FIG. 5

START

S1(T1)

FORM CARBON BOND ACTIVE MATERIAL

S2

FORM POSITIVE ELECTRODE MIX PASTE

S3

APPLY POSITIVE ELECTRODE MIX PASTE

S4

PRESS AND SHAPE

S5

DRY

END

(54) Title: ELECTRODE PLATE, SECONDARY BATTERY, AND METHOD FOR PRODUCING THE ELECTRODE PLATE

(57) Abstract: A method for producing an electrode plate (155, 156) is provided. In the method, carbon bond active material particles (154, 254) are formed in which a first conductive material (158) is evenly bound to a surface of active material particles (153) via a binder (161, 261). An electrode mix paste (30) is formed by mixing the carbon bond active material particles, a second conductive material (159), a binder (163) and a solvent (162) by rotation of a rotary blade (11) of a mixer (20) so that the carbon bond active material particles, the second conductive material, the binder and the solvent are pressed by the rotary blade to the inner circumferential surface (Bb) of a mixing vessel to be extended into a cylindrical thin film. The electrode mix paste is applied to a collector member (151).
Published: with international search report (Art. 21(3))
ELECTRODE PLATE, SECONDARY BATTERY, AND METHOD FOR PRODUCING THE ELECTRODE PLATE

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to an electrode plate and a method for producing the same, and a secondary battery that is made using the electrode plate.

2. Description of the Related Art


[0003] JP-A-2003-173777 describes the following method for producing a positive plate. First, lithium cobalt oxide (positive electrode active material), carbon powder and water are mixed to form a slurry. Then, after a PVA solution is added to the slurry and stirred, the slurry mixed with the PVA solution is sprayed and dried at 280 °C using a spray dryer, to obtain composite particles (carbon bond active material particles.) Then, the composite particles, a binder and a solvent are kneaded to form a positive electrode mix paste. The positive electrode mix paste is applied to an aluminum collector, dried and pressed to obtain a positive plate.

[0004] JP-A-2006-339184 describes the following method for forming composite particles (carbon bond active material particles.) First, a conductive material, a binder, a dissolved resin and ion-exchange water are mixed to prepare a slurry. Then, composite particles (carbon bond active material particles) are formed from the slurry and an
electrode active material using an Agglomaster (made by Hosokawa Micron Corporation.) More specifically, the electrode active material is supplied in a basin of the Agglomaster. While the electrode active material is fluidized by 80°C hot air, the slurry is sprayed into the basin. As a result, the electrode active material and the conductive material are bound to form composite particles (carbon bond active material particles).

[0005] Further, JP-A-2008-84665 describes the following method for producing a positive plate. A positive active material, a conductive material, a binder and a solvent are kneaded using a high shear dispersion device (e.g., a planetary mixer) to form a positive electrode mix paste. Then, the positive electrode mix paste is applied to a surface of a positive collector, and dried to produce a positive plate.

[0006] In the producing method described in JP-A-2003-173777, however, when the composite particles, binder and solvent are kneaded by using the planetary mixer, etc., to form the positive electrode mix paste, a portion of the conductive material bound to the surface of the positive active material by the spray dryer falls off the surface of the positive active material. Therefore, the secondary battery using the positive plate produced by the method described in JP-A-2003-173777 does not have sufficient battery characteristics (in particular, high-current discharge characteristics.)

[0007] If the composite particles (carbon bond active material particles) are formed by the method described in JP-A-2006-339184, and then the composite particles, binder and solvent are kneaded using the planetary mixer to form the electrode mix paste, a portion of the conductive material bound to the surface of the electrode active material by the Agglomaster falls off, while the electrode mix paste is being formed. Therefore, even if the electrode plate is made using the electrode mix paste, and the secondary battery is made using the electrode plate, sufficient battery characteristics (in particular, high-current discharge characteristics) cannot be obtained.

[0008] In the producing method described in JP-A-2008-84665, it takes long time to disperse the positive active material, conductive material, binder and solvent. Therefore, the production efficiency is not good. In addition, it is difficult to evenly disperse the
positive active material, conductive material, binder and solvent. As a result, the secondary battery using the positive plate produced by the method described in the JP-A-2008-84665 does not have sufficient battery characteristics (in particular, high-current discharge characteristics.)

[0009] In particular, when the secondary battery is used as an electric source of an electric vehicle or a hybrid vehicle, a high current (e.g., current equal to or higher than 20C) is discharged frequently. Thus, superior high rate characteristics are required. However, the secondary battery that is made using the positive plate produced by the above-described producing method cannot achieve such a requirement.

SUMMARY OF THE INVENTION

[0010] The present invention provides an electrode plate that reduces the internal resistance of a secondary battery and has improved high-current discharge characteristics, and a method for producing the electrode plate. The present invention also provides a secondary battery using the electrode plate.

[0011] A first aspect of the present invention provides a method for producing an electrode plate. In the method, active material particles and a first conductive material formed of a carbon material are bound with a first binder to form carbon bond active material particles in which the first conductive material are evenly bound over the surface of the active material particles. An electrode mix paste is formed by mixing the carbon bond active material particles, a second conductive material, a second binder and a first solvent with a mixer. The mixer has a cylindrical mixing vessel and a rotary blade that is provided in the mixing vessel, rotates and moves near an inner circumferential surface of the mixing vessel and includes a cylinder portion in which a plurality of holes are formed. To form the electrode mix paste, the carbon bond active material particles, the second conductive material, the second binder and the first solvent put in the mixing vessel are mixed by being pressed by the rotary blade to the inner circumferential surface of the mixing vessel to be extended into a cylindrical thin film. Then, the electrode mix paste is applied on a collector member.
According to the first aspect of the present invention, an electrode plate can be produced that includes an electrode mix in which the carbon bond active material particles and the second conductive material made of a carbon material are evenly dispersed. The carbon bond active material particles are formed of active material particles and the first conductive material evenly bound over the surface of the active material particles via a binder. The electrode mix is formed by drying an electrode mix paste.

In particular, in the producing method, after the process forming the carbon bond active material particles, the mixer having the cylindrical mixing vessel and the rotary blade that is provided in the mixing vessel, rotates and moves near an inner circumferential surface of the mixing vessel and includes a cylinder portion in which a plurality of holes are formed, is used to form the electrode mix paste. The carbon bond active material particles, the second conductive material, the binder and the solvent put in the mixing vessel are mixed by being pressed by the rotary blade to the inner circumferential surface of the mixing vessel to be extended into a cylindrical thin film. Such a mixing process enables the carbon bond active material particles, the second conductive material and the binder to be dispersed in the solvent in a short time.

In addition, such a mixing process prevents at least a portion of the first conductive material forming the carbon bond active material particles fall off the surface of the active material particles. In other words, even after the mixing process, each carbon bond active material particle maintains the condition that the particles of the first conductive materials are evenly bound over the surface of the active material particle.

Accordingly, by applying the electrode mix paste to the collector member and drying the electrode mix paste, the electrode plate including an electrode mix in which carbon bond active material particles, in which the first conductive material is evenly bound over the surface of the active material particles via a binder, and the second conductive materials made of a carbon material are evenly dispersed. With this electrode plate, the internal resistance of a battery is reduced and high-current discharge characteristics improve.
As described above, according to the first aspect of the present invention, an electrode plate that provides a reduced internal resistance of a battery and an improved high-current discharge characteristics of the battery, can be produced. Note that the producing method may be used to produce a positive plate or a negative plate.

In the method for producing the electrode plate, the carbon bond active material particles, the second conductive material, the second binder, and the first solvent may be mixed for five to ten minutes.

In this case, in the mixing process, the mixing is performed only for five to ten minutes. Thus, even if the mixing period is short, the carbon bond active material particles, the second conductive material and the binder are evenly dispersed in the solvent.

Because of the short mixing period, the production efficiency improves. Moreover, at least a portion of the first conductive material, which forms the carbon bond active material particles, is securely prevented from falling off the surface of the positive active material particle.

Further, in the method for producing the electrode plate, the carbon bond active material particles may be formed by a spray dry method.

