NEGATIVE ELECTRODE MATERIAL FOR LITHIUM SECONDARY BATTERIES AND METHOD FOR PRODUCING SAME

To provide a high-capacity lithium secondary battery at a low price that attains an increased reversibility of charge and discharge, by using a new negative electrode material different from the existing negative electrode materials, and to provide a lithium secondary battery that can use an existing electrolyte at a small risk of ignition or overheating.

There is provided a negative electrode material for a lithium secondary battery, comprising one of iron foil and iron-base alloy foil, wherein the one of iron foil and iron-base alloy foil which has a surface profile having a plurality of concave shaped hollows formed by heat treating with laser beam irradiation and the surface is a surface which contacts with an electrolyte solution for a lithium secondary battery. There is further provided a lithium secondary battery including a negative electrode of the negative electrode material, a positive electrode using a lithium compound as an active material, an electrolyte between the negative electrode and the positive electrode, and a separator dividing the negative electrode and the positive electrode from each other.
Fig. 1

PRESENT INVENTION

TEM IMAGE

EXISTING EXAMPLE

1: POSITIVE ELECTRODE COLLECTOR
2: POSITIVE ELECTRODE ACTIVE MATERIAL
3: ELECTROLYTE SOLUTION
4: SEPARATOR
5: NEGATIVE ELECTRODE ACTIVE MATERIAL
6: NEGATIVE ELECTRODE COLLECTOR
7: NEGATIVE ELECTRODE
Description

Technical Field

[0001] The present invention relates to a negative electrode material for a lithium secondary battery, a method for manufacturing the negative electrode material, and a lithium secondary battery using the negative electrode material.

Background Art

[0002] As motor-driving power sources for vehicles such as electric automobiles, high-performance secondary batteries have been recently developed. For secondary batteries to be used for motor driving, high capacities and excellent cycle characteristics are required. Accordingly, active development is being promoted of lithium ion secondary batteries with high theoretical energies.

[0003] As the negative electrode materials of existing lithium ion secondary batteries, there are known carbon-based materials, graphite-based materials, oxide-based materials such as CoO, Co3O4, Fe2O3, metal nitride-based materials such as Ge3N4, Zn3N2, and Cu3N, Li-Si-M-based materials such as Mg2Si, CrSi2, and NiSi, a Li metal, and a Li alloy. In practice, however, carbon-based materials and graphite-based materials are mainly used. In addition, there is known a non-aqueous electrolyte secondary battery using as a negative electrode material a metal carbide such as Cr4C, VC, Fe2C, or FeC (refer to Patent Literature 1), although such a non-aqueous electrolyte secondary battery is difficult to have a high capacity since the discharge capacity of its test cell is approximately 500 mAh/g, compared to a discharge capacity of 350 mAh/g obtained in a case where a graphite-based material is used for a negative electrode in a comparative example.

[0004] As materials that can offer higher capacities and higher energy densities to replace intercalation materials including carbon-based materials and graphite-based materials, Sn and Si alloyed with Li, and materials based on alloys of Sn and Si are receiving attention as negative electrode materials (refer to Non-Patent Literature 1).

[0005] Further, unlike the intercalation materials, an iron oxide such as Fe2O3 performs, as a negative electrode active material, charge and discharge reactions of a conversion type (decomposition and reproduction type). For example, it is reported that as a formula Fe2O3 + 6Li → 3Li2O + 2Fe shows, Fe2O3 decomposes and reduces when it absorbs Li ions at the time of charging so that iron (Fe) and lithium oxide (Li2O) are generated and that iron oxide (Fe2O3) is reproduced when the Li ions are desorbed at the time of discharging. Patents have been applied for a lithium secondary battery (refer to Patent Literature 2) having a negative electrode that includes an iron oxide film on a rough-surfaced conductive substrate as the conversion-type negative electrode active material, and further for a lithium secondary battery (refer to Patent Literature 3) using as the conversion-type negative electrode active material powders of iron oxide with particle diameters of 1 μm to 20 μm and crystallite sizes of 600 Å or smaller.

