Carbon Nanomaterials Used as Conductive Additives in Lithium Ion Batteries

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Abstract: As the vital part of lithium ion batteries, conductive additives play important roles on the electrochemical performance of lithium ion batteries. They construct a conductive percolation network to increase and keep the electronic conductivity of electrode, enabling it charge and discharge faster. In addition, conductive additives absorb and retain electrolyte, allowing an intimate contact between the lithium ions and active materials. Carbon nanomaterials are carbon black, Super P, acetylene black, carbon nanofibers, and carbon nanotubes, which all have superior properties such as low weight, high chemical inertia and high specific surface area. They are the ideal conductive additives for lithium ion batteries. This review will discuss some registered patents and relevant papers about the carbon nanomaterials that are used as conductive additives in cathode or anode to improve the electrochemical performance of lithium ion batteries.

Keywords: Carbon nanomaterials, carbon black, acetylene black, super P, carbon nanotubes, carbon fibers, conductive additives, cathode active materials, anode active materials, lithium ion batteries.

1. INTRODUCTION

Compared with other rechargeable batteries such as lead-acid batteries, Ni-Cd batteries and Ni-MH batteries, lithium ion batteries have high voltage, high energy density and long cyclic life. Therefore, they have attracted many researchers’ eyes and developed very fast since the birth of the early 1990s. The lithium batteries industry has undergone rapid expansion, now representing the largest segment of the portable battery industry and dominating the computer, cell phone, and camera power source industry. The large-scale lithium ion batteries for hybrid electric vehicles (HEV) or electric vehicles (EV) have arisen on the market. It reported that BYD E6 EV loading large-scale lithium ion batteries appeared on the market in the end of 2009.

The lithium ion batteries are visually called as ‘rocking chair’ batteries. The principal can be described as follows. When they charge, the lithium ions break away from the cathode, flow through the electrolyte and settle in the anode, whereas the electrons generated from the lithium ions moving, go through the external circuit. When they discharge, the lithium ions and electrons go the opposite directions. Thus, the electrode system of lithium ion batteries must allow for the flow of both lithium ions and electrons. That is, it must be both a good ionic conductor and an electronic conductor. As it is known, the cathode active materials are usually micro-sized materials with low electronic conductivity in the range of 10⁻³~10⁻⁹ S·cm⁻¹ [1]. In order to construct conductive percolation network, conductive additives are routinely added to the cathode active materials. The conductive network compensates for the low electronic conductivity of cathode active materials, maintains the electronic conductance of cathode during charge-discharge cycles, and increases batteries capacity, enabling it charge and discharge faster. The anode active materials are microsized materials with comparatively high electronic conductivity. But they expand and shrink repeatedly during the charge-discharge cycles. After several cycles, the anode active materials will separate each other and some of them will become the ‘dead’ active materials. Then, the electronic conductance and capacity of the anode will decrease rapidly after several charge-discharge cycles. Thus, conductive additives are usually added to keep their electronic conductance during the charge-discharge cycles. In addition, conductive additives absorb and retain electrolyte, which allows an intimate contact between lithium ions and the active material. In a word, the one role of conductive additives is to increase and keep the conductance of the electrode, and the other role is to absorb and retain electrolyte, allowing an intimate contact between lithium ions and active materials.

Compared with other key materials of lithium ion batteries such as cathode active materials, anode active materials, electrolyte and separator, conductive additives are a small but important part. Lithium ion batteries cannot properly work without them. Generally, all the conducting materials (including metal fibers, metal powders, graphite powders, carbon nanomaterials) can be used as conductive additives. Ann et al. [2] used metal fibers as conductive additives to develop high capacity, high rate lithium ion batteries. Shen et al. [3] used the mixture of metal fibers and metal powders as conductive additives to fabricate lithium ion batteries with low internal resistance, high rate and long cyclic life. Compared to those metal fibers or metal powders, carbon nanomaterials have superior properties such as low weight, high chemical inertia and high specific surface area.
Therefore, the most used conductive additives in lithium ion batteries are carbon nanomaterials such as carbon black, Super P, acetylene black, carbon nanofibers, and carbon nanotubes. This review will discuss them in the following text.