With the spray dry method, the carbon bond active material particles in which the first conductive material is evenly bound over the entire surface of the active material particles via the binder are appropriately formed. Note that, in the spray dry method, using a spray dryer (e.g., Micro Mist Dryer made by Fujisaki Electric Co. Ltd.), a slurry formed by mixing active material particles, first conductive material, the binder and the solvent is sprayed and the sprayed slurry is dried by hot air to bind the active material particles and the first conductive material with the binder.

Furthermore, in the method for producing the electrode plate, the active material particles and the first conductive material may be bound by the first binder by spraying a liquid formed by mixing the first binder and a second solvent into a basin while the active material particles and the first conductive material are fluidized in the basin, and then drying a mixture of the active material particles, the first conductive...
material and the liquid.

[0023] In the process for forming the carbon bond active material particles, the liquid
formed by mixing a binder and a solvent is sprayed into the basin while the active
material particles and the first conductive material are fluidized in the basin. In other
words, the liquid (sometimes referred to as a liquid binder, hereinafter) formed by mixing
the binder and the solvent is sprayed to the active material particles and the first
conductive material being fluidized in the basin. Due to this, the active material
particles and the first conductive material being fluidized in the basin contact each other
via the liquid binder. Under this condition, the liquid binder is dried to bind the active
material particles and the first conductive material with the binder. According to this
process for forming the carbon bond active material particles, the carbon bond active
material particles in which the first conductive material is evenly bound over the entire
surface of the active material particles via the binder are appropriately formed.

[0024] A second aspect of the present invention provides an electrode plate that
includes an electrode mix and a collector member that supports the electrode mix. The
electrode mix includes carbon bond active material particles including active material
particles and a first conductive material formed of a carbon material. The first
conductive material is evenly bound over a surface of the active material particles. The
electrode mix also includes a second conductive material formed of a carbon material.
The carbon bond active material particles and the second conductive material are evenly
dispersed in the electrode mix.

[0025] According to the second aspect of the present invention, the electrode plate
includes the carbon bond active material particles including active material particles and
the first conductive material that is evenly bound over the entire surface of the active
material particles. In other words, the electrode plate includes, as particles formed by
attaching or binding a conductive material formed of a carbon material on the active
material particle, the carbon bond active material particles in which the first conductive
material is evenly bound by the binder over the entire surface of the active material
particles. Thus, because the first conductive material is evenly bound over the surface
of the active material particles, the internal resistance (in particular, the DC resistance) of
the battery is reduced, and high-current discharge characteristics of the battery are
improved.

[0026] Further, the electrode plate according to the second aspect of the present
invention includes the electrode mix in which the carbon bond active material particles
and the second conductive material are evenly dispersed. Because the carbon bond
active material particles are evenly dispersed in the electrode mix, the internal resistance
of the battery is reduced and the high-current discharge characteristics are improved.
Moreover, because the second conductive material is evenly dispersed between the
carbon bond active material particles that are adjacent to each other, efficient conductive
network among the carbon bond active material particles is formed. Due to this, the
internal resistance is further reduced, and the high-current discharge characteristics can
be further improved.

[0027] Accordingly, with the electrode plate of the second aspect of the present
invention, the internal resistance of the battery is reduced and the high-current discharge
characteristics of the battery are improved. The electrode plate may be a positive plate
or a negative plate.

[0028] A third aspect of the present invention provides a secondary battery that
includes an electrode body having a positive plate, a negative plate and a separator. At
least one of the positive plate and the negative plate is made of the electrode plate
described above.

[0029] According to the third aspect of the present invention, the secondary battery
includes the electrode plate described above as at least one of the positive plate or the
negative plate. Therefore, the internal resistance (in particular, the DC resistance) of the
secondary battery is reduced, and the high-current discharge characteristics of the
secondary battery are improved.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] The foregoing and further objects, features and advantages of the invention
will become apparent from the following description of example embodiments with reference to the accompanying drawings, wherein like numerals are used to represent like elements and wherein:

FIG. 1 is a perspective view of a secondary battery according to first and second examples;
FIG. 2 is a vertical cross-sectional view of the secondary battery;
FIG. 3 is an enlarged view of a positive plate;
FIG. 4 is an enlarged view of a carbon bond active material particle;
FIG. 5 is a flowchart showing a process producing the positive plate;
FIG. 6 is a view showing a mixer used in a stirring and mixing process;
FIG. 7 is a view showing a positive electrode mix paste; and
FIG. 8 is a device used in a process for forming carbon bond active material particles according to the second example of the present invention.

DETAILED DESCRIPTION OF EMBODIMENTS

[0031] A first example of the present invention will be described with reference to drawings. FIG. 1 is a perspective view of a secondary battery 100 according to the first example of the present invention. FIG. 2 is a vertical cross-sectional view of the secondary battery 100. As shown in FIG. 1, the secondary battery 100 is a lithium-ion secondary battery provided with a cylindrical battery case 110.

[0032] As shown in FIG. 2, a battery case 110 is made of a stainless steel plate (SUS314), and has a cylindrical shape with an annular bottom portion Ilia and the thickness DH in a vertical direction. The battery case 110 includes a container 111 and a lid 112.

[0033] The container 111 is formed of an annular bottom portion Ilia and a cylindrical wall portion 111b that vertically extends from the periphery of the bottom portion Ilia and has an upper end bent inward to reduce the diameter thereof. The lid 112 is an annular plate and closes an opening 111c defined by the upper end of the cylindrical wall portion 111b. A gasket 113 is provided between the container 111 and
the lid 112. In the secondary battery 100, the container 111 is a positive external terminal and the lid 112 is a negative external terminal.

[0034] An electrode body 150 and a nonaqueous electrolyte solution (not shown), and the like, are accommodated in the battery case 110. The electrode body 150 has an annular shape, and as shown in FIG. 2, is a stacked electrode in which a positive plate 155 and a negative plate 156 are stacked in the vertical direction DH via a separator 157. The positive plate 155 is electrically connected to the bottom portion IIia of the container 111. The negative plate 156 is electrically connected to the lid 112. The gasket 113 covers the entire inner surface lllb of the cylindrical wall portion 111b of the container 111 and the peripheral portion of the inner surface lllx of the bottom portion IIia. Thus, the gasket 113 insulates the negative plate 156 from the container 111 serving as the positive external terminal.

[0035] The positive plate 155 will be described in detail. As shown in FIG. 3, the positive plate 155 includes a positive collector member 151 made of an aluminum foil and a positive electrode mix 152 applied to the surface of the positive collector member 151. The positive electrode mix 152 includes carbon bond active material particles 154, a second conductive material (acetylene black in the first example) 159, and a binder (not shown, polyvinylidene-fluoride in the first example). In the first example, the carbon bond active material particles 154 and the second conductive material 159 are evenly dispersed.

[0036] As shown in FIG. 4, the carbon bond active material particles 154 include positive active material particles (LiNiO₂ in the first example) 153 and a first conductive material 158 made of a carbon material (acetylene black in the first example). The first conductive material 158 is evenly bound over the entire surface of the positive active material particle 153 via a binder 161.

[0037] In the first example, the negative plate 156 is an annular lithium metal plate. The separator 157 is a porous sheet made of polypropylene and polyethylene. The nonaqueous electrolyte solution is formed by dissolving LiPF₆ at a concentration of 1 mol/liter into a solvent that is formed by mixing polycarbonate and diethyl carbonate in
the ratio of 1:1 by volume. The nonaqueous electrolyte solution is absorbed and supported by the separator 157.

[0038] The method for producing the secondary battery 100 according to the first example will be described hereinafter. First, the method for producing the positive plate 155 will be described. FIG. 5 is a flowchart illustrating a process producing the positive plate according to the first example.

[0039] In step S1, which is a carbon bond active material particle forming process, carbon bond active material particles 154 were formed by a spray dry method. More specifically, a slurry with the solid content of 15 wt% was formed by mixing LiNiO₂ (positive active material particles 153), acetylene black (first conductive material 158), polyvinylidene-fluoride and a solvent (N-methyl-2-pyrolidone). The compounding ratio of LiNiO₂ (positive active material particles 153), acetylene black (first conductive material 158) and polyvinylidene-fluoride was 87:5:1.5 by weight.