[0006] A negative electrode active material is usually used by being applied on a negative electrode collector in a mixture with a conduction assistant or a binder. For the collector, aluminum, titanium, copper, iron, stainless steel, etc. are used. Another patent (refer to Patent Literature 4) has been applied for a lithium battery that uses lithium foil or lithium alloy foil as a negative electrode active material. The lithium battery according to Patent Literature 4 is characterized in that the lithium foil or the lithium alloy foil is in a direct contact with a metal collector board of a stainless steel, for example, and that the main surface of the board is a rough surface provided with crater-like spots, by laser processing, having diameters of approximately 20 μm to 100 μm and differences in height of approximately 0.5 μm to 5 μm. The rough surfacing is performed for the purpose of enhancing the adhesive properties between the collector and the lithium foil.

Moreover, laser marking is carried out as processing of inscribing letters, figures, patterns, etc. on various materials. As an example of the laser marking, there is known a surface processing method with which a surface of Ti, a stainless steel, etc. is irradiated with a YVO4 laser having a spot diameter of 20 μm to 80 μm, whereby an ornament excellent in durability and aesthetically pleasing can be created (refer to Patent Literature 5). This method, however, is not used for forming a surface layer part having a functionality of a chemical reaction, for example.

Citation List

Patent Literature

[0008]

Patent Literature 2: JP 2011-129344 A
Patent Literature 5: JP 2003-138384 A

Non Patent Literature

Summary of Invention

Technical Problem

[0010] An existing lithium ion secondary battery mainly uses a carbon-based material or a graphite-based material as a negative electrode active material, and uses as an electrolyte solution a solution obtained by dissolving LiPF$_6$ into a mixture solvent of ethylene carbonate and dialkyl carbonic acid ester. Such a lithium ion secondary battery suffers from disadvantages that a carbon-based material has an intercalation voltage as low as 0.05 V to 0.25 V and that the initial irreversible capacity is increased due to the presence of an SEI (solid electrolyte interphase) film, which is a several-nm-thick coating film, formed on a surface of the negative electrode by an initial charge. Another disadvantage is that when a carbon-based material or a graphite-based material is used as a negative electrode active material, over-charge and over-discharge, for example, cause precipitation of Li metal and this leads to easy occurrence of ignition. Moreover, although Fe$_2$O$_3$ as a replacement of a carbon-based material has an intercalation voltage as low as 0.05 V to 0.25 V and that the initial irreversible capacity is increased due to the presence of an SEI (solid electrolyte interphase) film, which is a several-nm-thick coating film, formed on a surface of the negative electrode by an initial charge. Another disadvantage is that when a carbon-based material or a graphite-based material is used as a negative electrode active material, over-charge and over-discharge, for example, cause precipitation of Li metal and this leads to easy occurrence of ignition. Moreover, although Fe$_2$O$_3$ as a replacement of a carbon-based material has a theoretical capacity of 1008 mAh/g and thus an extremely high capacity, it is reported that the irreversible capacity becomes extremely large and the durability is degraded when a conversion reaction is used.

[0011] In the meanwhile, since high capacities are difficult to obtain with the use of a carbon-based material or a graphite-based material, a lithium ion secondary battery is being proposed that uses Sn, Si, or a material based on an Sn alloy or an Si alloy as a negative electrode active material. The proposed type of lithium ion secondary battery is advantageous in that a high capacity can be obtained and a conventional process of preparing an electrode using a conduction assistant or a binder is not necessary. On the other hand, it is disadvantageous in that since the volumes of the above metals change to a large extent due to absorption and discharge of Li, the metals become finer and the cycle characteristics are degraded due to repeated charges and discharges, and therefore the battery has difficulty in having a long life. Under these circumstances, improving a durability while maintaining a high capacity with the use of an alloy-based material for a negative electrode active material has been a goal. Enhancement of the energy density of a lithium secondary battery requires increases in the capacities of a positive electrode and a negative electrode and in an operating voltage, and development is being promoted of a new electrolyte solution having resistances to flame and oxygen and using a solvent other than ethylene carbonate.

[0012] An object of the present invention is to provide a high-capacity lithium secondary battery at a low price that attains an increased reversibility of charge and discharge by using a new negative electrode material different from the existing negative electrode materials. Another object is to provide a lithium secondary battery that can use an existing electrolyte solution at a small risk of ignition or overheating.