2. CONDUCTIVE ADDITIVES IN CATHODE

Cathode active materials are LiCoO$_2$, LiMn$_2$O$_4$, LiNiO$_2$, LiNi$_{1-x}$Mn$_x$O$_2$, LiNi$_{1/3}$Co$_{1/3}$Al$_{1/3}$O$_2$, LiMPO$_4$ (M is Fe, Mn, Co, Ni, Cu or V) and Li$_2$MSiO$_4$ (M is Fe, Mn, Co or Ni). They are semiconductors or insulators. Several common cathode active materials and their electronic conductivities are listed in the Table 1.

<table>
<thead>
<tr>
<th>Cathode active materials</th>
<th>LiCoO$_2$</th>
<th>LiNiO$_2$</th>
<th>LiMn$_2$O$_4$</th>
<th>LiFePO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic conductivity (S·cm$^{-1}$)</td>
<td>$10^{-3}$</td>
<td>$10^{-2}$</td>
<td>$10^{-3}$</td>
<td>$10^{-9}$</td>
</tr>
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</table>

The ideal cathode of lithium ion batteries should have high electronic and ionic conductivity. The electronic conduction depends on the electronic conductance of the cathode. The ionic conduction depends on the ionic diffusibility which is closely related to the pores in the cathode. The porous structure, especially mesoporous structure can absorb and retain electrolyte solution, allowing an intimate contact between the lithium ions and cathode active material. In addition, the cathode active materials expand and shrink repeatedly during the charge-discharge cycles. Therefore, another role of conductive additives is to keep the conductance constantly during charge-discharge cycles. Thus, the functions of conductive additives in cathode can be summarized in the following: (1) enhancing the electronic conductance of cathode, (2) absorbing and retaining electrolyte solution, allowing an intimate contact between the lithium ions and cathode active material, (3) maintaining the electronic conductance of cathode during the charge-discharge cycles. The primary function of conductive additives in cathode is to enhance the electronic conductance of cathode.

2.1. Single Conductive Additives

Single conductive additives are those containing only one conducting material. They include particulate carbon and fiber-like carbon. Particulate carbon mainly includes carbon black, acetylene black, Super P and graphite. They all have spherical primary particles. The conducting networks formed by them are dominated by the degree of inter-particle resistance which in turn depends on the degree of inter-particle contact. Fiber-like carbon mainly includes carbon fibers and carbon nanotubes. They are fibers or tubes with high aspect ratio which is over 100. The conducting networks formed by them are less sensitive to inter-particle contact. The curve of conductive additive’s theoretical percolation threshold versus the aspect ratio is shown in Fig. (1). Clearly, the high-aspect-ratio additives are more efficient in increasing overall electronic conductivity for a given volume fraction. But, the fiber-like carbon is usually much more expensive than the particulate carbon. Thus, the particulate carbon is the conventional conductive additive in lithium ion batteries.
2.1.1. Particulate Carbon

Liu et al. [5] investigated the effects of carbon black on the electrochemical performance of LiCoO₂ and LiMn₂O₄ cathode. They found that LiCoO₂ cathode is more sensitive to the amount of carbon black. The nonperformance of LiCoO₂ or LiMn₂O₄ results primarily from incomplete charging caused by deteriorating particle contacts between the oxides and carbon black. Good capacity retention at high charging rate (2 mA·cm⁻²) may be attained in practice with 5~10 wt.% of carbon for the LiCoO₂ cathodes, and 2~5 wt.% of carbon for the LiMn₂O₄ cathodes. Jang et al. [6] investigated the surface state on the spinel dissolution and capacity losses in 4 V Li/Li₃Mn₂O₄ rechargeable cells. The observed spinel capacity losses were accounted to two factors: the material losses arising from spinel dissolution and polarization losses caused by an increment in cell resistances. The relative importance between the two seems to be determined by carbon surface area: The material losses are dominant with larger surface area carbons since spinel dissolution is severe in this case, while the polarization losses are more of a problem as carbon surface area becomes smaller.

Besides the dosage and own properties of conductive additives, the dispersing extent is an important factor to influence the electrochemical performance of cathode. Many researches had proved it. Because the comminuted expanded graphite is easily dispersed with cathode active material particles, Kurosa et al. [7] had utilized it as conductive additives to enhance the capacity and cyclic life of cathode. Liu et al. [8] found significant decrease of contact resistance between the oxide phase and carbon black. Through extensive ball milling of the spinel with carbon black during the preparation of the cathode mixture. The spinel LiCo₀.₉Mn₁₀.₁O₄ cathode so prepared showed good cyclic life and rate capability.