[0040] Then, the slurry prepared as described above was sprayed and dried by a spray dryer to obtain carbon bond active material particles 154 in which LiNiO₂ (positive active material particles 153) and acetylene black (first conductive material 158) are bound by polyvinylidene-fluoride (binder 161). The carbon bond active material particle 154 was observed with a scanning electron microscope (SEM). As shown in FIG. 4, the particles of the first conductive material 158, formed of the carbon material (acetylene black), were bound evenly over the entire surface of the positive active material particles (LiNiO₂) 153.

[0041] In the first example, Micro Mist Dryer (MDL-050M) made by Fujisaki Electric Co. Ltd. was used as the spray dryer. Also, in the first example, in the spray dryer, the inlet temperature of the heated air was set to 220 °C, and the heated air (hot air) was supplied into the drying chamber. Further, the amount of compressed air supplied to the spray nozzle and the amount of slurry supplied to the spray nozzle were respectively set to 50 L/min and 10 mL/min, and the slurry was sprayed from the spray nozzle.

[0042] Next, in step S2, which is a stirring and mixing process, a positive electrode
mix paste 30 (see FIG. 7) is formed. More specifically, with a mixer (T.K.Filmics made by Primix Corporation, see FIG. 6) 20, the carbon bond active material particles 154, the second conductive material (acetylene black) 159, a binder (polyvinylidene-fluoride) 163 and a solvent (N-methyl-2-pyrolidone) 162 were stirred and mixed to obtain the positive electrode mix paste 30.

[0043] In the first example, the positive electrode mix paste 30 was formed such that the compounding ratio of the carbon bond active material particle 154, the second conductive material 159 and the binder 163 was 93.5:5:1.5 by weight. Further, the acetylene black (the second conductive material 159) supplied into the mixer 20 was generally the same as the acetylene black (the first conductive material 158) used in step Sl. Further, the binder (polyvinylidene-fluoride) 163 supplied into the mixer 20 was generally the same as polyvinylidene-fluoride used to form the slurry in step Sl.

[0044] The mixer (T.K.Filmics made by Primix Corporation) 20 used in the first example will be described hereinafter. As shown in FIG. 6, the mixer 20 is provided with a mixing vessel 1 having a cylindrical inner circumferential surface 1b, and an outer vessel 2 surrounding the mixing vessel 1. A cooling water tank 3 is formed between the mixing vessel 1 and the outer vessel 2. Cooling water is supplied to the cooling water tank 3 through an inflow pipe 4, absorbs friction heat caused by mixing, and is discharged from an effluent pipe (not shown). Feed pipes 5 and 6 respectively having valves 5a and 6a are connected to the bottom portion of the mixing vessel 1. The feed pipes 5 and 6 may be used to supply raw materials, or may be used to discharge the product during batch production.

[0045] A flash board 7 is disposed at the upper portion of the mixing vessel 1, and a upper vessel 8 is attached on the flash board 7. An effluent pipe 9 is connected to the upper vessel 8. The upper vessel 8 has a lid 8a and a cooling water tank 8b, and is used when the product is continuously produced. In such a case, the flash board 7 is replaced with the one having an opening whose inner diameter is larger than that of shown in FIG. 6, raw materials are continuously supplied from the feed pipes 5 and 6, and the liquid after mixing continuously flows out through the flash board 7. The cooling water tank
8b is connected to a water passage to be parallel to the cooling water tank 3.

[0046] A rotating shaft 10 penetrates the lid 8a so as to keep the upper vessel airtight, and is arranged coaxially with the mixing vessel 1. The rotating shaft 10 is driven by a motor provided at the upper portion thereof to rotate at high speed. A rotary blade 11 is attached to the lower end of the rotating shaft 10.

[0047] The rotary blade 11 has a cylindrical portion 12. The cylindrical portion 12 is attached to the rotating shaft 10 with a boss 14 via an arm 13. The cylindrical portion 12 has many holes 12a. The arm 13 has an appropriate number of communicating holes 13a.

[0048] In the first example, the carbon bond active material particles 154, the second conductive material (acetylene black) 159, the binder 163 and the solvent 162 were supplied into the mixing vessel 1 through the feed pipes 5 and 6 of the mixer 20, and were stirred and mixed in the following manner. FIG. 6 shows a state in which the carbon bond active material particles 154, the second conductive material 159, the binder 163 and the solvent 162 (collectively referred to as raw materials L) are placed in the mixing vessel 1.

[0049] In the first embodiment, the raw materials L were pressed in a radial direction by the high speed revolution of the rotary blade 11, and rotated while tightly contacting the inner circumferential surface 1b of the mixing vessel 1 to be a cylindrical thin-film due to the centrifugal force generated by the high speed revolution of the rotary blade 11. At this moment, the raw materials L were mixed by a difference of speeds between the raw materials L and the inner circumferential surface 1b of the mixing vessel 1. Further, the rotation of holes 12a applied a strong rotating force to the raw materials L flowing into the holes 12a. Thus, the raw materials L further flow into the gap S from the holes 12a, and the pressure of the raw materials L increased. Further, the raw material L flowing into the gap S from the holes 12a disrupted the flow of raw materials L located in the gap S, and enhanced the mixing operation. By stirring and mixing as described above, the carbon bond active material particles 154, the second conductive material 159 and the binder 163 can be evenly dispersed in the solvent 162 in a short time. Thus, the
positive electrode mix paste 30 was obtained.

[0050] In the first example, the raw materials L were stirred and mixed by the mixer 20 only for ten minutes. The carbon bond active material particles 154, the second conductive material 159, and the binder 163 can be evenly dispersed in the solvent 162, even if the raw materials L are mixed for such a short period of time. FIG. 7 shows the positive electrode mix paste 30 formed as described above contained in a container 35. When the positive electrode mix paste 30 was observed, as shown in FIG. 7, the carbon bond active material particles 154, the second conductive material 159, it was found that the binder 163 were evenly dispersed in the solvent 162.

[0051] Because the raw materials L are stirred and mixed for such a short period of time (10 minutes in the first example), the production efficiency improves. Moreover, at least a portion of the first conductive material 158, which forms the carbon bond active material particles 154, is securely prevented from falling off the surface of the positive active material particle 153.

[0052] Next, the process proceeds to step S3, which is an application process. In step S3, the positive electrode mix paste 30 was applied to the surface of an aluminum foil. Then, the process proceeds to step S4, in which the positive electrode mix paste 30 applied to the surface of the aluminum foil was pressed and compressed, and stamped out along with the aluminum foil into a disc. Then, the process proceeds to step S5, in which the positive electrode mix paste 30 was dried to obtain the positive plate 155 (see FIG. 3) having the positive electrode mix 152. When the positive electrode mix 152 was observed with an SEM, the carbon bond active material particles 154 and the second conductive material 159 were evenly dispersed.

[0053] Incidentally, whether, in step S2 (the stirring and mixing process), at least a portion of the first conductive material 158, which forms the carbon bond active material particle 154, falls off the surface of the positive active material particle 153 may be determined as follows.

[0054] In the carbon bond active material particles 154, the binder (PVDF) 161 that binds the positive active material particles 153 and the first conductive material 158 may
change its nature due to the hot air (high-temperature dry gas) of the spray dryer. More specifically, the cross-linking reaction progresses and the degree of crystallization increases. Meanwhile, in step S2 (the stirring and mixing process), the binder (PVDF) supplied into the mixer 20 separate from the carbon bond active material particles 154 does not change its nature due to the stirring and mixing. Accordingly, the binder 161 and the binder 163 are different from each other in their cross-linked structure and the degree of crystallization.

[0055] When a portion of the first conductive material 158 bound to the surface of the positive active material particle 153 by the binder 161 falls off the surface of the positive active material particle 153, a portion of the binder 161 also falls off together with the first conductive material 158. Therefore, it is possible to determine whether at least a portion of the first conductive material 158 forming the carbon bond active material particle 154 falls off the surface of the positive active material particle 153 by examining the binder that is not a part of the carbon bond active material particle 154, i.e., that does not bind the positive active material particle 153 and the first conductive material 158.