Solution to Problem

[0013] The inventors of the claimed invention have found out that they can provide a lithium secondary battery having a high capacity and excellent charge and discharge characteristics without using an existing negative electrode including an active material layer coated on a surface of a collector, if they form a surface profile having a plurality of minute, concave shaped hollows such as holes or recesses in a surface layer part of an iron foil or an iron-base alloy foil conventionally used as a collector by irradiating the surface of the iron foil or the iron-base alloy foil with a laser beam, and bring the surface into a direct contact with an electrolyte solution for a lithium secondary battery.

[0014] In other words, the present invention provides a negative electrode material for a lithium secondary battery (1) comprising one of an iron foil and an iron-base alloy foil, wherein the one of the iron foil and the iron-base alloy foil has a surface profile having a plurality of concave shaped hollows formed by heat treating with laser beam irradiation and the surface is a surface which contacts with an electrolyte solution for a lithium secondary battery.

[0015] Further, the present invention provides a negative electrode material for a lithium secondary battery (2) according to (1), in which the hollow is one of a hole and a recess.

[0016] Furthermore, the present invention provides a negative electrode material for a lithium secondary battery (3) according to (1) or (2), in which the one of the iron foil and the iron-base alloy foil serves as a negative electrode collector.

[0017] Furthermore, the present invention provides a negative electrode material for a lithium secondary battery (4) according to any one of (1) to (3), in which the one of the iron foil and the iron-base alloy foil has a thickness of 5 μm to 20 μm and a depth from a plane surface of the concave shaped hollow at an edge of the hollow to the lowermost part of the hollow is 0.5 μm to 2.5 μm.

[0018] Moreover, the present invention provides a negative electrode material for a lithium secondary battery (5) according to any one of (1) to (4), in which the one of the iron foil and the iron-base alloy foil which is included is provided with a concave shaped hollow formed by heat treating a surface of the iron foil or the iron-base alloy foil by irradiating and scanning the surface with a laser beam.

[0019] Moreover, the present invention provides a lithium secondary battery (6) including: a positive electrode using a lithium compound as an active material; an electrolyte solution between the negative electrode and the positive electrode; and a separator dividing the negative electrode and the positive electrode from each other.
Fig. 1 schematically illustrates a cross-sectional configuration of a lithium secondary battery using a negative electrode material according to the present invention, and the configuration of a typical type of existing lithium secondary battery for comparison. A lithium battery usually includes a positive electrode having a positive electrode collector 1 and a positive electrode active material 2, an electrolyte solution 3, a separator 4, and a negative electrode having a negative electrode active material 5 and a negative electrode collector 6. Formation of the negative electrode active material according to the present invention does not require application of the negative electrode active material layer 5 on a surface of the negative electrode material. In the lithium secondary battery of the present invention, one of an iron foil and an iron-base alloy foil alone can complete the negative electrode 7. Using the negative electrode 7 promotes a reaction, caused by charging, between an electrolyte solution and a surface layer part of the iron foil or the iron-base alloy foil of the negative electrode 7, so that a compound layer is generated at an interface between the negative electrode and the electrolyte solution, as the TEM observed image of Fig. 1 shows.

It is known that when a lithium ion secondary battery using a carbon material as a negative electrode active material is subjected to an initial charge in a non-aqueous electrolyte, the solvent in the electrolyte is reactive and a coating film called an SEI film is formed on a surface of the negative electrode active material. The SEI film is a passivation film of a lithium compound such as Li$_2$O, Li$_2$CO$_3$, and LiF. The lithium ions consumed for forming the lithium compound cannot contribute to a charge capacity, so that an irreversible capacity at the initial charge, that is, a difference between a charge capacity and a discharge capacity is increased. The irreversible capacity becomes larger as the SEI film is formed in a larger amount. Therefore, the amount of the SEI film to be formed on a surface of the negative electrode is preferably made as small as possible.

The inventors have not yet clearly figured out the reason for increases in the reversibility of charge and discharge and in the capacity occurred when they use as the negative electrode material an iron foil or an iron-base alloy foil having a surface profile formed by laser beam irradiation. They infer, however, from the results of the TEM observation of the interface between the negative electrode and the electrolyte solution after charging, that the reason is that a surface of the negative electrode which is in a direct contact with the electrolyte solution chemically reacts with the electrolyte solution at the charging and a thick Li compound layer is resultantly formed, unlike a known intercalation phenomenon of Li or a known alloying reaction with Li ions made by Si-based and Sn-based active materials, for example. The inventors speculate that the above chemical reaction is caused in a manner such that crystal grains modified by heat treating or nano-particles of Fe$_3$O$_4$ generated by heat treating serve to allow the surface layer part to have a strong reduction power and a low potential and further to perform catalysis. Given the result of the TEM observation and an excellent function exercised on the charge and discharge characteristics, the inventors have considered that an essential difference exists between the existing SEI film and the Li compound layer formed at the interface between the electrolyte solution and a surface of the negative electrode according to the present invention not using a carbon material as the negative electrode active material.

