

DESCRIPTION

TITLE OF THE INVENTION: NEGATIVE ELECTRODE FOR LEAD-ACID BATTERY, AND LEAD-ACID BATTERY

TECHNICAL FIELD

[0001]

The present invention relates to a negative electrode for a lead-acid battery, and a lead-acid battery.

BACKGROUND ART

[0002]

Lead-acid batteries have been used widely in various applications such as in-vehicle use and industrial use. For example, an in-vehicle lead-acid battery has been used as a power source for driving a cell motor and a power source for electric equipment in a vehicle.

[0003]

In a lead-acid battery, additives such as carbon are added to a negative active material in order to improve various performances (cf. Patent Document 1.). Patent Document 1 proposes a lead-acid battery in which sodium lignin sulfonate, barium sulfate, and oil furnace black are added to a negative active material.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0004]

Patent Document 1: JP-A-2008-152955

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

In recent years, a system for stopping the idling of an engine has become widespread for the purpose of improving the fuel efficiency of automobiles. In a lead-acid battery provided in an automobile (idling stop vehicle) adopting the system, the frequency of charge and discharge is higher than in an energy storage device provided in a conventional automobile. Further, more power is required to be chargeable in a short time. As described above, a lead-acid battery for an idling stop vehicle is required to be capable of efficient charge. However, conventional lead-acid batteries are not sufficient to meet this requirement. For example, as an idling stop life test, a test method of repeating charge and discharge for a predetermined short time is specified in the Battery Association of Japan (BAJ) Standard SBAS0101. When the charge efficiency is low, the discharge voltage drops quickly and the life becomes short in such an idling stop life test.

[0006]

An object of the present invention is to provide a negative electrode for a lead-acid battery capable of improving the charge efficiency of a lead-acid battery, and a lead-acid battery having good charge efficiency.

MEANS FOR SOLVING THE PROBLEMS

[0007]

One aspect of the present invention made to solve the above problems is a negative electrode (A) for a lead-acid battery, which includes a negative composite containing lead, and in an X-ray diffraction spectrum of

the negative composite present on the surface of the negative electrode, the ratio of a peak height near a diffraction angle of 30.3° to a peak height near a diffraction angle of 31.2° is 0.05 or more.

[0008]

Another aspect of the present invention is a negative electrode (B) for a lead-acid battery, which includes a negative composite containing lead, and at least a part of the negative composite present on the surface of the negative electrode has a scale-like shape, and an aspect ratio of the scale-like shape is 3 or more and 10 or less.

[0009]

Another aspect of the present invention is a lead-acid battery provided with the negative electrode (A) for the lead-acid battery or the negative electrode (B) for the lead-acid battery.

ADVANTAGES OF THE INVENTION

[0010]

According to the present invention, it is possible to provide a negative electrode for a lead-acid battery capable of improving the charge efficiency of a lead-acid battery, and a lead-acid battery having good charge efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

Fig. 1 is a partially cut-out exploded perspective view illustrating an external appearance and an internal structure of a lead-acid battery according to an embodiment of the present invention.

Fig. 2 is an X-ray diffraction spectrum of a negative composite

present on the surface of a lead-acid battery of Example 4.

Fig. 3 is an X-ray diffraction spectrum of a negative composite present on the surface of a lead-acid battery of Comparative Example 5.

Fig. 4 is an electron micrograph of a negative composite on the surface of a lead-acid battery of Example 4.

Fig. 5 is an electron micrograph of a negative composite on the surface of a lead-acid battery of Comparative Example 5.

MODE FOR CARRYING OUT THE INVENTION

[0012]

A negative electrode for a lead-acid battery according to one embodiment of the present invention is a negative electrode (A) for a lead-acid battery, which includes a negative composite containing lead, and in an X-ray diffraction spectrum of the negative composite present on the surface of the negative electrode, the ratio of a peak height near a diffraction angle of 30.3° to a peak height near a diffraction angle of 31.2° is 0.05 or more.

[0013]

The negative electrode (A) for the lead-acid battery can improve the charge efficiency of the lead-acid battery. The reason for this is not clear, but the following reasons are presumed. It is known that lead sulfate, which is coarsened in the negative composite by repeating charge and discharge, is one of the causes of lowering charge acceptability and the like. The lead sulfate present in the negative composite or on the surface of the negative composite is reduced and eluted into the electrolyte solution during charge, but as the charge and discharge are repeated, the lead sulfate becomes less likely to be reduced and eluted, and the coarsening proceeds.