[0056] In other words, if, in the examined binder, greatly different cross-linked structures or greatly different degrees of crystallization exist, it may be concluded that both the binder 161 and the binder 163 exist together. In this case, it may be determined that at least a portion of the first conductive material 158 forming the carbon binding active material particle 154 falls off the surface of the positive active material particle 153.

[0057] When the carbon bond active material particles 154 included in the positive electrode mix 152 was observed with an SEM, similar to the carbon bond active material particles 154 formed in step S1, the first conductive material (acetylene black) 158 was bound evenly over the entire surface of the positive active material particle (LiNiO₂) 153 (see FIG. 4). Thus, in step S2 (the stirring and mixing process) of the first example, the first conductive material 158 bound to the surface of the positive active material particle 153 in step S1 is prevented from falling off the surface of the positive active material
particle 153. In other words, it can be concluded that even after the stirring and mixing process (the process in step S2) is performed, each carbon bond active material particle 154 maintains the state in which the first conductive material 158 is bound evenly over the entire surface of the positive active material particle 153.

[0058] Next, an electrode body 150 was formed by stacking the positive plate 155, the negative plate (lithium metal plate) 156 and the separator 157. Further, the container 111 and the lid 112 made of stainless steel plate (SUS314) were prepared. Then, the gasket 113 and the electrode body 150 were placed in the container 111, and the nonaqueous electrolyte solution was injected into the container 111. Note that the nonaqueous electrolyte solution was formed by dissolving LiPF$_6$ at a concentration of 1 mol/liter into a solvent that was formed by mixing polycarbonate and diethyl carbonate in the ratio of 1:1 by volume. Then, the lid 112 closed the opening 111c of the container 111 to complete the secondary battery 100 (see FIGs. 1 and 2).

[0059] As comparative examples, two kinds of secondary batteries (comparative examples 1 and 2) using the positive plates produced by conventional methods were prepared. More specifically, in the comparative example 1, the positive plate was made by the producing method described in JP-A-2008-84665. In detail, the positive active material (LiNiO$_2$) 153, acetylene black, a binder (PVDF) and a solvent (NMP) were kneaded using a high shear dispersion device (a planetary mixer in the first comparative example) to form the positive electrode mix paste. The compounding ratio of positive active material particles (LiNiO$_2$) 153, acetylene black and the binder (PVDF) was 87:10:3 by weight.

[0060] In this comparative example 1, it took about four to five hours to disperse the positive active material 153, acetylene black and the binder (PVDF) into the solvent (NMP) 162 by kneading them with the planetary mixer. Then, the positive electrode mix paste was applied to the surface of an aluminum foil, pressed, shaped and dried to obtain a disc-shaped positive plate having the same dimension as that of the first example. Then, in the same manner as the first example, a secondary battery of the comparative example 1 was made using the positive plate.
In the comparative example 2, a positive plate was formed with reference to the producing method described in JP-A-2003-173777. More specifically, similar to the step S1 of the first example, the carbon bond active material particles 154 were formed by the spray dryer (Micro Mist Dryer (MDL-050M) made by Fujisaki Electric Co. Ltd.) Note that, similar to the first example, the compounding ratio of LiNiO₂ (positive active material particles 153), acetylene black (first conductive material 153) and PVDF (binder) was 87:5:1.5 by weight.

Then, a positive electrode mix paste was formed by kneading the carbon bond active material particles 154, acetylene black (second conductive material 159), the binder (PVDF) 163 and the solvent (NMP) 162 by the planetary mixer. In the comparative example 2, it took about two to three hours to evenly disperse the carbon bond active material particles 154, acetylene black and the binder (PVDF) 163 into the solvent (NMP) 162 by kneading them with the planetary mixer. Similar to the first example, the compounding ratio of the carbon bond active material particle 154, the second conductive material (acetylene black) 159 and the binder (PVDF) 163 was 93.5:5:1.5 by weight.

Then, the positive electrode mix paste was applied to the surface of an aluminum foil, pressed, shaped and dried to obtain a disc-shaped positive plate having the same dimension as that of the first example. Then, in the same manner as the first example, a secondary battery of the comparative example 2 was made using the positive plate. In the comparative examples 1 and 2, the positive plate was formed by mixing the positive active material 153, acetylene black (conductive material) and the binder (PVDF), the respective amounts of which were the same as those in the first example.

The battery characteristics of the secondary battery 100 of the first example and the secondary batteries of the comparative examples 1 and 2 were evaluated.

First, the high-current load discharge characteristics of each secondary battery was evaluated. More specifically, each secondary battery was charged at constant current of 1C until the battery voltage became 4.1V, and then charged with the constant voltage of 4.1V until the secondary battery was fully charged. Then, the secondary...
battery is discharged at constant current of 1C until the battery voltage became 3.0V. At this time, the discharged capacity D1 (mAh/g) per gram of the positive active material was obtained by dividing the product of the current value and the discharge duration by the mass (g) of the positive active material (LiNiO2) 153. Note that 1C is a current value to charge the secondary battery to the theoretical electric capacity in one hour. The theoretical electric capacity is the maximum value that the positive active material included in the secondary battery can theoretically store.

[0066] Alternatively, each secondary battery was charged at the constant current of 20C until the battery voltage became 4.1V, and then charged with the constant voltage of 4.1 V until the secondary battery was fully charged. Then, the secondary battery was discharged at constant current of 20C until the battery voltage became 3.0V. At this time, the discharged capacity D2 (mAh/g) per gram of the positive active material was obtained by dividing the product of the current value and the discharge duration by the mass (g) of the positive active material (LiNiO2) 153. Then, D2/D1 was calculated as an evaluation criterion of the high-current load discharge characteristics. The results are shown in TABLE 1.

<table>
<thead>
<tr>
<th></th>
<th>D1(mAh/g)</th>
<th>D2(mAh/g)</th>
<th>D2/D1</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Example</td>
<td>129.37</td>
<td>94.53</td>
<td>0.73</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>125.45</td>
<td>70.67</td>
<td>0.56</td>
</tr>
<tr>
<td>Comparative Example 2</td>
<td>140.53</td>
<td>85.78</td>
<td>0.61</td>
</tr>
</tbody>
</table>

[0067] The values of D1 were compared among the first example and the comparative examples 1 and 2. In the secondary battery of the comparative example 1, D1 was 125.45mAh/g, and in the secondary battery of the comparative example 2, D1 was 140.53mAh/g. On the other hand, in the secondary battery 100 of the first example, D1 was 129.37mAh/g, which is a value between the comparative example 1 and the comparative example 2. Thus, there was no significant difference in the discharged capacity when discharged at the current of 1C among the first example, comparative example 1 and the comparative example 2.
The values of D2 were compared among the first example and the comparative examples 1 and 2. In the secondary battery of the comparative example 1, D2 was 70.67 mAh/g. In the secondary battery of the comparative example 2, D2 was 85.78 mAh/g. Both were significantly reduced from the respective values of D1.

More specifically, in the comparative examples 1 and 2, the value of D2 was reduced by about 55 mAh/g, compared to the value of D1. On the other hand, in the secondary battery 100 of the first example, D2 was 94.53 mAh/g, which is reduced only by 35 mAh/g, compared to the value of D1. Thus, D2 of the secondary battery of the first example was larger than the comparative examples 1 and 2.

Further, the values of D2/D1 were compared among the first example and the comparative examples 1 and 2. In the secondary battery of the comparative example 1, D2/D1 was 0.56. In the secondary battery of the comparative example 2, D2/D1 was 0.61. Thus, in the comparative examples 1 and 2, the discharged capacity when discharged at a high current of 20C was reduced by about 40%, compared to the discharged capacity when discharged at a current of 1C.

On the contrary, in the secondary battery 100 of the first example, D2/D1 was 0.73, which is greater than that of the comparative examples 1 and 2. Thus, in the first example, the discharged capacity when discharged at a high current of 20C was reduced only by 27%, compared to the discharged capacity when discharged at a current of 1C. According to the result described above, it may be concluded that the secondary battery 100 of the first example is superior to the secondary batteries of the comparative examples 1 and 2, in the high-current discharge characteristics.