Advantageous Effects of Invention

According to the present invention, it is possible to provide a lithium secondary battery with excellent charge and discharge characteristics by using as a negative electrode material an iron foil or an iron-base alloy foil having a surface profile with a plurality of concave shaped hollows formed by laser beam scanning. Further, it is possible to provide a lithium ion secondary battery having a function of an iron foil or an iron-base alloy additionally serving as a collector and resistances to corrosion and heat. Furthermore, a simple manufacturing process and a low cost are attained, since a collector alone can complete the negative electrode and therefore steps of mixing, coating, drying, etc. of a negative electrode active material are not necessary for forming an active material layer on a surface of the collector. Moreover, since over-charge and over-discharge, for example, do not easily lead to precipitation of Li metal at least in principle, notably advantageous effects such as great safety and high capacity of a secondary battery can be obtained.

Brief Description of Drawings

Fig. 1 is a cross-sectional schematic drawing that illustrates a comparison between two lithium secondary batteries using negative electrode materials according to an existing example and the present invention, respectively.

Fig. 2 is a drawing-substituting photograph that shows an SIM image in a case where holes are regularly arranged like dots in a surface of a stainless steel foil by irradiating the surface with a laser beam. Fig. 3 is a schematic drawing that illustrates a cross-sectional configuration of a crater-like hole with a small depth, which is seen in an exemplary surface profile of the negative electrode material according to the present invention.

Fig. 4 is a drawing-substituting photograph that shows an SIM image of a surface profile of a stainless steel foil on which heat treating has been performed by a laser in Experiment 1.

Fig. 5 is a drawing-substituting photograph that
The negative electrode material according to the present invention will be hereinafter described in detail. The negative electrode material according to the present invention is formed by scanning a surface of an iron foil or an iron-base alloy foil by a laser beam and thereby modifying the crystals of a surface layer part by heat treating. The iron foil or the iron-base alloy foil can additionally serve as a negative electrode collector.

As an iron foil to be used as the negative electrode material according to the present invention, a pure iron foil or an iron-base alloy foil defined by JIS C2504 or a carbon steel foil defined by JIS G4305, for example, may be used. The standard electromagnetic soft iron foil on which heat treating has been performed by a laser in Experiment 2. The iron foil or the iron-base alloy foil is used. Examples of the iron-base alloy foil include iron-based alloys such as an iron nickel alloy, an iron chromium alloy, an iron molybdenum alloy, a stainless steel, and a low-alloy steel.

As the stainless steel, any type of stainless steel foil is usable. Specifically, there may be used austenitic stainless steel foils (SUS304, SUS304-L, SUS302, SUS301, SUS310S, SUS321, SUS316, SUS316-L, for example), ferritic stainless steel foils (SUS430, SUS434, for example), martensitic stainless steel foils (SUS410S, SUS420J2, for example), precipitation hardening stainless steel foils (SUS631, ASL-350, for example), etc., as defined in JIS G4305: 2005, “cold-rolled stainless steel and steel band”.

Although the thickness of the iron foil or the iron-base alloy foil to be used is not particularly limited as long as the thickness is not larger than approximately 1 mm, it is desirable that the thickness is approximately 5 µm to 100 µm, which corresponds to the thickness of an existing collector, and is more desirable that the thickness is approximately 5 µm to 20 µm for practical use.

Examples of types of lasers include various gaseous lasers such as a CO₂ laser, an Ar laser, and an excimer laser, and various solid lasers such as a YAG laser, a YLF laser, and a YVO₄ laser. In particular, a YVO₄ laser, where a single mode oscillation is possible, is advantageous for adjusting the diameter of a beam to a smallest possible value or for forming fine dots or recesses so as to be periodically arranged with a high precision.