It is thus considered that when the negative composite is formed in a shape in which the lead sulfate is easily reduced and eluted, the coarsening of the lead sulfate is prevented, and the charge efficiency is improved. The inventors have found that a peak near a diffraction angle of 30.3° in an X-ray diffraction spectrum appears when a scale-like shape (a shape in which scale-like protrusions are formed) is formed in a negative composite containing lead. When the negative composite present on the surface includes such a scale-like shape, the lead sulfate is produced in the narrow gap of the scale-like material and is thus considered to be hardly coarsened. Further, with the electrolyte solution permeating into the gap of the scale-like shape, the area where the produced lead sulfate is in contact with the electrolyte solution is large. Therefore, when the negative electrode (A) for the lead-acid battery is used, it is presumed that the lead sulfate produced in the negative electrode is easily reduced and dissolved upon reduction, and the charge efficiency has been improved. Alternatively, since the peak near 30.3° is considered to correspond to lead oxide, it is also presumed that the presence of lead oxide in the negative composite present on the surface itself contributes to the improvement in charge efficiency, for example, by facilitating the reduction of lead sulfate, regardless of whether or not the scale-like shape has been formed.

[0014]

The surface of the negative electrode for the lead-acid battery is the surface facing the positive electrode when the negative electrode is incorporated into the lead-acid battery, and the negative composite present on the surface is the negative composite exposed on the surface facing the

positive electrode. In the present specification, the X-ray diffraction spectrum of the negative composite present on the surface is a value measured by the following method.

I. Pretreatment

First, the lead-acid battery is fully charged (state of charge (SOC) 100%). The charge conditions for bringing the lead-acid battery into the fully charged state are as follows. In the case of a flooded-type (vent-type) battery, the constant current charge is performed at 25°C in a water bath at 0.2 C until the voltage reaches 2.5 V/cell, and then, the constant current charge is further performed at 0.2 C for two hours. In the case of a valve regulated (sealed type) battery, the constant current constant voltage charge is performed at 25°C in an air bath at 0.2 C and 2.23 V/cell, and the charge is terminated when the charge current during constant voltage charge becomes 1 mC or less. Note that 1C is a current value for discharging a battery with a nominal capacity in one hour, and for example, in the case of a battery with a nominal capacity of 30 Ah, 1C is 30 A. The fully charged lead-acid battery is disassembled, and the negative electrode is taken out and washed with running water for four hours. Then, vacuum drying is performed at a drying temperature of 70°C and a vacuum degree of about 150 kPa for 12 hours.

II. Measurement

For the negative electrode subjected to the above pretreatment, the negative composite is collected from the surface in an amount of 0.048 g per 1 cm² with a spatula and pulverized in a mortar. The sample stage is filled with 2 g of the pulverized negative composite, and measurement is

performed. The measurement conditions are as follows:

Measuring instrument: SmartLab Horizontal Goniometer θ - θ type,
manufactured by Rigaku Corporation

Target: Cu

Voltage/Current: 40 kV/30 mA

Detector: Dtex 250 (H)

X-ray diffraction chart measurement

Scan mode: continuous scan

Measurement angle: $2\theta = 20^\circ$ to 60°

Scan speed: $10^\circ/\text{min}$

Scan step: 0.02°

[0015]

A negative electrode for a lead-acid battery according to another embodiment of the present invention is a negative electrode (B) for a lead-acid battery, which includes a negative composite containing lead, and at least a part of the negative composite present on the surface of the negative electrode has a scale-like shape, and an aspect ratio of the scale-like shape is 3 or more and 10 or less. The charge efficiency of the lead-acid battery can also be improved by the negative electrode (B) for the lead-acid battery. The reason for this is not clear but is assumed to be similar to the reason in the negative electrode (A) for the lead-acid battery described above.

[0016]

In the present specification, the scale-like shape simply means a thin shape, and its planar shape is not particularly limited. The aspect ratio of the scale-like shape is a value measured by the following method: A

mass of the negative composite is collected from the negative electrode which has been subjected to pretreatment similar to that in “I. Pretreatment”. The collected mass of the negative composite is broken to obtain a fracture surface. Gold vapor deposition is performed on the obtained fracture surface portion of the negative composite. Then, the negative composite is placed into an electron microscope device, and the fracture surface is observed. Conditions for observation by the electron microscope are as follows: From the observed image, the maximum width and the maximum thickness are obtained for one having a scale-like shape present on the surface, and the ratio of the maximum width to the maximum thickness (max width/max thickness) is taken as an aspect ratio.

Measuring instrument: Scanning Electron Microscope SM-300, manufactured by TOPCON CORPORATION.

Acceleration voltage: 15 kV

Magnifications: 50×, 100×, 500×, 1000×, 2000× (Among these magnifications, a magnification at which the shape of the negative composite present on the surface can be most clearly observed is adopted.)