This is because the secondary battery 100 of the first example is provided with the positive plate 155 including the carbon bond active material particles 154 that has the positive active material particles 153 and the first conductive material particles 158 evenly bound to the entire surface of the positive active material particles 153. By evenly binding the first conductive material 158 to the entire surface of the positive active material particles 153, the internal resistance of the battery is reduced, and the high-current discharge characteristics are improved.
Moreover, this is because the electrode plate (positive plate) 155 of the first example has the positive electrode mix 152 in which the carbon bond active material particles 154 and the second conductive material 159 are evenly dispersed. Because the carbon bond active material particles 154 are evenly dispersed in the positive electrode mix 152, the internal resistance of the battery is reduced and the high-current discharge characteristics are improved. In addition, because the second conductive material 159 is evenly dispersed between the carbon bond active material particles 154 that are adjacent to each other, efficient conductive network among the carbon bond active material particle 154 is formed, the internal resistance is further reduced, and the high-current discharge characteristics can be further improved.

Incidentally, the positive electrode mix of the comparative example 1 was observed with an SEM. The positive active material particles 153 and the conductive material (acetylene black) were not evenly dispersed. Thus, it may be concluded that efficient conductive network is not formed, and as a result, sufficient battery characteristics (in particular, the high-current discharge characteristics) cannot be obtained. In addition, because it takes four to five hours to knead the raw materials with the planetary mixer, the production efficiency is not good.

When the carbon bond active material particles included in the positive electrode mix of the comparative example 2 were also observed with an SEM, the first conductive material particles 158 were unevenly bound to the surface of the positive active material particle 153. More specifically, the number of particles of the first conductive material 158 bound to the surface of the positive active material particle 153 was significantly smaller, compared to the carbon bond active material particles 154 of the first example.

In view of the above, it may be concluded that in the producing method of the comparative example 2, when the carbon bond active material particles 154, the acetylene black, the binder and the solvent are kneaded by the planetary mixer, a portion of the first conductive material 158 falls off the surface of the positive active material particles 153 forming the carbon bond active material particles 154. Therefore, the internal resistance
of the secondary battery of the comparative example 2 is larger than that of the secondary battery 100 of the first example, and the high-current discharge characteristics are inferior to that of the secondary battery 100.

[0076] Impedance of each secondary battery was measured by a Solartron 1255WB electrochemical measuring system (a frequency analyzer + a potentiogalvanostat). More specifically, the impedance was measured as follows. While a potential amplitude of 5 mV was given to each secondary battery with battery voltage of 3.8V, the measurement frequency was varied in the range of 0.01 Hz - 100 kHz. The impedance was measured from a synchronized current value. A DC resistance (Ω) and a reaction resistance (Ω) were calculated from the obtained impedance. The results are shown in TABLE 2.

<table>
<thead>
<tr>
<th>TABLE 2</th>
<th>DC Resistance</th>
<th>Reaction Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Example</td>
<td>1.48</td>
<td>7.59</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>4.40</td>
<td>10.45</td>
</tr>
<tr>
<td>Comparative Example 2</td>
<td>2.53</td>
<td>9.16</td>
</tr>
</tbody>
</table>

[0077] The DC resistances were compared among the secondary batteries of the comparative examples 1 and 2 and the secondary battery 100 of the first example. As shown in TABLE 2, the DC resistances in the comparative examples 1 and 2 were respectively 4.40Ω and 2.53Ω. On the other hand, the DC resistance in the first example was 1.48Ω, which is significantly smaller than those in the comparative examples 1 and 2.

[0078] Further, the reaction resistances were compared among the secondary batteries of the comparative examples 1 and 2 and the secondary battery 100 of the first example. As shown in TABLE 2, the reaction resistances in comparative examples 1 and 2 were respectively 10.45Ω and 9.16Ω. On the other hand, the reaction resistance in the first example was 7.59Ω, which is smaller than those in the comparative examples 1 and 2. Thus, the internal resistance (in particular, the DC resistance) of the secondary battery 100 of the first example is smaller than those of the secondary batteries of the
comparative examples 1 and 2.

[0079] The internal resistance of the secondary battery 100 of the first example is small, because the secondary battery 100 is provided with the positive plate 155 including carbon bond active material particles 154 that have positive active material particles 153 and the first conductive material particles 158 evenly bound over the entire surface of the positive active material particles 153. Thus, the internal resistance of the battery can be reduced by evenly binding the first conductive material 158 to the entire surface of the positive active material particles 153.

[0080] Further, another factor causing the reduction of the internal resistance may be that the electrode plate (positive plate) 155 of the first example includes the positive electrode mix 152 in which the carbon bond active material particles 154 and the second conductive material 159 are evenly dispersed. Thus, because the carbon bond active material particles 154 are evenly dispersed in the positive electrode mix 152, the internal resistance of the battery is reduced. In addition, because the second conductive material 159 is evenly dispersed between the carbon bond active material particles 154 that are adjacent to each other, efficient conductive network among the carbon bond active material particles 154 is formed, and the internal resistance is further reduced.

[0081] A second example of the present invention will be described with reference to drawings. The second example is different from the first example in the method producing the positive plate (more specifically, the carbon bond active material particles); but the rest is generally the same. Accordingly, those points different from the first example will be mainly described hereinafter, and the explanation of the rest will be omitted or simplified.

[0082] As shown by the bracketed reference numerals in FIGs. 1 and 2, only the positive plate of the secondary battery 200 of the second example is different from that of the secondary battery 100 of the first example. Other portions are the same between the secondary batteries of first and second examples. As shown by the bracketed reference numerals in FIG. 3, in the positive plate 255 of the secondary battery 200, only the positive electrode mix (more specifically, the carbon bond active material particle) is
different from that of the secondary battery 100 of the first example, and the rest is the same. Similar to the positive electrode mix 152 of the first example, the carbon bond active material particles 254 and the second conductive material 159 are evenly dispersed in the positive electrode mix 252 of the second example.

[0083] As shown in FIG 4, the carbon bond active material particles 254 has the positive active material particles (LiNiO₂, in the second example as well) 153 and the first conductive material 158 made of carbon material (acetylene black in the second example). The first conductive material 158 is evenly bound over the entire surface of the positive active material particle 153 via the binder (PVDF) 261.

[0084] The method for producing the secondary battery 200 according to the second example will be described. First, the method for producing the positive plate 255 will be described. FIG. 5 is a flowchart showing the process for producing the positive plate according to the second example.

[0085] In step T1, which is a carbon bond active material particle forming process, the carbon bond active material particles 254 were formed with a processing device (Agglomerator AMG-MINI made by Hosokawa Micron Corporation in the second example) 60. The method for forming the carbon bond active material particles 254 of the second example will be described in detail with reference to FIG. 8. FIG. 8 is a schematic diagram of the processing device 60 according to the second example.

[0086] The processing device 60 includes a processing vessel 65 and a powder-supply portion 61 that stores fine particles (positive active material and conductive material in the second example) and supplies the fine particles into the processing basin 65. The processing device 60 also has a binder container 62 that stores a liquid binder, which is a mixture of a binder and a solvent. Further, an air filter 66 and a heater 67 are connected to the processing basin 65 via an inlet pipe. Air inducted from the exterior through the air filter 66 is heated by the heater 67, and the heated air is supplied into the processing basin 65. Further, a rotor 64 is provided in the processing basin 65. Rotation (Revolution) of the rotor 64 generates an air current in the processing basin 65, and thus fluidizes the fine particles (a positive active material and a
conductive material in the second example) supplied to the processing basin 65 in the processing basin 65. Moreover, a nozzle 63 that sprays the liquid binder is provided in the processing basin 65.

[0087] In the second example, the powder-supply portion stored the fine particles in which LiNiO₂ (positive active material particles 153) and acetylene black (first conductive material 158) are mixed. Further, the binder container 62 stored a liquid of a mixture of PVDF (binder) and NMP (solvent). In the second example, the ratio of LiNiO₂ (positive active material particles 153), acetylene black (first conductive material 158) and PVDF (binder) was 87:5:1.5 by weight.