In the meanwhile, a laser marker is known as a means for forming letters, patterns, etc. on a surface layer part of a metal material such as a stainless steel. A laser marker itself is a processing means with which an area of a surface layer part of a material is vaporized, scratched, or changed thermally or chemically by a laser beam. Such a commercially available laser marker machine may be employed for modifying the surface layer part by heat treating in the present invention.

A desirable type of laser in the present invention is a YVO₄/SHG laser with a wavelength of 532 nm suitable for weak heat treating, since the present invention does not require laser beam irradiation necessary for forming a hollow such deep as to melt and penetrate an iron foil or an iron-base alloy foil. By narrowing down an SHG laser with a high absorption as much as possible, a power density can be increased to a large extent and highly efficient heat treating is enabled.

Although it is preferable that regularly-arranged concave shaped hollows, such as hole patterns or recess patterns, are formed by adjusting the conditions for laser beam irradiation so as to heat-treat a surface layer part.
of an iron foil or an iron-base alloy foil and by performing
scanning by a laser beam, the pattern of each concave
shaped hollow on a two-dimensional level is not particu-
larly limited. The concave shaped hollow may be not
only a shallow crater-like hole but also a recess in the
shape of a shallow tub, for example. Although the envi-
ronments for the laser beam irradiation are not particu-
larly limited, performing the irradiation in the atmosphere
is desirable in terms of productivity.

Unlike the other iron foils and iron-base alloy
foils, a stainless steel includes a passive coating film on
a surface thereof. The passivation film usually has a thick-
ness of approximately 1 nm to 3 nm, and includes a chro-
mium oxide film and a film of Fe hydroxide and Cr hy-
droxide. The passivation film, however, will be removed
through laser beam irradiation by a laser maker machine,
other than the part of the passivation film at the edges of
a concave shaped hollow, in a manner such that the laser
beam irradiation instantaneously heats a surface layer
part of the stainless steel and melts the surface layer part
other than the hollows.

Fig. 2 illustrates an SIM image in a case where
holes are regularly arranged like dots in a surface of a
stainless steel foil by irradiating the surface with a laser
beam. Fig. 3 is a schematic diagram that illustrates a
cross section of a single hole. Descriptions will be made
of a case where shallow crater-like holes, each of which
is shown in Fig. 3, are arranged in a surface of the stain-
less steel foil as concave shaped hollows. In that case,
heat treating using a laser instantaneously melts a sur-
face layer part of a stainless steel 1, whereby the surface
layer part is transformed, which causes formation of a
shallow crater-like hole having an edge part 2 and a
curved part 3. In the formation, the surface layer part of
the stainless steel 1 is subjected to heat treating, and as
a result, the passivation film mainly including a chromium
oxide on a surface of the hole is removed, so that a crys-
talline surface of the stainless steel base material is ex-
posed. Further, the inventors consider that in the forma-
tion of the hole, a cooling rate for the region from the
diameter D1 of dots illustrated in Fig. 3 is preferably set
approximately 5 μm to 20 μm. When recesses are
formed, a space between recesses next to each other may
be the same as that between dots.

Unlike the other iron foils and iron-base alloy
foils, a stainless steel includes a passive coating film on
a surface thereof. The passivation film usually has a thick-
ness of approximately 1 nm to 3 nm, and includes a chro-
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a concave shaped hollow, in a manner such that the laser
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part of the stainless steel and melts the surface layer part
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droxide. The passivation film, however, will be removed
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mium oxide film and a film of Fe hydroxide and Cr hy-
droxide. The passivation film, however, will be removed
through laser beam irradiation by a laser maker machine,
other than the part of the passivation film at the edges of
a concave shaped hollow, in a manner such that the laser
beam irradiation instantaneously heats a surface layer
part of the stainless steel and melts the surface layer part
other than the hollows.
The present invention will be hereinafter described in detail based on experiments and embodiments. It is to be noted that the present invention is not limited to the embodiments.

[Experiment 1]

[0043] A test cell using the negative electrode material according to the present invention is manufactured and a charge state of the test cell is checked. A square with a side of 40 mm is formed by a 1 mm-thick stainless steel foil SUS316 (manufactured by Nippon Steel & Sumikin Stainless Steel Corporation, NSSC, TP-316) so that a negative electrode material is prepared. Anapasive coating film on a surface of the stainless steel foil is left as it is. As a laser device, a laser marker MD-T1010 (manufactured by Keyence Corporation) is used. A surface of the stainless steel foil is irradiated with a laser beam for heat treating while the surface is scanned in a full discharge state. The inventors consequently consider that a reversible reaction proceeds unlike in the case of an SEI film formed on a surface of a negative electrode of an existing carbon-based or graphite-based material.