[0017]

The specific surface area of the negative composite on each of the negative electrode (A) for the lead-acid battery and the negative electrode (B) for the lead-acid battery is preferably $0.55 \text{ m}^2/\text{g}$ or more and $0.8 \text{ m}^2/\text{g}$ or less. Such a setting improves the charge efficiency. The reason for this is presumed to be that when the specific surface area of the negative composite is within the above range, lead sulfate produced in the gap between the negative composite is dissolved more easily.

[0018]

In the present specification, the specific surface area of the negative composite is a value (BET specific surface area) measured by the following method: A mass of the negative composite is collected from the negative electrode which has been subjected to pretreatment similar to that in “I. Pretreatment”. The collected negative composite (about 3.5 g) is placed into the measuring cell. After vacuum degassing at 100°C for one hour, the measuring cell is attached to the device, and measurement is performed in the following conditions:

Measuring instrument: Specific Surface Area/Pore Distribution
measuring device TriStar 3000, manufactured by Shimadzu Corporation

Measurement condition: BET eight-point method

Adsorption gas: Nitrogen

[0019]

The specific surface area of the negative composite on each of the negative electrode (A) for the lead-acid battery and the negative electrode (B) for the lead-acid battery is more preferably 0.6 m²/g or more and 0.75 m²/g or less. Such a setting further improves the charge efficiency.

[0020]

A lead-acid battery according to one embodiment of the present invention is a lead-acid battery provided with the negative electrode (A) for the lead-acid battery or the negative electrode (B) for the lead-acid battery. The lead-acid battery has good charge efficiency since including the negative electrode (A) for the lead-acid battery or the negative electrode (B) for the lead-acid battery according to one embodiment of the present invention

described above.

[0021]

The lead-acid battery is preferably for an idling stop vehicle. The lead-acid battery has high charge efficiency and can thus be suitably used for an idling stop vehicle requiring efficient charge in a short time.

[0022]

Hereinafter, a negative electrode for a lead-acid battery, and a lead-acid battery, according to one embodiment of the present invention will be described in detail in order.

[0023]

<Negative electrode (A) for lead-acid battery>

A negative electrode plate, which is an example of the negative electrode (A) for the lead-acid battery according to one embodiment of the present invention, includes a negative current collector and a negative composite. The negative composite is held by the negative current collector.

[0024]

(Negative current collector)

The negative current collector is usually in the form of a grid plate. The negative current collector may be formed by casting lead (Pb) or a lead alloy or may be formed by processing a lead or a lead alloy sheet. Examples of the processing method include expansion and punching.

[0025]

Examples of the lead alloy used for the negative current collector include a Pb-Sb based alloy, a Pb-Ca based alloy, and a Pb-Ca-Sn based

alloy. These lead or lead alloys may further contain elements such as Ba, Ag, Al, Bi, As, Se, and Cu as additional elements. The negative current collector may have lead alloy layers with different compositions, and a plurality of lead alloy layers may be used.

[0026]

(Negative composite)

The negative composite contains lead.

[0027]

Lead is a component that functions as a negative active material and is usually the main component in the negative composite. The content of lead in the negative composite may be, for example, 90 to 99.99% by mass. Part of or all the lead in the negative composite may be present as lead sulfate, lead oxide, or the like.

[0028]

In the negative composite, it is possible to contain additives in addition to lead, such as a carbonaceous material like carbon black, barium sulfate, and lignin, when necessary.

[0029]

In the X-ray diffraction spectrum of the negative composite present on the surface of the negative composite, the ratio of a peak height near the diffraction angle of 31.2° to a peak height near the diffraction angle of 30.3° is 0.05 or more. The peak near the diffraction angle of 31.2° is a peak as a reference which appears strongly in general lead. When the ratio of the peak height near the diffraction angle of 31.2° to the peak height near the diffraction angle of 30.3° is high, it is considered that the lead has become

lead oxide and grown in the scale-like shape. The peak near the diffraction angle of 31.2° may be a peak appearing within $31.2^\circ \pm 0.3^\circ$ or a peak appearing within $31.2^\circ \pm 0.1^\circ$. The peak near the diffraction angle of 30.3° may be a peak appearing within $30.3^\circ \pm 0.3^\circ$ or a peak appearing within $30.3^\circ \pm 0.1^\circ$.

[0030]

The lower limit of the ratio of the peak height is 0.05 but is preferably 0.1 and more preferably 0.15. The charge efficiency is further improved by increasing the peak height ratio. On the other hand, the upper limit of the peak height ratio is, for example, 1 and may be 0.5, 0.4, or 0.3.