[0088] While the rotor 64 kept rotating, the power-supply portion 61 supplied LiNiO₂ (positive active material particles 153) and acetylene black (the first conductive material 158) into the processing basin 65, so as to fluidize the positive active material particles 153 and the first conductive material 158 in the processing basin 65. Under this condition, the liquid binder (liquid mixture of a binder and a solvent) was sprayed into the processing basin 65 through the nozzle 63. At this time, the positive active material particles 153 and the first conductive material 158 being fluidized in the processing basin 65 contacted each other via the liquid binder. At this time, because the temperature in the processing basin 65 was high (about 150°C, for example), the liquid binder is immediately dried (i.e., the solvent was evaporated). Thus, the positive active material particles 153 and the first conductive material 158 were bound with the binder (PVDF).

[0089] In the second example, the carbon bond active material particles 254 in which LiNiO₂ (positive active material particles 153) and acetylene black (the first conductive material 158) are bound via polyvinylidene-fluoride (binder 261) were thus obtained. The carbon bond active material particle 254 was observed with a scanning electron microscope (SEM). As shown in FIG. 4, the first conductive material particles 158, formed of the carbon material (acetylene black), was bound evenly over the entire surface of the positive active material particles (LiNiO₂) 153.

[0090] In the second example, in the processing device (Agglomerator AMG-MINI
made by Hosokawa Micron Corporation), the heated air (hot air) was supplied into the processing basin 65 while setting the amount of air inducted from the exterior to the air filter 66 is to 150m³/min, and setting the inlet temperature of the heated air to 150°C. Further, the amount of compressed air supplied to the nozzle 63 was set to 20L/min, and the amount of liquid binder supplied to the nozzle 63 was set to 1.2g/min to spray the liquid binder from the nozzle 63.

[0091] Next, as shown in FIG. 5, in step S2, which is an stirring and mixing process, positive electrode mix paste 230 (see FIG. 7) was formed in a manner similar to the first example. In the second example as well as the first example, the raw materials L (including carbon bond active material particles 254, the second conductive material 159, the binder 163 and solvent 162) were stirred and mixed by the mixer 20 only for ten minutes. The carbon bond active material particles 254, the second conductive material 159, the binder 163 were evenly dispersed in the solvent 162, even if the raw materials L were mixed for such a short period of time. More specifically, when the positive electrode mix paste 230 was observed, the carbon bond active material particles 254, the second conductive material 159, the binder 163 were evenly dispersed in the solvent 162 as shown in FIG. 7.

[0092] Because the raw materials L are stirred and mixed for such a short period of time (10 minutes in the second example), the production efficiency improves. Moreover, at least a portion of the first conductive material 158, forming the carbon bond active material particles 254, can be securely prevented from falling off the surface of the positive active material particle 153.

[0093] Next, the process proceeds to step S3, which is an application process. In step S3, the positive electrode mix paste 230 was applied to the surface of an aluminum foil. Then, similar to the first example, the process of steps S4 and S5 were performed to obtain the positive plate 255 (see FIG. 3) having the positive electrode mix 252. When the positive electrode mix 252 was observed with an SEM, the carbon bond active material particles 254 and the second conductive material 159 were evenly dispersed.

[0094] Incidentally, whether, in step S2 (the stirring and mixing process), at least a
portion of the first conductive material 158, forming the carbon bond active material particle 254, falls off the surface of the positive active material particle 153 may be determined as follows.

[0095] In the carbon bond active material particles 254, the binder (PVDF) 261 that binds the positive active material particle 153 and the first conductive material 158 may change its nature because the temperature in the processing basin 65 of the processing device 60 is high (e.g., about 150°C). More specifically, the cross-linking reaction progresses and the degree of crystallization increases. Meanwhile, in step S2 (the stirring and mixing process), the binder (PVDF) 163 supplied into the mixer 20 separate from the carbon bond active material particles 254 does not change its nature by stirring and mixing. Accordingly, the binder 261 and the binder 163 are different from each other in their cross-linked structure and the degree of crystallization.

[0096] When a portion of the first conductive material 158 bound to the surface of the positive active material particle 153 by the binder 261 falls off the surface of the positive active material particle 153, a portion of the binder 161 also falls off together with the first conductive material 158. Therefore, it is possible to determine whether at least a portion of the first conductive material 158 forming the carbon bond active material particle 254 falls off the surface of the positive active material particle 153 by examining the binder that is not a part of the carbon bond active material particle 254, i.e., that does not bind the positive active material particle 153 and the first conductive material 158.

[0097] In other words, if, in the examined binder, greatly different cross-linked structures or greatly different degrees of crystallization exist, it may be concluded that both the binder 261 and the binder 163 exist together. In this case, it may be determined that at least a portion of the first conductive material 158 forming the carbon binding active material particle 254 falls off the surface of the positive active material particle 153.

[0098] The carbon bond active material particles 254 included in the positive electrode mix 252 was observed with an SEM. Similar to the carbon binding active
material particles 254 formed in step T1, the first conductive material (acetylene black) 158 was bound evenly over the entire surface of the positive active material particle (LiNiO$_2$) 153 (see FIG. 4). Thus, in step S2 (the stirring and mixing process) of the second example, the first conductive material 158 bound to the surface of the positive active material particle 153 in step T1 is prevented from falling off the surface of the positive active material particle 153. In other words, it can be concluded that even after the stirring and mixing process (the process in step S2) is performed, each carbon bond active material particle 254 maintains the state in which the first conductive material particles 158 are bound evenly over the entire surface of the positive active material particle 153.

[0099] Then, in the same manner as the first example, the secondary battery 200 (see FIGs. 1 and 2) was produced using the positive plate 255 formed as described above. Note that, in the second example as well as the first example, the nonaqueous electrolyte solution was formed by dissolving LiPF$_6$ at a concentration of 1 mol/liter into a solvent that was formed by mixing polycarbonate and diethyl carbonate in the ratio of 1:1 by volume.

[0100] As comparative examples, two kinds of secondary batteries (comparative examples 1 and 3) produced by conventional methods were prepared. The secondary battery of comparative example 1 has been described above.

[0101] In the comparative example 3, the positive plate was made as follows. First, similar to step S2 of the second example, the carbon bond active material particles 254 were formed with the processing device 60 (Agglomeram AMG-MINI made by Hosokawa Micron Corporation). Similar to the second example, the compounding ratio of the positive active material particles (LiNiO$_2$) 153, acetylene black and the binder (PVDF) was 87.5:1.5 by weight.

[0102] Then, the carbon bond active material particles 254, acetylene black (the second conductive material 159), the binder (PNDF) 163 and the solvent (NMP) 162 were kneaded with the planetary mixer to form the positive electrode mix paste. In the comparative example 3, it took about two to three hours to evenly disperse the carbon
bond active material particles 254, acetylene black and the binder (PVDF) 163 into the solvent (NMP) 162 by kneading them with the planetary mixer. Similar to the second example, the compounding ratio of the carbon bond active material particle 254, the second conductive material (acetylene black) 159 and the binder (PVDF) 163 was 93.5:5:1.5 by weight.

[0103] Then, the positive electrode mix paste was applied to the surface of an aluminum foil, pressed, shaped and dried to obtain a disc-shaped positive plate having the same dimension as that of the second example. Then, in the same manner as the second example, a secondary battery of the comparative example 3 was made using the positive plate. In the comparative examples 1 and 3, the positive plate was produced by mixing the positive active material 153, acetylene black (conductive material) and the binder (PVDF), the respective amounts of which were the same as those in the second example.

[0104] The battery characteristics of the secondary battery 200 of the second example and the secondary batteries of the comparative examples 1 and 3 were evaluated.