Momchilov et al. [9] used polyvinyl pyrrolidone (PVP) as a dispersant in N-methyl pyrrolidone (NMP) to prepare nonaqueous ultrafine carbon suspensions (UFC). They aslo explored them as conductive additives in LiMn₂O₄ cathodes. The ultrafine carbon here is teflonized acetylene black (TAB) and it was firstly dispersed well in UFC. The electrochemical cycling test showed that the discharge capacity of cathodes containing 20% UFC + TAB at a ratio from 1:3 to 1:1 are 5 to 10% higher than that of the cathodes with only 20% TAB. The better electrochemical behaviors of the cathodes with UFC are due to the two factors: decreasing of the specific resistivity and increasing of the pore volume of the cathodes.

Kuroda et al. [10] investigated the influence of the dispersion state of conductive additives on the properties of lithium ion batteries. They prepared suspensions of ketjen black (KB) which is one kind of acetylene black. The required amount of KB was slowly added to NMP with/wihtout a dispersant that was a derivative of vinylpyrrolidone. Then, they were pulverized by a three-rolled mill. The obtained two types of KB suspensions were D0 and D1, with and without the dispersant, respectively. The average particle size of these suspensions (d₅₀) was 0.3 mm for D0 suspension and 3.0 mm for the D1 suspension. 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 suspensions (D0 suspension: 0.5 wt.%, D1 suspension: 2.0 wt.%) was kept constant, while 4.5 wt.% KB power content was needed to keep the similar durability performance. They concluded that an electro-conductive network made of KB can transmit electrons smoothly from active materials to the collector, formed in the cathode when the cathode was prepared from a well-dispersed suspension.

Dominko et al. [11] studied the influence of carbon black distribution or arrangement in composite cathode on the cathode performance by using three types of cathode active materials: LiMn₂O₄, LiCoO₂, and LiFePO₄. To the active materials, carbon black is added in two different ways: (a) using a conventional mixing procedure (cathode active materials, carbon black and binder were directly mixed) and (b) using a novel coating technology (NCT) (Gelatin pretreated the cathode active particles, and then mixed with a dispersion of carbon black). Different technologies result in different distribution of carbon black around active particles. It is shown that the uniformity of carbon black distribution affects significantly the cathode kinetics, regardless of the type of active particles used. For example, in the case of LiCoO₂, even a much lower content (2 wt.%) of uniformly distributed carbon black shows better kinetics than a higher content (10 wt.%) of non-uniformly distributed carbon black. A simple model explaining the influence of carbon black distribution on cathode kinetics is presented in Fig. (2). In order for insertion to occur without excessive polarisation, both the Li⁺ ion and the electron have to be available at the same spot Fig. (2b), by contrast, if a part of active material is not in contact with an electronic conductor Fig. (2a), the supply of electrons to this spot will be reflected in additional polarization, and thus, in a lower reversible capacity.
black coated powder was also separated and washed three times with NMP to remove the unbound carbon black. The carbon black coated LiCoO$_2$ has very high specific conductivity. Kim et al. [13] used a polyacrylate dispersant to prepare Super P suspension and then coat the dispersed carbon black on the cathode material by a gelatin being an amphoteric surfactant. This technology reduces the carbon content in the electrode without sacrificing the cyclic performance of the cell, and also improves the rate capability of the Li-ion cell. Hibino et al. [14] used two-step acetylene black addition to prepare hydrated sodium manganese oxide (HSMO). Acetylene black was added twice, first while synthesizing HSMO and next while preparing the electrode. Acetylene black added in the synthesis resulted in an additional redox reaction below 2 V versus Li/Li$^+$ and was effective in enlarging the charge-discharge capacity. On the other hand, Acetylene black added during electrode fabrication reduced resistance and improved cyclic performance.