[0042] The present invention will be hereinafter described in detail based on experiments and embodiments. It is to be noted that the present invention is not limited to the embodiments.

[0041] TEM observation is carried out of product materials at the interface between the electrolyte solution and the negative electrode, which are generated when an initial charge is performed on a lithium secondary battery using the negative electrode material according to the present invention. As a result of the observation, it is found that a thick compound layer is formed to have a thickness of approximately tens of nm to 100 nm. From a depth-directional XPS analysis of charged and discharged states, the inventors infer that a layer including Li$_2$O$_3$ as the main component and a mixture of a Li hydroxide, carbon oxide, fluoride, and phosphorus oxide as the rest of the components is formed on a surface of the negative electrode in a full charge state to have a thickness of approximately tens of nm to 100 nm and that Li is absorbed in the layer. The Li compound layer is made thinner due to discharge, and mostly disappears in a full discharge state. The inventors consequently consider that a reversible reaction proceeds unlike in the case of using an SEI film formed on a surface of a negative electrode of an existing carbon-based or graphite-based material.

[0044] Next, a disc with a diameter of 16 mm is formed by punching the stainless steel foil which has been heat-treated by the laser beam irradiation as described above, so that the disc can be used as a negative electrode additionally serving as a negative electrode collector. A surface of the thus obtained negative electrode is brought into contact with an electrolyte solution, and a counter electrode is made of lithium metal. Further, a coin battery for a test cell is manufactured using the negative electrode, the counter electrode, and the electrolyte solution, and the charge characteristics of the coin battery are measured. For the facility for evaluating the characteristics, CELTEST-8 system (1470E) manufactured by Solatron is used.

[0046] TEM observation is carried out of a surface of the negative electrode material at an initial charge. As a result of the observation, it is found that a thick compound layer (gray area) with a thickness of approximately 50 nm is formed at the interface between the negative electrode (black area) and the electrolyte solution, as Fig. 5 illustrates. Fig. 6 shows initial charge characteristics of the test cell. The charge capacity is 192.6 μAh.

[Experiment 2]

[0047] A test cell using the negative electrode material according to the present invention is manufactured and a discharge state of the test cell is checked. A stainless steel foil is irradiated with a laser beam so as to be heat-treated with a laser output set to 4w x 30%. The crater-like holes have a diameter D1 of approximately 20 μm and a depth D2 of approximately 1.5 μm. The depth D2 is measured with a surface profiler. By the above irradiation, shallow crater-like holes are regularly opened into the vertical and horizontal directions. It takes 72 seconds to carry out dot processing on the entire surface. The crater-like holes have a diameter D1 of approximately 15 μm and a depth D2 of approximately 1.0 μm. The depth D2 is measured with a laser microscope VK series. Fig. 4 illustrates an SIM observed image of the surface profile of the stainless steel which has been heat-treated by the laser beam irradiation.
thick compound layer generated in Experiment 1 at the interface between the negative electrode (black area) and the electrolyte solution has disappeared, as Fig. 7 illustrates. Fig. 8 shows initial charge and discharge characteristics of the test cell. The charge capacity is as high as 555.0 μAh and the discharge capacity is as high as 483.9 μAh.

[Embodiment 1]

[0049] A full cell is manufactured using the negative electrode obtained in Experiment 2. A separator is inserted into a battery container made of stainless steel. On both sides of the separator, a positive electrode and a negative electrode are placed. As the positive electrode, an electrode having one surface coated with lithium cobalt oxide so as to have a capacity of 1.6 mAh/cm² is used. Further, the negative electrode is made of the stainless steel foil manufactured in Experiment 2 which is brought in a direct contact with an electrolyte solution. The positive electrode is brought into contact with an aluminum collector, and the aluminum collector is brought into contact with the battery container. The negative electrode material is allowed to additionally serve as a negative electrode collector and is brought into contact with the battery container. The separator, the electrolyte solution, and the electrolyte are the same as those employed in Experiments 1 and 2.