[0105] First, high-current load discharge characteristics of each secondary battery were evaluated. More specifically, each secondary battery was charged at constant current of 1C until the battery voltage became 4.1V, and then charged with the constant voltage of 4.1V until the secondary battery was fully charged. Then, the secondary battery was discharged at the constant current of 1C until the battery voltage became 3.0V. At this time, the discharged capacity D1 (mAh/g) per gram of the positive active material was obtained by dividing the product of the current value and the discharge duration by the mass (g) of the positive active material (LiNiO₂) 153.

[0106] Alternatively, each secondary battery was charged at the constant current of 2OC until the battery voltage became 4.1V, and then charged with the constant voltage of 4.1V until the secondary battery was fully charged. Then, the secondary battery was discharged at the constant current of 2OC until the battery voltage became 3.0V. At this time, the discharged capacity D2 (mAh/g) per gram of the positive active material was obtained by dividing the product of the current value and the discharge duration by the mass (g) of the positive active material (LiNiO₂) 153. Then, D2/D1 was calculated as
an evaluation criterion of the high-current load discharge characteristics. The results are shown in TABLE 3.

<table>
<thead>
<tr>
<th></th>
<th>D1(mAh/g)</th>
<th>D2(mAh/g)</th>
<th>D2/D1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second Example</td>
<td>135.5</td>
<td>104.02</td>
<td>0.77</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>125.45</td>
<td>70.67</td>
<td>0.56</td>
</tr>
<tr>
<td>Comparative Example 3</td>
<td>137.19</td>
<td>79.82</td>
<td>0.58</td>
</tr>
</tbody>
</table>

[0107] The values of D1 were compared among the second example and the comparative examples 1 and 3. In the secondary battery of the comparative example 1, D1 was 125.45mAh/g, and in the secondary battery of the comparative example 3, D1 was 137.19mAh/g. On the other hand, in the secondary battery 200 of the second example, D1 was 135.5mAh/g, which is a value between the comparative example 1 and the comparative example 3. Thus, there was no significant difference in the discharged capacity when discharged at the current of 1C among the second example, comparative example 1 and the comparative example 3.

[0108] The values of D2 were compared among the second example and the comparative examples 1 and 3. In the secondary battery of the comparative example 1, D2 was 70.67mAh/g. In the secondary battery of the comparative example 3, D2 was 79.82mAh/g. Both were significantly reduced from the respective values of D1. More specifically, in the comparative examples 1 and 3, the value of D2 was reduced by about 55mAh/g, compared to the value of D1. On the other hand, in the secondary battery 200 of the second example, D2 was 104.02mAh/g, which is reduced only by 30mAh/g, as compare to the value of D1. Thus, D2 of the secondary battery of the second example was larger than that of the comparative example 1 by about 35mAh/g, and was larger than that of the comparative example 3 by about 25mAh/g.

[0109] Further, the values of D2/D1 were compared among the second example and the comparative examples 1 and 3. In the secondary battery of the comparative example 1, D2/D1 was 0.56. In the secondary battery of the comparative example 3, D2/D1 was 0.58. Thus, in the comparative examples 1 and 3, the discharged capacity when
discharged at a high current of 20C was reduced by more than 40%, compared to the discharges capacity when discharged at a current of 1C.

[0110] On the contrary, in the secondary battery 200 of the second example, D2/D1 was 0.77, which is greater than those of the comparative examples 1 and 3. Thus, in the second example, the discharged capacity when discharged at a high current of 20C was reduced only by 23%, compared to the discharged capacity when discharged at a current of 1C. According to the result described above, it may be concluded that the secondary battery 200 of the second example is superior to the secondary batteries of the comparative examples 1 and 3, in the high-current discharge characteristics.

[0111] This is because the secondary battery 200 of the second example is provided with the positive plate 255 including the carbon bond active material particles 254 that has the positive active material particles 153 and the first conductive material 158 evenly bound to the entire surface of the positive active material particles 153. By evenly binding the first conductive material 158 to the entire surface of the positive active material particles 153, the internal resistance of the battery is reduced, and the high-current discharge characteristics are improved.

[0112] Moreover, this is because the electrode plate (positive plate) 255 of the second example has the positive electrode mix 252 in which the carbon bond active material particles 254 and the second conductive material 159 are evenly dispersed. Because the carbon bond active material particles 254 are evenly dispersed in the positive electrode mix 252, the internal resistance of the battery is reduced and the high-current discharge characteristics are improved. In addition, because the second conductive material 159 is evenly dispersed between the carbon bond active material particles 254 that are adjacent to each other, efficient conductive network among the carbon bond active material particle 254 is formed, the internal resistance is further reduced, and the high-current discharge characteristics can be further improved.

[0113] Incidentally, the carbon bond active material particle included in the positive electrode mix of the comparative example 3 was observed with an SEM. The first conductive material was unevenly bound to the surface of the positive active material
particles 153. Thus, in the producing method of the comparative example 3, when the carbon bond active material particle 254, acetylene black, the binder and the solvent are kneaded with the planetary mixer, a portion of the first conductive material 158 falls off the surface of the positive active material particle 153 forming the carbon bond active material particle 254. Accordingly, the internal resistance of the secondary battery of the comparative example 3 is larger than that of the secondary battery 200 of the second example, and the high-current discharge characteristics thereof are inferior to those of the secondary battery 200.

[0114] Impedance of each secondary battery was measured by a Solartron 1255WB electrochemical measuring system (a frequency analyzer + a potentiogalvanostat). More specifically, the impedance was measured as follows. While a potential amplitude of 5 mV was given to each secondary battery with battery voltage of 3.8V, the measurement frequency was varied in the range of 0.01Hz - 100kHz. The impedance was measured from a synchronized current value. A DC resistance and a reaction resistance were calculated from the obtained impedance. The results are shown in TABLE 4.

<table>
<thead>
<tr>
<th></th>
<th>DC Resistance</th>
<th>Reaction Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second Example</td>
<td>1.81</td>
<td>9.28</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>4.40</td>
<td>10.45</td>
</tr>
<tr>
<td>Comparative Example 3</td>
<td>2.82</td>
<td>10.23</td>
</tr>
</tbody>
</table>

[0115] The DC resistances were compared among the secondary batteries of the comparative examples 1 and 3 and the secondary battery 200 of the second example. As shown in TABLE 4, the DC resistances in comparative examples 1 and 3 were respectively 4.40Ω and 2.82Ω. On the other hand, the DC resistance in the second example was 1.81Ω, which is significantly smaller than those in the comparative examples 1 and 3.

[0116] Further, the reaction resistances were compared among the secondary batteries of the comparative examples 1 and 3 and the secondary battery 200 of the
second example. As shown in TABLE 4, the reaction resistances in comparative examples 1 and 3 were respectively 10.45Ω and 10.23Ω. On the other hand, the reaction resistance in the second example was 9.28Ω, which is smaller than those in the comparative examples 1 and 3. Thus, the internal resistance (in particular, the DC resistance) of the secondary battery 200 of the second example is smaller than those of the secondary batteries of the comparative examples 1 and 3.

[0117] The internal resistance of the secondary battery 200 of the second example is small, because the secondary battery 200 is provided with the positive plate 255 including carbon bond active material particles 254 that have positive active material particles 153 and the first conductive material 158 evenly bound over the entire surface of the positive active material particles 153. Thus, the internal resistance of the battery can be reduced by evenly binding the first conductive material 158 over the entire surface of the positive active material particles 153.

[0118] Further, another factor causing the reduction of the internal resistance may be that the electrode plate (positive plate) 255 of the second example includes the positive electrode mix 252 in which the carbon bond active material particles 254 and the second conductive material 159 are evenly dispersed. Thus, because the carbon bond active material particles 254 are evenly dispersed in the positive electrode mix 252, the internal resistance of the battery is reduced. In addition, because the second conductive material 159 is evenly dispersed between the carbon bond active material particles 254 that are adjacent to each other, efficient conductive network among the carbon bond active material particles 254 is formed, and the internal resistance of the battery is further reduced.

[0119] In the above description, the first and second examples of the present invention are described; however, this invention is not limited thereto. Rather, the examples may be appropriately modified as long as the gist thereof is not changed.