[0031]

In the X-ray diffraction spectrum of the negative composite present on the surface of the negative composite, when the ratio of the peak height near the diffraction angle of 31.2° to the peak height near the diffraction angle of 30.3° is 0.05 or more, at least a part of the negative composite present on the surface usually has a scale-like shape. A component constituting the scale-like shape is presumed to be a component containing lead. The planar shape of the negative composite in the scale-like shape is not particularly limited but may be, for example, a fan-shaped or semi-circular shape. The lower limit of the aspect ratio of the scale-like shape is preferably 3 and more preferably 5. On the other hand, the upper limit of the aspect ratio may be, for example, 10 or may be 8 or 7.

[0032]

When the negative composite present on the surface is divided into

ones having the scale-like shape and ones having other shapes (spherical shape, massive shape, etc.), the number of ones having the scale-like shape is preferably 50% or more, more preferably 70% or more, and still more preferably 90% or more. The classification based on the difference in the shape of the negative composite is performed from the image of the electron microscope obtained in the conditions for measuring the “aspect ratio of the scale-like shape” described above.

[0033]

The lower limit of the specific surface area of the negative composite may be, for example, 0.4 m²/g or 0.5 m²/g but is preferably 0.55 m²/g and more preferably 0.6 m²/g. When the specific surface area of the negative composite is equal to or larger than the lower limit, the electrolyte solution can sufficiently penetrate into the negative composite and the like, so that the lead sulfate is more easily eluted during charge, and the charge efficiency is improved. The upper limit of the specific surface area of the negative composite may be, for example, 1 m²/g but is preferably 0.8 m²/g and more preferably 0.75 m²/g. When the specific surface area of the negative composite is equal to or lower than the upper limit, the electrolytic reaction in which gas is generated is suppressed, and hence the charge efficiency is improved.

[0034]

(Manufacturing method for negative electrode)

The negative electrode plate is obtained by subjecting a non-chemically converted negative electrode plate to chemical conversion treatment. The non-chemically converted negative electrode plate is

usually produced using a lead powder, which is a raw material of the negative active material and contains lead monoxide as the main component. Specifically, the negative current collector is filled with a negative composite paste, and the negative electrode plate is cured and dried in accordance with a conventional method to produce a non-chemically converted negative electrode plate. The negative composite paste can be obtained, for example, by mixing a lead powder containing lead monoxide as the main component with carbon black, lignin, and barium sulfate as additives in a predetermined ratio, and then mixing water and 50% dilute sulfuric acid in a predetermined ratio. The curing and drying of the non-chemically converted negative electrode plate are preferably performed at a temperature higher than room temperature and at a high humidity.

[0035]

The obtained non-chemically converted negative electrode plate is subjected to the chemical conversion treatment to obtain a negative electrode plate in which the lead powder has become spongy lead. The chemical conversion can be performed by charging the element in a state where the element including the non-chemically converted negative electrode plate is immersed in the electrolyte solution containing sulfuric acid in the container of the lead-acid battery. However, the chemical conversion may be performed before the lead-acid battery or the element is assembled. By the chemical conversion, spongy lead is generated and can be used as the negative electrode plate.

[0036]

Here, the negative composite having the above peak height ratio,

that is, the negative composite in which at least a part of the negative composite present on the surface has a scale-like shape, can be obtained by adjusting the chemical conversion treatment conditions and the additive to the negative composite. Specifically, when carbon black having a relatively small specific surface area, barium sulfate having a relatively small average particle size, and lignin having a relatively small molecular weight are used in combination, and the chemical conversion treatment is performed in predetermined conditions, the negative composite can be obtained easily. For example, the specific surface area of the carbon black used may be from 70 to 240 m²/g and is preferably from 100 to 200 m²/g. The average particle size of the barium sulfate used may be from 0.1 to 0.5 μm and is preferably 0.2 to 0.4 μm. The average molecular weight of the lignin used may be from 1,000 to 10,000 and is preferably from 3,000 to 8,000. The amount of carbon black added may be, for example, from 0.1 to 1% by mass relative to the lead powder. The amount of barium sulfate added may be, for example, from 1 to 5% by mass relative to the lead powder. The amount of lignin added may be, for example, from 0.01 to 0.5% by mass relative to the lead powder. The specific surface area of the negative composite can be adjusted by the particle size, the specific surface area, or the like of each component used, the chemical conversion treatment conditions, or the like.