Among the cathode active materials for lithium ion batteries, LiFePO$_4$ has advantages such as rich in raw materials, stable voltage platform, resistance to overcharge, and good safety performance. It is an ideal cathode active material for large-scale batteries for HEV and EV. But it has very poor electronic conductivity. Nano carbon doping is a feasible way to enhance the electronic conductivity of LiFePO$_4$.

Wang et al. [15] mixed Fe$^{3+}$, Li$^+$ and chelating agent containing PO$_4^{3-}$ in molecule scale. Then the mixture was dried and calcined in inert atmosphere. Pyrolyzed carbon from the chelating agent hinders the LiFePO$_4$ particles from growing up and increases its’ electronic conductivity. Therefore, the LiFePO$_4$/C shows excellent electrochemical performance. Yang et al. [16] mixed Li$_2$CO$_3$, ferrite, chrome salt and phosphor precursor by ball-milling. The mixture was then mixed with 5 wt. % carbon black, 10 wt. % sucrose in step by ball-milling. After that, the mixture was calcined at 350 °C for 5h, milled again and then calcined at 600 °C in inert atmosphere for 8 h. The acquired LiFe$_{1-x}$Cr$_x$PO$_4$/C has good cyclic performance. Zhang et al. [17] mixed 1:1:1 mole ratio of LiOH·H$_2$O, Fe powders and H$_3$PO$_4$ in aqueous solution and stirred for 2~10 h under N$_2$ atmosphere. Glucose or cyclodextrin was added to the suspension and then sprayed to prepare the LiFePO$_4$/C precursor. The LiFePO$_4$/C precursor calcined at 300 °C for 3h and then 300 °C for 3~24 h in inert atmosphere. The precursors of Li, Fe, P and C was mixed together and then calcined in inert atmosphere. It is a common way to prepare LiFePO$_4$/C composite with high electrochemical performance. Similar works were also done by Nathalie [18], Li [19], Feng [20], Liu [21], Singhal [22], Audemer [23], Doeff [24] and Jack [25].

### 2.1.2. Fiber-Like Carbon

Compared with particulate carbon, fiber-like carbon can fix the cathode active materials to the current collector firmly. Some researchers call it "physical binder". Frysz et al. [26] utilized carbon filaments as conductive additives to prepare MnO$_2$ composite cathode without using a binder. The composite cathode shows higher volumetric energy density than the carbon black counterpart.

Kotaro et al. [27] prepared LiMn$_2$O$_4$ composite cathode containing less than 5 wt. % graphitized carbon fibers. The cathode has high rate charge-discharge performance. Masayuki [28] utilized fiber type carbon as conductive additives to restrict an increase of the batteries resistance when being used in the high-temperature surroundings. In addition, the cathode has excellent heavy load discharge characteristic. Nishimura et al. [29] used vapor-grown carbon fibers (VCF) agglomerates to prepare composite cathode with low resistance and high energy density. Masataka et al. [30] used 0.1~2 wt.% carbon fibers with a mean fiber diameter of 1~200 nm to fabricate a composite cathode. The cathode has an excellent electrolyte permeability and electrolyte retention. Therefore, it is very adapted to be used in high-density lithium batteries. Tetsuharu [31], Hideyuki et al. [32] and Tsuneo et al. [33] also used carbon fibers as conductive additives to prepare composite cathodes. The prepared cathodes have high discharge capacity and low cyclic deterioration.

Carbon nanotubes (CNTs) have high aspect ratio, large surface area, high electronic conductivity, high thermal conductivity, high flexibility and tensile strength. High aspect ratio and high electronic conductivity are effective in forming conductive networks with high electronic conductivity. Large specific area means CNTs can adsorb and retain electrolyte allowing an intimate contact of lithium ions and cathode active materials. High thermal conductivity means CNTs can easily transfer out the heat generated from electrochemical reactions in battery. High flexibility and tensile strength means CNTs can form a firm and resilient conductive network to improve the battery cyclic performance. Therefore, CNTs are the ideal conductive additives for lithium ion batteries.