[0120] For example, in the first and second example, a positive plate is produced. However, a negative plate as well as the positive plate may be produced using the method for producing an electrode plate according to the present invention. For example,
Li$_4$Tl$\text{Si}_2$O$_5$ may be used as a negative active material to produce a negative plate by the method for producing an electrode plate according to the present invention.

[0121] More specifically, in step S1 (or Tl), carbon bond active material particles are formed by binding acetylene black on the negative active material particles (Li$_4$Tl$\text{Si}_2$O$_5$).

Then the process proceed to step S2, similar to the first and second example, the carbon bond active material particles, acetylene black, the binder and the solvent are stirred and mixed by the mixer 20 to form negative electrode mix paste. Then, in step S3, the negative electrode mix paste is applied to the surface of a negative collector member (e.g., a copper foil). Then, the process of step S4 and S5 are performed in the same manner as the first and second examples to obtain the negative plate. By using this negative plate, the internal resistance of the battery is reduced and the high-current discharge characteristics are improved.

[0122] If a positive plate is produced by the method for producing an electrode plate, the active material particle is not limited to a specific one, but may be a lithium-containing metal oxide expressed by LiMO$_2$ or LiM$_2$O$_4$, where the element M is one or more of the metal elements Co, Ni, Mn, Fe and Cu. More specifically, the active material particle may be a lithium containing metal oxide including lithium-cobalt oxide such as LiCoO$_2$, lithium manganese oxide such as LiMnO$_4$, a lithium-nickel oxide such as LiNiO$_2$, or composite oxide including them as a basic structure (for example, a dissimilar metal doped material). The active material particle may also be a metal oxide including manganese dioxide, vanadium pentoxide, chrome oxide or composite oxide including them as a basic structure, or may be metal sulfide including a titanium disulfide and molybdenum disulfide. Only one of these active material particles may be solely used, or two or more of them may be used together as a mixture or a solid solution. In particular, if a battery is formed with lithium containing composite oxide that shows an open-circuit voltage on charging higher than that of lithium by 4V, such as LiCoO$_2$, LiMnO$_4$, and LiNiO$_2$, the energy density of the battery increases.

[0123] If a negative plate is produced by the method for producing an electrode plate, the active material particle is not limited to a specific one as long as a lithium-ion can be
doped to and dedoped from the active material particles (negative active material particles). More specifically, the active material may be a carbon material such as black lead, pyrolytic carbon, coke, glassy carbon, a burned substance of an organic high polymer, mesocarbon microbeads, a carbon fiber, and an activated carbon, or an alloy of Si, Sn, In, or the like, or an oxide of Si, Sn, In, or the like, that can charge and discharge with a low voltage, as Li does. One of the active material particles may be solely used, or two or more of them are used together.

[0124] The first conductive material and the second conductive material may be a carbon black, such as a furnace black and a Ketjen black, acetylene black, a scale black lead, a fibrous carbon and an activated carbon. The first conductive material and the second conductive material may be the same carbon material, or mutually different carbon materials.

[0125] The binder may be a resin binder, such as polytetrafluoroethylene, polyvinylidene-fluoride (PVDF), polyethylene, polypropylene, polyethylene oxide, polyvinylpyrrolidone, polyester resin, acrylic resin, phenol resin and epoxy resin, a rubber binder, such as an ethylene-polypropylene-diene copolymer resin, styrene-butadiene rubber (SBR), polybutadiene and fluoro-rubber, or a polysaccharide like a cellulose resin including hydroxypropylcellulose, carboxymethyl cellulose (CMC) or the like. One of these binders may be solely used, or two or more of them may be used together.

[0126] The solvent may be an aprotic organic solvent, such as N-methyl-2-pyrolidone (NMP), dimethylacetamide, and dimethylformamide. One of these solvents may be solely used, or two or more of them may be used together.

[0127] Incidentally, for binding the active material particles and the first conductive material to form the carbon bond active material particles according to the claimed invention, a spray dryer such as a Micro Mist Dryer made by Fujisaki Electric Co. Ltd., or Agglomaster made by Hosokawa Micron Corporation, or a rotary fluidized coater made by Pawrex Corporation may be used, for example. T.K.Filmics made by Primix Corporation may be used as a mixer in the mixing process.

[0128] Further, to bind the active material particles and the first conductive material
by the binder by spraying a liquid formed by mixing the binder and the solvent into the
basin, while the active material particles and the first conductive material are fluidized in
the basin according to the claimed invention, Agglomaster made by Hosokawa Micron
Corporation, or a rotary fluidized coater made by Pawrex Corporation may be used, for
example.

[0129] While some embodiments of the invention have been illustrated above, it is to
be understood that the invention is not limited to details of the illustrated embodiments,
but may be embodied with various changes, modifications or improvements, which may
occur to those skilled in the art, without departing from the spirit and scope of the
invention.
CLAIMS

1. A method for producing an electrode plate, comprising:
   binding active material particles and a first conductive material formed of a carbon material with a first binder to form carbon bond active material particles in which the first conductive material is evenly bound over the surface of the active material particles;
   forming an electrode mix paste by mixing the carbon bond active material particles, a second conductive material, a second binder and a first solvent with a mixer having a cylindrical mixing vessel and a rotary blade that is provided in the mixing vessel, rotates and moves near an inner circumferential surface of the mixing vessel and includes a cylinder portion in which a plurality of holes are formed, wherein the carbon bond active material particles, the second conductive material, the second binder and the first solvent put in the mixing vessel are mixed by being pressed by the rotary blade to the inner circumferential surface of the mixing vessel to be extended into a cylindrical thin film; and
   applying the electrode mix paste on a collector member.

2. The method for producing the electrode plate according to claim 1, wherein the carbon bond active material particles, the second conductive material, the second binder, and the first solvent are mixed for five to ten minutes.

3. The method for producing the electrode plate according to claim 1 or 2, wherein the carbon bond active material particles are formed by a spray dry method.

4. The method for producing the electrode plate according to claim 1 or 2, wherein the active material particles and the first conductive material are bound by the first binder by spraying liquid formed by mixing the first binder and a second solvent into a basin while the active material particles and the first conductive material are fluidized in the
basin, and then drying a mixture of the active material particles, the first conductive material and the liquid.

5. An electrode plate comprising:

   an electrode mix that includes:
   
   carbon bond active material particles including active material particles and a first conductive material formed of a carbon material, wherein the first conductive material is evenly bound over a surface of the active material particles; and
   
   a second conductive material formed of a carbon material; and
   
   a collector member that supports the electrode mix,

   wherein the carbon bond active material particles and the second conductive material are evenly dispersed in the electrode mix.

6. A secondary battery comprising an electrode body that includes a positive plate, a negative plate, and a separator,

   wherein at least one of the positive plate and the negative plate is made of the electrode plate according to claim 5.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M4/13 H01M4/04

According to International Patent Classification (IPC) into both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

HOIM

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>JP 2002 083585 A (TOKYO SHIBAURA ELECTRIC CO) 22 March 2002 (2002-03-22) the whole document</td>
<td>5, 6</td>
</tr>
<tr>
<td>Y</td>
<td>EP 1 547 973 A (NAT INST OF ADVANCED IND SCIEN [JP]) 29 June 2005 (2005-06-29) page 4, paragraph 33; claims 21-23</td>
<td>3</td>
</tr>
<tr>
<td>X</td>
<td>WO 2007/126400 A (SHEMBEL ELENA MOISEEVNA [UA]; GLOBA NATALYA IVANOVNA [UA]; RYABCHUK AN) 8 November 2007 (2007-11-08) claims 1,20,21,25</td>
<td>1, 2, 4-6</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered prior art and cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

4 August 2009

Date of mailing of the international search report

11/08/2009

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2380 HV Rijswijk

Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer

Boussard, Nadege

Form PCT/ISA/210 (second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>JP 2002083585 A</td>
<td>22-03-2002</td>
<td>NONE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2004022484 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 20050057237 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2006154071 A1</td>
</tr>
<tr>
<td>US 2005034299 A1</td>
<td>17-02-2005</td>
<td>CN 1577920 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 4077432 B2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2005044794 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 2005006074 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TW 257633 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 9092265 A</td>
</tr>
</tbody>
</table>