[0037]

<Negative electrode (B) for lead-acid battery>

The negative electrode (B) for the lead-acid battery according to one embodiment of the present invention is similar to the negative electrode (A) for the lead-acid battery described above except that at least a part of the

negative composite present on the surface of the negative electrode has a scale-like shape, the aspect ratio of the scale-like shape is 3 or more and 10 or less, and in the X-ray diffraction spectrum of the negative composite present on the surface, the ratio of the peak height near the diffraction angle of 30.3° to the peak height near the diffraction angle of 31.2° in the X-ray diffraction spectrum of the negative composite on the surface is not limited to 0.05 or more. The specific form, preferred form, and manufacturing method of the negative electrode (B) for the lead-acid battery can be made similar to those of the negative electrode (A) for the lead-acid battery described above.

[0038]

The lower limit of the aspect ratio of the scale-like shape of the electrode (B) for the lead-acid battery is preferably 4 and more preferably 5. By setting the aspect ratio equal to or higher than the lower limit, the charge efficiency is improved. On the other hand, the upper limit of the aspect ratio may be 10 or may be 8 or 7.

[0039]

<Lead-acid battery>

The lead-acid battery according to one embodiment of the present invention includes a negative electrode plate as a negative electrode, a positive electrode plate as a positive electrode, and an electrolyte solution. A separator is disposed between the negative electrode plate and the positive electrode plate. The negative electrode plate, the positive electrode plate, and the separator are immersed in the electrolyte solution. The lead-acid battery may be a flooded-type lead-acid battery or a valve regulated

lead-acid battery but is preferably the flooded-type lead-acid battery.

[0040]

(Negative electrode plate)

As the negative electrode plate, the negative electrode (A) for the lead-acid battery or the negative electrode (B) for the lead-acid battery according to one embodiment of the present invention is used.

[0041]

(Positive electrode plate)

The positive electrode plate can be classified into a paste type, a clad type, and the like.

[0042]

The paste-type positive electrode plate usually includes a grid plate-shaped positive current collector and a positive composite. The positive composite is held on the positive current collector. The positive current collector may be formed similarly to the negative current collector and can be formed by casting lead or a lead alloy or processing a lead or a lead alloy sheet.

[0043]

The clad-type positive electrode plate includes a plurality of porous tubes, a spine inserted into each tube, a positive composite with which the spine inserted tube is filled, and a joint that joins the plurality of tubes.

[0044]

As the lead alloy used for the positive current collector, a Pb-Ca based alloy, a Pb-Ca-Sn based alloy, or the like is preferred in terms of corrosion resistance and mechanical strength. The positive current

collector may have lead alloy layers having different compositions, and a plurality of lead alloy layers may be used. It is preferable to use the Pb-Sb-based alloy for the spine.

[0045]

The positive composite includes a positive active material (usually lead dioxide or lead sulfate). In addition to the positive active material, the positive composite may contain additives such as tin sulfate and red lead when necessary.

[0046]

A non-chemically converted paste-type positive electrode plate is obtained by filling the positive current collector with a positive composite paste, obtained by the conventional method, and curing and drying the same as in the case of a negative electrode plate. The positive composite paste can be prepared by kneading a lead powder, additives, water, sulfuric acid, and the like. Thereafter, the non-chemically converted positive electrode plate is converted chemically. The clad-type positive electrode plate is formed by filling the spine inserted porous glass tube with a lead powder or a slurry-like lead powder and joining the plurality of tubes with the joint.

[0047]

(Electrolyte solution)

The electrolyte solution is an aqueous solution containing sulfuric acid. The electrolyte solution may further contain metal ions such as sodium ions.

[0048]

The electrolyte solution may be gelled when necessary. The degree

of gelation is not particularly limited. A gel-like electrolyte solution from a sol having fluidity may be used, or a gel-state electrolyte solution having no fluidity may be used. The lower limit of the specific gravity of the electrolyte solution at 20°C in the fully charged lead-acid battery is, for example, 1.1 g/cm³ and preferably 1.2 g/cm³. On the other hand, the upper limit of the specific gravity is, for example, 1.4 g/cm³ and preferably 1.35 g/cm³.

[0049]

(Separator)

A nonwoven fabric, a microporous film, or the like is used as the separator. The thickness and the number of separators interposed between the negative electrode plate and the positive electrode plate may be appropriately selected in accordance with the distance between the electrodes. The nonwoven fabric sheet is a sheet mainly composed of polymer fibers and glass fibers, and for example, 60% by mass or more is formed of fiber components. On the other hand, the microporous film is obtained by, for example, extruding a composition containing a polymer powder, a silica powder, and oil into a sheet and then extracting the oil to form pores. The material constituting the separator is preferably one having acid resistance, and the polymer component is preferably polyolefin such as polyethylene or polypropylene.