Junji et al. [34] utilized carbon nanotubes to prepare a composite cathode. The composite cathode has very low resistance. Wang et al. [35, 36] compared three conductive additives: acetylene black (AB), VCF and CNTs. The initial discharge capacities at various charge-discharge rates are shown in Fig. (3). Clearly, carbon nanotubes are the most effective in enhancing charge-discharge rate performance of the composite cathode. They investigated other electrochemical performance (including cathode resistance, cyclic performance and discharge voltage profile) of the three composite cathodes. All results indicated that electrochemical performance of CNTs loaded cathode is the best. They thought the reasons are as follows. The CNTs’ wire-like shape, crystallinity and nano-size are all considered to be important factors. The wire-like shape favors forming continuous conductive network and then assures an efficient electronic transport throughout the cathode. The higher crystalline and nano-size make them show better ability to rapidly transfer electrons and lower percolation threshold in comparison with VCF. Moreover, the higher surface energy guarantees their close contact with the cathode active materials LiCoO$_2$.

Single wall carbon nanotubes have a high thermal conductivity of 1800~6000 W-m$^-1$K$^-1$. Ochao et al. [37] used them as conductive additives in lithium ion batteries. The results indicated that the use of single wall carbon nanotubes as conductive additives in the electrode materials, even in
very small amounts, improves the capacity, thermal stability, and safety of the electrode materials. Since the CNTs with opened ends have a uniform pore shape, when used as a capacitor material, diffusion resistance at low temperature is lower than that of activated carbon and the like, and output characteristics are enhanced. Masaya et al. [38] used this kind of CNTs to fabricate composite cathode being fit for high rate discharging under low temperature.

Li et al. [39, 40] used CNTs to prepare composite cathodes. They found that CNTs conductive network wirings connect the LiNi_{0.7}Co_{0.3}O_{2} or LiFePO_{4} particles and are effective in improving reversible capacity and cycle efficiency. Sheem et al. [41] compared CNTs and Super P as conductive additives on the electrochemical performance of LiCoO_{2} composite cathodes. The CNTs loaded cathode showed some superiority over the Super P Loaded cathode. They thought that CNTs aggregates form resilient conductive bridges between particles of the active material. These resilient bridges maintain intimate contacts between the particles even when the composite expands on cycling. By contrast, similar but rigid bridges of carbon black in the Super P cathode are broken on cycling. Figure 4 is a schematic presentation of the two kinds of bridges in the composite cathodes.

2.2. Multiple Conductive Additives

Compared with single conductive additives, multiple conductive additives can take advantages of two or more than two conductors. And thus synergistic effects came into being. Therefore, multiple conductive additives usually show some superiority over single conductive additives. Micro-sized graphite is easily dispersed with cathode active materials, but cannot form a valid conductive network with a small dosage. When nano-sized Super P or like is also added, a valid conductive network is usually formed. Then the cathode has improved cyclic life and higher discharge capacity. This study had been done by Cheon et al. [42] and Hong et al. [43].

Cheon et al. [44] used multiple conductive additives comprising a first conductor with a specific surface area ranging from about 200 to about 1500 m^{2}·g^{-1} and a second conductor with a specific surface area of about 100 m^{2}·g^{-1} or less. The composite cathode has low resistance and high energy density. Zhang et al. [45, 46] used mesoporous carbon containing multiple conductive additives to improve the electrochemical performance of LiCoO_{2} composite cathodes. The results showed that the electrochemical performance (including the discharge capacity, the discharge voltage and the total internal resistance) of a multiple conductive additives loaded LiCoO_{2} composite cathode was better than that of a cathode loaded with AB. The possible mechanism is that the mesoporous carbon can adsorb and retain electrolyte solution, which allows an intimate contact between the lithium ions and the cathode active material LiCoO_{2} due to its large mesopore specific surface area. Figure 5 is a schematic view of the LiCoO_{2} composite cathode loaded with multiple conductive additives. In Fig. (5), A, B and C are LiCoO_{2} particles, mesoporous carbon particles and AB particles, respectively.

**Fig. (3).** Comparison of initial discharge capacities of LiCoO_{2} composite cathodes loaded with different conductive additives at various discharge rates [35, 36].

**Fig. (4).** (a) Schematic representation of changes in Super P loaded cathode; (b) schematic representation of changes in CNTs loaded cathode [41].
As discussed, fiber-like carbon easily form a conductive network. But fiber-like carbon has less contact point with cathode active materials compared with particulate carbon. If particulate carbon and fiber-like carbon are mixed together to form multiple conductive additives, they will take advantages of the two kinds of conductors.