[0050] The conditions for charge and discharge are that a thermostatic chamber is set at a temperature of 25 °C, the charge is constant-current charge performed at 30 μA, and charging and discharging voltages range from 4.3 V to 2.5 V. Fig. 9 illustrates the charge and discharge characteristics of the full cell. The charge capacity and discharge capacity in a first cycle are 1467 μAh and 1466 μAh, respectively, and the charge capacity and discharge capacity in a second cycle are 1458 μAh and 1441 μAh, respectively. The irreversible capacity can be reduced to a large extent and an initial charge and discharge efficiency is nearly 100%.

[Experiment 3]

[0051] A square with a side of 50 mm is formed by punching a 10 μm-thick electromagnetic soft iron foil (SU-YP JIS C 2504) instead of the stainless steel foil in Experiment 1 so that a negative electrode material is prepared. Shallow crater-like holes are regularly opened into the vertical and horizontal directions in the same manner as in Experiment 1 using a laser device under the conditions that the output is 4 W × 25%, the scanning speed is 1200 mm/s, and the frequency is 80 KHz. As the laser device, the same laser device as that employed in Experiment 1 is used. It takes 181 seconds to carry out dot processing on the entire surface. The crater-like holes have a diameter D1 of approximately 15 μm and a depth D2 of approximately 1.2 μm. Fig. 10 illustrates an SIM observed image of the surface of the electromagnetic soft iron foil which has been heat-treated by the laser beam irradiation.

[0052] A disc with a diameter of 16 mm is formed by punching the electromagnetic soft iron foil thus obtained, a test cell is manufactured as a negative electrode additionally serving as a negative electrode collector, and the charge and discharge capacities of the test cell are measured under the same conditions as those employed for Experiments 1 and 2. Fig. 11 illustrates the results of charge and discharge of the test cell. The charge capacities in the first, second, and third cycles are 49 μAh, 26 μAh, and 23 μAh, respectively, and the discharge capacities in the first, second, and third cycles are 24 μAh, 21 μAh, and 19 μAh, respectively.

[Embodiment 2]

[0053] A full cell is manufactured using the negative electrode manufactured in Experiment 3 under the same conditions as those employed for Embodiment 1, except that the capacity of lithium cobalt oxide is set at 3 mAh/cm², and the charge and discharge characteristics are evaluated. Fig. 12 illustrates the charge and discharge characteristics of the full cell. The charge capacities in the first, second, and third cycles are 4783 μAh, 3169 μAh, and 2080 μAh, respectively, and the discharge capacities in the first, second, and third cycles are 2608 μAh, 1882 μAh, and 1268 μAh, respectively.

[Experiment 4]

[0054] A square with a side of 50 mm is formed by punching a 1 mm-thick cold-rolled steel foil (SPCC JIS G 3141) instead of the stainless steel foil in Experiment 1 so that a negative electrode material is prepared. As a laser device, a laser marker SUNXLP-Z250 (manufactured by PanasonicElectricWorksCo., Ltd.) is used. Shallow crater-like holes are regularly opened into the vertical and horizontal directions in the same manner as in Experiment 1, using a YAG laser, under the conditions that the laser power is 1 W, the scanning speed is 120 mm/s, and the printing pulse is 10 μs. The YAG laser has a wavelength of 532 nm, an average output of 1 W, and a maximum printing speed of 12000 mm/s. The crater-like holes have a diameter D1 of approximately 15 μm and a depth D2 of approximately 2 μm. Fig. 13 illustrates an optical microscope image of the surface of the cold-rolled steel foil which has been heat-treated by the laser beam irradiation.

[0055] A disc with a diameter of 16 mm is formed by punching the cold-rolled steel foil thus obtained, a test cell is manufactured as a negative electrode additionally serving as a negative electrode collector, and the charge and discharge capacities of the test cell are measured under the same conditions as those employed for Experiments 1 to 3. Fig. 14 illustrates the results of charge and discharge of the test cell. The charge capacity and the discharge capacity in the first cycle are 65 μAh and 43
Ah, respectively.