[0050]

(Applications)

The lead-acid battery has good charge efficiency. Therefore, the lead-acid battery can be widely used in various applications in which a

general lead-acid battery is used, such as for automobiles. In particular, the lead-acid battery can be suitably used for an idling stop vehicle in which a large number of charges and discharges are repeated, and excellent charge efficiency is required.

[0051]

Fig. 1 illustrates an external appearance of an example of a lead-acid battery according to an embodiment of the present invention. A lead-acid battery 1 includes an element 11, an electrolyte solution (not illustrated), and a container 12 for housing those. The inside of the container 12 is partitioned by a partition wall 13 into a plurality of cell chambers 14. In each cell chamber 14, one element 11 is stored. The opening of the container 12 is sealed by a lid 15 having a negative electrode terminal 16 and a positive electrode terminal 17. The lid 15 is provided with a vent plug 18 for each cell chamber. At the time of water addition, the vent plug 18 is removed to supply a water addition liquid. The vent plug 18 may have a function of discharging gas generated in the cell chamber 14 to the outside of the battery.

[0052]

The element 11 is configured by laminating a plurality of negative electrode plates 2 and positive electrode plates 3 with a separator 4 interposed therebetween. Although the bag-shaped separator 4 housing the negative electrode plate 2 is illustrated here, the form of the separator is not particularly limited. In the cell chamber 14 located at one end of the container 12, a negative electrode shelf 6 for connecting the plurality of negative electrode plates 2 in parallel is connected to a through-connector 8,

and a positive electrode shelf 5 for connecting the plurality of positive electrode plates 3 in parallel is connected to a positive electrode pole 7. The positive electrode pole 7 is connected to the positive electrode terminal 17 outside the lid 15. In the cell chamber 14 located at the other end of the container 12, a negative electrode pole 9 is connected to the negative electrode shelf 6, and the through-connector 8 is connected to the positive electrode shelf 5. The negative electrode pole 9 is connected to the negative electrode terminal 16 outside the lid 15. Each through-connector 8 passes through a through-hole provided in the partition 13 and connects the elements 11 of the adjacent cell chambers 14 in series.

[0053]

The present invention is not limited to the above embodiment but can be carried out in various modified and improved aspects in addition to the above modes. For example, in the above embodiment, the positive electrode and the negative electrode have been described as the positive electrode plate and the negative electrode plate, respectively, but each of the positive electrode and the negative electrode is not limited to a plate shape.

EXAMPLES

[0054]

Hereinafter, the present invention will be described more specifically by way of examples, but the present invention is not limited to the following examples.

[0055]

<Example 1>

(1) Production of non-chemically converted negative electrode plate

To a lead powder containing lead monoxide as the main component, 0.3% by mass of carbon black having a specific surface area of 165 m²/g, 2.1% by mass of barium sulfate having an average particle size of 0.3 μm, and 0.05% by mass of lignin having a mass average molecular weight of 6000 were added. Water and 50% dilute sulfuric acid were further added to the mixture, which was then kneaded to obtain a negative composite paste. A mesh portion of an expanded grid made of a Pb-Ca-Sn alloy was filled with the negative composite paste, which was then cured and dried to obtain a non-chemically converted negative electrode plate.

[0056]

(2) Production of non-chemically converted positive electrode plate

A lead oxide powder, which is a raw material, was mixed with a sulfuric acid aqueous solution to obtain a positive composite paste. A mesh portion of an expanded grid made of a Pb-Ca-Sn alloy was filled with the positive composite paste, which was then cured and dried to obtain a non-chemically converted positive electrode plate.

[0057]

(3) Preparation of the electrolyte solution

Sulfuric acid was added to water to prepare an electrolyte solution.

[0058]

(4) Production of lead-acid battery

A non-chemically converted negative electrode plate was housed into a bag-shaped separator formed using a polyethylene microporous film, and an element was formed using seven non-chemically converted negative electrode plates and six non-chemically converted positive electrode plates.

The element was housed into a polypropylene container together with the electrolyte solution, and chemical conversion was performed in the container to assemble a flood-type lead-acid battery of Example 1. The chemical conversion was performed on the negative composite at an electric quantity of 3.3 Ah/g.

[0059]

<Example 2>

A lead-acid battery of Example 2 was assembled similarly to in Example 1 except that the amount of lignin added was 0.07% by mass.

[0060]

<Example 3>

A lead-acid battery of Example 3 was assembled similarly to in Example 1 except that 0.3% by mass of carbon black having a specific surface area of 140 m²/g was added, and the amount of lignin added was 0.10% by mass.