Thorat et al. [47] fabricated and tested LiFePO₄ cathodes for hybrid vehicle applications. The cathodes contained combinations of three different carbon conductivity additives: vapor-grown carbon fibers (VCF), carbon black (CB) and graphite (GR). With all other factors held constant, cathodes with a mixture of VCF+CB were found to have the best power-performance, followed by cells containing VCF only and then by CB+GR. Thus, the use of carbon fibers as conductive additive was found to improve the power performance of cells compared to the baseline (CB + GR). The enhanced electrode performance due to the fibers also allows an increase in energy density while still meeting power goals. Keisuke [48] fabricated spinel LiMn₂O₄ cathodes with a mixture of VCF + CB. The highest charge-discharge efficiency was achieved with the mixture of 8:2 weight ratio of VCF/CB. Yusuke et al. [49] fabricated cathodes with a mixture of carbon nanofiber and particulate carbon. The content of the multiple conductive additives to the total weight of the activator is 0.5–15 wt.%. In the multiple additives, the content of the carbon nanofiber is 80–99.5 wt.% and that of the particulate carbon is 0.5–20 wt.%. The cathodes can charge-discharge at high rate. Shiyuuko et al. [50] used multiple conductive additives containing a fiber-like carbon (1–20 wt.%), a granular carbon (99–80 wt.%). The granular carbon contains the crystal carbon (90–60 wt.%) and the non-crystalline carbon (10–40 wt.%). The cathodes have long cyclic life and high rate charge-discharge capacity. Koji [51] fabricated a cathode with a mixture of CB, VCF and flake natural graphite (FNG). The CB adheres on the surface of the cathode active material to enhance the conductivity of the cathode active material. The VCF couples the cathode active material. The FNG increases the contact area of the VCF. Therefore, the multiple conductive additives enhance the conductivity of the cathode and the lithium ion batteries using this cathode can charge-discharge at very high rate. The schematic view of the composite cathode loaded with the multiple conductive additives is shown in Fig. (6).

Fig. (5). Schematic of the LiCoO₂ composite cathode loaded with mesoporous carbon containing multiple conductive additives [45, 46].

Zhang et al. [52, 53] used nano carbon composites (NCC) formed by sonication of CNTs and AB as conductive additives to improve the electrochemical performance of LiCoO₂ composite cathode. CNTs formed valid conducting networks to enhance the electronic conductivity, while the AB particles, which were on the surface of or in the internal space of LiCoO₂ particles, were partly in contact with CNTs, and therefore, the contact surface area of NCC and LiCoO₂ particles increased. The electrochemical performance of LiCoO₂ cathode loaded with NCC was greatly improved. Yu et al. [54, 55] prepared a composite of CNTs and particulate carbon by different methods. The composite is effective in improving the high rate charge-discharge capacity and cyclic life of the cathode.

3. CONDUCTIVE ADDITIVES IN ANODE

The most common anode active materials are carbon materials such as natural graphite and artificial graphite. Carbon materials have high electronic conductivity compared with the cathode active materials. In principle, it is not necessary to add conductive additives into anode to construct conductive network. But, carbon materials expand and shrink again and again when charging and discharging. The carbon particles separate from each other after several cycles. Then, some carbon materials will be “dead” active materials and the discharged capacity decrease rapidly. The anode electronic conductivity also decreases rapidly. Therefore, conductive additives are usually needed to keep the discharged...
capacity and electronic conductivity during the charge-discharge cycles. Other anode active materials like silicon and metal alloy have higher capacity and larger expansion ratio. They also need conductive additives to keep their electrochemical performances. In addition, conductive additives usually have some discharged capacity. They can enhance the discharged capacity along with anode active material.

3.1 Single Conductive Additives

3.1.1. Particulate Carbon

Takamura et al. [56] compared the electrochemical performance of graphitized mesophase carbon fiber (MCF) loaded with three particulate carbons such as GP, AB and Ketjen black. The results indicated that dispersion of particulate carbon in anode was a key factor for obtaining a reliable anode of lithium ion secondary batteries for high rate use. Improvement of the anode performance due to the particulate carbon loading includes: (1) remarkable increase of the cyclic life; (2) increasing of the initial irreversible capacity to a great extent; (3) increasing of the charge-discharge rate and (4) increased utilization efficiency of anode active materials. Using the same dosage of AB, the electrochemical performance of the mechanical made anode was higher than that of manual made anode. Thus, homogenization of slurry mix was found to be a key factor for obtaining a high performance anode irrespective of the presence of the conductive additives.