[Embodiment 3]

[0056] A full cell is manufactured using the negative electrode manufactured in Experiment 4 under the same conditions as those for Embodiment 1 except that the capacity of lithium cobalt oxide is set at 3 mAh/cm², and the charge and discharge characteristics are evaluated. Fig. 15 illustrates the charge and discharge characteristics of the full cell. The charge capacity and the discharge capacity in the first cycle are 2960 μAh and 1344 μAh, respectively.

Industrial Applicability

[0057] The negative electrode material according to the present invention can be easily manufactured using publicly-available iron foil or iron-base alloy foil and a laser marking technique. Further, the negative electrode material can be manufactured at a low cost since a conventional step is unnecessary of applying an expensive active material on a surface of a negative electrode. The negative electrode material is being expected to be used as a new revolutionary negative electrode material that has an excellent resistance to heat and allows a lithium secondary battery to have increased safety, reliability, and capacity.

Claims

1. A negative electrode material for a lithium secondary battery, comprising one of iron foil and iron-base alloy foil, wherein
   the one of the iron foil and the iron-base alloy foil has a surface profile having a plurality of concave shaped hollows formed by heat treating with laser beam irradiation, and
   the surface is a surface which contacts with an electrolyte solution for a lithium secondary battery.

2. The negative electrode material for a lithium secondary battery according to claim 1, wherein the hollow is one of a hole and a recess.

3. The negative electrode material for a lithium secondary battery according to claim 1 or 2, wherein the one of the iron foil and the iron-base alloy foil serves as a negative electrode collector.

4. The negative electrode material for a lithium secondary battery according to any one of claims 1 to 3, wherein
   the one of the iron foil and the iron-base alloy foil has a thickness of 5 μm to 20 μm, and
   a depth from a plane surface of the concave shaped hollow at an edge of the hollow to a lowermost part of the hollow is 0.5 μm to 2.5 μm.

5. A method for manufacturing the negative electrode material for a lithium secondary battery according to any one of claims 1 to 4, wherein
   providing a surface profile having a plurality of concave shaped hollows on the surface of the one of the iron foil and the iron-base alloy foil by heat treating the surface of the foil by irradiating and scanning the surface with a laser beam.

6. A lithium secondary battery comprising:
   a negative electrode of the negative electrode material according to any one of claims 1 to 4;
   a positive electrode using a lithium compound as an active material;
   an electrolyte between the negative electrode and the positive electrode; and
   a separator dividing the negative electrode and the positive electrode from each other.
Fig. 7

STAINLESS STEEL FOIL

50 nm

Fig. 8

POTENTIAL

CHARGE AND DISCHARGE CAPACITY (μ Ah)

<p>| | |</p>
<table>
<thead>
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<tr>
<td>CHARGE CAPACITY (μ Ah)</td>
<td>555.0</td>
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<td>DISCHARGE CAPACITY (μ Ah)</td>
<td>483.9</td>
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Fig. 9

Charge and discharge capacity (μ A h)

Fig. 10
Fig. 11

Fig. 12
Fig. 13

Fig. 14
Fig. 15
# INTERNATIONAL SEARCH REPORT

**International application No.**

PCT/JP2014/056004

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**A. CLASSIFICATION OF SUBJECT MATTER**

H01M4/134(2010.01)i, H01M4/38(2006.01)i, H01M4/66(2006.01)i, H01M10/052 (2010.01)i, H01M10/0566(2010.01)i

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

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**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

H01M4/134, H01M4/38, H01M4/66, H01M10/052, H01M10/0566

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

Jitsuyo Shinan Koho 1922-1996
Jitsuyo Shinan Toroku Koho 1996-2014
Rokai Jitsuyo Shinan Koho 1971-2014
Toroku Jitsuyo Shinan Koho 1994-2014

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

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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>JP 2011-129344 A (Toyota Motor Corp.), 30 June 2011 (30.06.2011), entire text; all drawings (Family: none)</td>
<td>1-6</td>
</tr>
<tr>
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<td>JP 2006-066696 A (TDK Corp.), 09 March 2006 (09.03.2006), entire text; all drawings (Family: none)</td>
<td>1-6</td>
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* Further documents are listed in the continuation of Box C.  
See patent family annex.

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**Date of the actual completion of the international search**

31 March, 2014 (31.03.14)

**Date of mailing of the international search report**

08 April, 2014 (08.04.14)

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**Name and mailing address of the ISA/ Japanese Patent Office**

Authorized officer

**Facsimile No.**

Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description