[0061]

<Example 4>

A lead-acid battery of Example 4 was assembled similarly to Example 1 except that the amount of lignin added was 0.10% by mass.

[0062]

<Example 5>

A lead-acid battery of Example 5 was assembled similarly to in Example 1 except that 0.3% by mass of carbon black having a specific surface area of 183 m²/g was added, and the amount of lignin added was 0.10% by mass.

[0063]

<Example 6>

A lead-acid battery of Example 6 was assembled similarly to in Example 1 except that 0.3% by mass of carbon black having a specific surface area of 140 m²/g was added, and the amount of lignin added was 0.15% by mass.

[0064]

<Example 7>

A lead-acid battery of Example 7 was assembled similarly to Example 1 except that the amount of lignin added was 0.15% by mass.

[0065]

<Example 8>

A lead-acid battery of Example 8 was assembled similarly to in Example 1 except that 0.3% by mass of carbon black having a specific surface area of 183 m²/g was added, and the amount of lignin added was 0.15% by mass.

[0066]

<Example 9>

A lead-acid battery of Example 9 was assembled similarly to Example 1 except that the amount of lignin added was 0.20% by mass.

[0067]

<Example 10>

A lead-acid battery of Example 10 was assembled similarly to Example 1 except that the amount of lignin added was 0.25% by mass.

[0068]

<Comparative Example 1>

A lead-acid battery of Comparative Example 1 was assembled similarly to in Example 1 except that 0.5% by mass of carbon black having a specific surface area of 214 m²/g was added as carbon black, 2.1% by mass of barium sulfate having an average particle size of 0.6 μm was added as barium sulfate, and 0.05% by mass of lignin having a mass average molecular weight of 12000 was added as lignin.

[0069]

<Comparative Example 2>

A lead-acid battery of Comparative Example 2 was assembled similarly to in Comparative Example 1 except that lignin having an average molecular weight of 12000 was added by 0.07% by mass as lignin.

[0070]

<Comparative Example 3>

A lead-acid battery of Comparative Example 3 was assembled similarly to in Comparative Example 1 except that lignin having an average molecular weight of 12000 was added by 0.10% by mass as lignin.

[0071]

<Comparative Example 4>

A lead-acid battery of Comparative Example 4 was assembled similarly to in Comparative Example 1 except that lignin having an average molecular weight of 12000 was added by 0.15% by mass as lignin.

[0072]

<Comparative Example 5>

A lead-acid battery of Comparative Example 5 was assembled

similarly to in Comparative Example 1 except that lignin having an average molecular weight of 12000 was added by 0.20% by mass as lignin.

[0073]

<Comparative Example 6>

A lead-acid battery of Comparative Example 6 was assembled similarly to in Comparative Example 1 except that lignin having an average molecular weight of 12000 was added by 0.25% by mass as lignin.

[0074]

[Measurement]

The specific surface area of the negative composite and the X-ray diffraction (XRD) spectrum of the surface were measured for the negative electrode of each of the obtained lead-acid batteries by the method described above. Fig. 2 shows the XRD spectrum of Example 4, and Fig. 3 shows the XRD spectrum of Comparative Example 5. Table 1 shows the obtained specific surface area and the ratio of the peak height near the diffraction angle (2θ) of 30.3° to the peak height near the diffraction angle (2θ) of 31.2° in the X-ray diffraction spectrum.

[0075]

The shape of the surface of the negative composite was observed for the negative electrode of each of the obtained lead-acid batteries by the method described above. Table 1 shows the shape and the aspect ratio based on the shape. In the column of the shape in Table 1, the term “Normal” means a massive shape or a spherical shape having a low aspect ratio.

[0076]

Fig. 4 shows an electron micrograph of the surface of the negative composite in the lead-acid battery of Example 4. Fig. 5 shows an electron micrograph of the surface of the negative composite in the lead-acid battery of Comparative Example 5. It can be seen from Fig. 4 that in Example 4, a plurality of scale-like protrusions (scale-like shape) have been formed on the surface. On the other hand, it can be seen from Fig. 5 that such a scale-like shape has not been formed in Comparative Example 5.

[0077]

[Evaluation]

<Idling stop (IS) life>

An idling stop life test was conducted on each lead-acid battery as follows: In an atmosphere of 0°C, 6h-small current (20 mA) discharge was performed every time discharge at 300 A for 1.0 seconds, discharge at 25 A for 25 seconds, and charge at 14.0 V for 30 seconds were repeated for 30 cycles. Note that the small current discharge simulates dark current discharge when the engine is stopped. The above 30 cycles and the 6h-small current discharge were repeated, and the time point when the discharge voltage in the 300 A discharge falls below 7.2 V was taken as the life. When the IS life is long, the charge efficiency can be determined to be excellent.