Joho et al. [57] proved that conductive additives such as carbon black may prolong the cyclic life of a graphite anode by preventing the electrode resistance from increasing during prolonged cycling. Nishizawa et al. [58] developed a novel electrochemical technique based on a filament-type and an array-type microelectrodes to in situ study the conductance change of a mesocarbon microlead (MCMB) particle and its composite film during electrochemical lithium insertion/extraction reactions. The filament-type microelectrode studies for a material's single particle, and the array-type microelectrode studied for the material's film. The results indicated that the conductance and redox activity of its film decreased continuously during successive charge/discharge, while an MCMB particle itself is stable. This behavior is presumably caused by the break of electrical contact between MCMBs in composite due to their volume change induced by lithium insertion/extraction reactions. Addition of AB was found to be effective in retaining the inter-particle connection. Figure 7 is the schematic of the presentation anode.

Takao et al. [59] added a non-graphitized carbon material with a mean particle diameter of not more than 70nm to a graphitized carbon to form a composite anode. The anode has excellent discharge capacity and cyclic performance. Takeshi et al. [60] added conductive cokes to natural graphite to fabricate composite anode. The anode has high reversible capacity during charge-discharge cycles. Jiro et al. [61] covered the non-flake graphite with amorphous carbon and then mixed the graphite material with flake graphite particles. The cells using the composite anodes have large capacity and excellent charge and discharge efficiency.

3.1.2. Fiber-like Carbon

Fiber-like carbon has high aspect ratio. It can form valid conductive network and fix the anode active material to the collector firmly. That is to say, fiber-like carbon can keep the conductance of composite anode constant during the prolonged cycling. Many researchers paid attention on this issue and used fiber-like carbon as conductive additives to improve electrochemical performance of the composite anode.

Yoshiyuki et al. [62] mixed MCMB with carbon fibers to increase the strength of the composite anode. The cells with the improved anode have a high voltage, a high energy density and an excellent cyclic performance. Yoshiyuki et al. [63] also calcined VCF to enhance its crystallinity and mixed the treated VCF with anode active materials. The batteries with the composite anodes have a high voltage and a high capacity. Chiaki et al. [64] mixed anode active materials with 2 wt.% carbon fibers having a diameter of 1~1000nm. The composite anode has low electrode resistance, superior electrode strength and superior in electrolyte permeability. It can charge and discharge at very high rates. Atsushi et al. [65] added 3~20 wt.% VCF to the mesophase graphite. A battery with the composite anode has superior cyclic performance in a wide temperature range, from high temperatures to low temperatures. Aiichiro [66] mixed mesophase pitch carbon fibers and VCF to fabricate polymer lithium secondary batteries with a long cyclic life. Seigi et al. [67] added carbon fiber to amorphous carbon. The cell with composite anode is excellent in safety and charge-discharge cyclic performance. Kunihiko et al. [68] mixed a precursor of a graphite material A and a precursor of a fibrous graphite material B. The precursor of the fibrous graphite material B is stuck to the precursor of the graphite material A, and thereafter, graphitization is performed. The composite anode material is capable of affording high discharge capacity and initial charge-discharge efficiency, excellent rapid charge-
In order to disperse CNTs or VCF with anode materials uniformly, some researchers employed chemical vapor deposition to *in situ* growth CNTs or VCF on the surface of anode materials. Sheem *et al.* [76] coated the graphite sphere with a catalyst layer and grew VCF or CNTs on the surface of graphite sphere. Since VCF or CNTs are formed on the surface of the graphite sphere, the anode active material not only forms a fine path between active materials but also improves conductivity between neighboring active materials. Therefore, a battery having improved high rate and cyclic performance can be got. Figure 9 is the schematic view of the composite anode active material.

