer cycleability, but higher electrode conductivity observed with the carbon black loaded cathodes seems to originate from an uneven distribution of the electrode components. The SEM images shown in Fig. 6(a) and (c) reveal that the carbon blacks are agglomerated and become isolated from the $LiCoO_2$-rich region. The contact points of $LiCoO_2$|carbon are then less populated, which leads to poorer utilization of active material and poorer cycleability (Fig. 2). It is, likely, however, that the carbon–carbon contact points are rich such that electrical conduction is facilitated along the channel of carbon agglomerates.

4. Conclusions

This study demonstrates that carbon additives play an important role in influencing the electrode conductivity, utilization of active materials and cycleability. It is proposed, with some experimental evidence, that all these properties are primarily determined by the extent of dispersion between the electrode ingredients. The following observations are made.

(i) The larger-sized Lonza KS6 is well dispersed with the $LiCoO_2$ particles due to the similarity in particle size. The poorer mixing between the carbon blacks and active material can then be ascribed to the significant difference in size of the two components.

(ii) Better utilization of active material and longer electrode life is observed with the Lonza KS6 loaded cathode. This feature comes from the enlargement of the active surface-area of the carbon|$LiCoO_2$ interface as a result of a more uniform dispersion between the electrode ingredients. The poorer electrode conductivity of this cathode may, however, be attributed to the larger size of Lonza KS6. The number of carbon–carbon contact points is expectedly less abundant in this cathode.

(iii) The addition of smaller-sized carbon blacks to the larger-sized Lonza KS6/$LiCoO_2$ further enhance the cathodic performance of composite electrodes. The carbon blacks probably fill the void spaces made by the larger grains, which leads to a better network formation between the carbon components and enlarges the effective surface-area of the carbon|$LiCoO_2$ interface. The former feature enhances the electrode conductivity and cathode life, whereas the latter allows greater utilization of active material.

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