[0078]

Table 1 shows the evaluation results. Note that the IS life in Table 1 is shown as a relative value with Comparative Example 1 as a reference (100%).

[0079]

[Table 1]

	Negative additive				Negative composite				Evaluation
	Carbon black Specific surface area [m²/g]	Barium sulfate Particle size [µm]	Lignin		Specific surface area [m²/g]	XRD spectrum	Shape		IS life [%]
			Mass average molecular weight	Added amount [mass%]		Peak height ratio [-]	-	Aspect ratio [-]	
Comparative Example 1	214	0.6	12000	0.05	0.5	0.02	Normal	-	100
Example 1	165	0.3	6000	0.05		0.18	Scale-like	3	134
Comparative Example 2	214	0.6	12000	0.07	0.55	0.03	Normal	-	112
Example 2	165	0.3	6000	0.07		0.18	Scale-like	4	172
Comparative Example 3	214	0.6	12000	0.10	0.6	0.02	Normal	-	124
Example 3	140	0.3	6000	0.10		0.10	Scale-like	4	207
Example 4	165	0.3	6000	0.10		0.18	Scale-like	5	212
Example 5	183	0.3	6000	0.10		0.22	Scale-like	6	213
Comparative Example 4	214	0.6	12000	0.15	0.75	0.02	Normal	-	129
Example 6	140	0.3	6000	0.15		0.10	Scale-like	6	212
Example 7	165	0.3	6000	0.15		0.18	Scale-like	7	216
Example 8	183	0.3	6000	0.15		0.22	Scale-like	8	218
Comparative Example 5	214	0.6	12000	0.20	0.8	0.02	Normal	-	118
Example 9	165	0.3	6000	0.20		0.18	Scale-like	9	174
Comparative Example 6	214	0.6	12000	0.25	0.85	0.03	Normal	-	97
Example 10	165	0.3	6000	0.25		0.18	Scale-like	10	132

[0080]

As shown in Table 1, each of the lead-acid batteries of Example 1 to 10 had an IS life of 130% or more, resulting in good charge efficiency. Further, in comparison among the examples, it can be seen that the IS life becomes longer when the specific surface area of the negative composite is 0.55 m²/g or more and 0.8 m²/g or less, or when the peak height ratio in the X-ray diffraction spectrum is higher. On the other hand, each of the lead-acid batteries of Comparative Examples 1 to 6, in which the surface shape of the negative composite is not scale-like and the peak height ratio in the X-ray diffraction spectrum is low, has a short IS life, resulting in insufficient charge efficiency.

INDUSTRIAL APPLICABILITY

[0081]

The lead-acid battery of the present invention is used as a power

source for automobiles, motorcycles, electric vehicles (forklifts, etc.), industrial energy storage apparatuses, and the like and is particularly preferably used as a power source for idling stop vehicles.

DESCRIPTION OF REFERENCE SIGNS

[0082]

- 1: lead-acid battery
- 2: negative electrode plate
- 3: positive electrode plate
- 4: separator
- 5: positive electrode shelf
- 6: negative electrode shelf
- 7: positive electrode pole
- 8: through-connector
- 9: negative electrode pole
- 11: element
- 12: container
- 13: partition
- 14: cell chamber
- 15: lid
- 16: negative electrode terminal
- 17: positive electrode terminal
- 18: vent plug

CLAIMS

1. A negative electrode for a lead-acid battery, the electrode comprising
a negative composite containing lead,
wherein in an X-ray diffraction spectrum of the negative composite present on a surface of the negative electrode, a ratio of a peak height near a diffraction angle of 30.3° to a peak height near a diffraction angle of 31.2° is 0.05 or more.
2. A negative electrode for a lead-acid battery, the electrode comprising
a negative composite containing lead,
wherein at least a part of the negative composite present on a surface of the negative electrode has a scale-like shape, and an aspect ratio of the scale-like shape is 3 or more and 10 or less.
3. The negative electrode for the lead-acid battery according to claim 1 or 2, wherein a specific surface area of the negative composite is 0.55 m^2/g or more and 0.8 m^2/g or less.
4. The negative electrode for the lead-acid battery according to claim 3, wherein the specific surface area of the negative composite is 0.6 m^2/g or more and 0.75 m^2/g or less.
5. A lead-acid battery comprising

the negative electrode for the lead-acid battery according to any one of claims 1 to 4.

6. The lead-acid battery according to claim 5, wherein the lead-acid battery is for an idling stop vehicle.