Tatsuo *et al.* [77] conglutinated catalyst on the surface of Si, Sn or Sb and grew VCF on the surface. The composite anode material exhibited excellent conductivity and cyclic performance. Yoshinori *et al.* [78] used the similar method to fabricate VCF coated graphite particles. The graphite-carbon material has excellent conductivity and can be used as anode material or conductive additives in lithium ion batteries. Dasgupta *et al.* [79] grew a small amount of VCF or CNTs by high temperature on the surface of meso-phase graphite. The composite anode has excellent cyclic performance.

### 3.2 Multiple Conductive Additives

Multiple conductive additives can take advantages of different conductors. Thus, synergistic effects come into being when they were been used in anode.

Kim *et al.* [80] fabricated a core/shell type composite of silicon/carbon nanotubes (Si/CNTs). Firstly, a Ni catalyst is deposited on a Si surface. Secondly, the growth of CNTs is performed by chemical vapour deposition at 600 °C using C2H2/H2. They used Super P as conductive additives. Here, Super P and CNTs formed multiple conductive additives. The anodic performance of a Si/CNTs composite electrode is superior to that observed with bare Si and Si/CNTs mixed electrodes. This beneficial feature is ascribed to the conductive buffering role of the CNTs layer. It is likely that the void space and the flexible characteristics in the CNTs buffer layer on the Si surface allow volume expansion of the Si core without severe electrode swelling. Because of this,
the electric conductive network made among Si particles, carbon network and current-collector is well maintained, which reduces the charge-transfer resistance. Figure 10 is the schematic view of failure mode encountered in Si anode.

Yusuke et al. [81] used carbon nanofiber and graphite of 10-500 nm to improve the electrochemical performance of carbon material. High rate charge and discharge characteristics are successfully improved. Kunihiko et al. [82] used carbon or graphite material of low crystallinity as an adhesive material to mix granulated graphite material and fibrous graphite material together. The composite anode has excellent electrochemical performance. Yamaguchi et al. [83] used carbon flakes and CF as multiple additives. CF improves the retention of the electrolyte solution and carbon flakes improve conductivity between the anode active material particles. Synergistic effects came into being. Therefore, the composite anode can absorb and extract lithium ions rapidly, and has high capacity in the high-load current mode. Aruna et al. [84] provides a mixed nano-filament composition for use as an electrode. Here, the multiple conductive additives are processed to form an aggregate or web, characterized in that these additives are intersected, overlapped, somehow bonded together to form a network of electron-conducting paths. Thus, the composition anode has high electronic conductivity which enables facile collection of electrons produced by the anode active materials (e.g., Si nanowires). A cell containing this composite anode has high cyclic life and high reversible capacity.

4. CURRENT & FUTURE DEVELOPMENTS

With low weight, high chemical inertia, high specific surface area and high electronic conductivity, carbon nanomaterials meet the needs of conductive additives for lithium ion batteries and thus are widely used as conductive additives in lithium ion batteries. Carbon nanopowders such as acetylene black, carbon black and Super P are comparatively cheap. They are firstly and widely used as conductive additives in lithium ion batteries. In order to enhance the electronic conductivity, graphite powders are usually added. Carbon nanofibers like VCF and CNTs have high aspect ratio. They are more effective in forming valid conductive networks than carbon nanopowders. But carbon nanofibers have less contact points compared with carbon nanopowders. Combining carbon nanofibers and carbon nanopowders to form multiple conductive additives is an ideal way to improve the electrochemical performance of lithium ion batteries. Therefore, using different conductors to form multiple conductive additives is a developing direction of conductive additives in lithium ion batteries. With the development of new nanomaterials, there will be more kinds of multiple conductive additives to fabricate lithium ion batteries with high electrochemical performance.

As it is known, the electrode of lithium ion batteries must be both a good ionic conductor and an electronic conductor. The ionic conductivity also greatly influences the electrochemical performance of lithium ion batteries besides the electronic conductivity. Mesoporous materials have large mesopores which enable lithium ions penetrate and move quickly. Mesoporous carbon containing multiple conductive additives had been proved to be effective in improving the electrochemical performance of LiCoO2 composite cathode [45, 46]. Other mesoporous materials like mesoporous silica, MCM-41, MCM-48, MCM-50 and SBA-15 have more uniform and stable mesopores. The multiple conductive additives containing them and carbon nanomaterials like CNTs or VCF may be greatly improve the electrochemical performance of lithium ion batteries.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.
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