

DESCRIPTION

TITLE OF THE INVENTION: LEAD-ACID BATTERY

TECHNICAL FIELD

[0001]

The present invention relates to 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, in order to improve various performances, generally, an additive such as carbon is added to a negative active material, and an additive such as sodium ion is added to an electrolyte solution (cf. Patent Documents 1 and 2.). 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. Patent Document 2 proposes a lead-acid battery using an electrolyte solution containing aluminum ions in the range of 0.03 to 0.27 mol/L and sodium ions in the range of 0.03 to 0.28 mol/L.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004]

Patent Document 1: JP-A-2008-152955

Patent Document 2: JP-A-2016-115396

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

It is important that a lead-acid battery used in an automobile and the like has a long life even when used in a severe environment. However, the life of the lead-acid battery is shortened, especially when the overcharge is repeated at a high temperature, because the corrosion of a positive current collector progresses. Conventional lead-acid batteries do not sufficiently have such a high-temperature overcharge life.

[0006]

Meanwhile, a system for stopping the idling of an engine has become widespread for the purpose of improving the fuel efficiency of automobiles. In automobiles employing the system, the state of charge (SOC) of the lead-acid battery tends to be controlled in a lower range than in conventional vehicles. Hence, the lead-acid battery is often used at intermediate SOC. When the lead-acid battery is used at intermediate SOC, there is a disadvantage that the subsequent electric capacity is difficult to recover sufficiently. As a technique for improving charge acceptability in the lead-acid battery used in the idling stop system used at intermediate SOC, it has been conventionally proposed to add Al ions to an electrolyte solution or to add carbon having a high specific surface area to a negative active material. However, as idling stop vehicles are put on the market and sold, the following new issues have become apparent. That is, an idling stop vehicle

in stock for a long period of time at a vehicle dealer or a short-distance idling stop vehicle running once a week or once a month has insufficient capacity recoverability due to overdischarge or deep discharge and may reach the service life earlier than expected.

[0007]

The present invention has been made based on such circumstances as above, and an object of the present invention is to provide a lead-acid battery having a long high-temperature overcharge life and having sufficient capacity recoverability after overdischarge or deep discharge.

MEANS FOR SOLVING THE PROBLEMS

[0008]

One aspect of the present invention made to solve the above problems is a lead-acid battery including: a negative electrode having a negative composite that contains lead and carbon black; and an electrolyte solution containing sodium ions. The carbon black has a di-butyl phthalate (DBP) oil absorption of 170 mL/100 g or less, and the content of the sodium ions in the electrolyte solution is more than 0 mmol/L and 30 mmol/L or less.

ADVANTAGES OF THE INVENTION

[0009]

According to the present invention, it is possible to provide a lead-acid battery having a long high-temperature overcharge life and having sufficient capacity recoverability after overdischarge or deep discharge.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

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.

MODE FOR CARRYING OUT THE INVENTION

[0011]

A lead-acid battery according to one aspect of the present invention is a lead-acid battery including a negative electrode having a negative composite that contains lead and carbon black; and an electrolyte solution containing sodium ions. The carbon black has a DBP oil absorption of 170 mL/100 g or less, and the content of the sodium ions in the electrolyte solution is more than 0 mmol/L and 30 mmol/L or less.

[0012]

The lead-acid battery has a long high-temperature overcharge life and has sufficient capacity recoverability after overdischarge or deep discharge. The reason for this is not clear, but the following reasons are presumed. By using a carbon black having a small DBP oil absorption as the carbon black contained in the negative composite and reducing the content of the sodium ions in the electrolyte solution, the amount of overcharge during charge in a high-temperature environment can be reduced. In such a lead-acid battery, with the accumulated amount of overcharge being reduced, it is presumed that the positive current collector is less likely to be corroded and the overcharge life at high temperature is extended. The lead-acid battery has sufficient capacity recoverability after overdischarge or deep discharge due to the sodium ions being contained in the electrolyte solution. Further, the lead-acid battery has a small decrease in the amount of electrolyte solution accompanying charge and discharge

and has good charge acceptability.

[0013]

In the present specification, the DBP oil absorption is assumed to be a value measured in accordance with Japanese Industrial Standards (JIS) K 6217-4. The content of each component is assumed to be a content in a fully charged state (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.

[0014]

It is preferable that the content of the carbon black relative to the lead be 0.01% by mass or more and 0.6% by mass or less. Setting the content of the carbon black in the above range makes the amount of overcharge during charge in a high-temperature environment more moderate to further improve the high-temperature overcharge life. It is preferable that the content of the carbon black relative to the lead be 0.1% by mass or more and 0.4% by mass or less. In this case, the high-

temperature overcharge life and the capacity recoverability after overdischarge or deep discharge are improved

[0015]

It is preferable that the negative composite further contain barium sulfate and that a content of the barium sulfate relative to the lead be 0.5% by mass or more and 10% by mass or less. It is more preferable that the content of the barium sulfate relative to the lead be 2% by mass or more and 10% by mass or less. By containing such an amount of barium sulfate in the negative composite, the high-temperature overcharge life and the capacity recoverability after overdischarge or deep discharge are improved. It is also preferable that the content of the barium sulfate relative to the lead be 0.5% by mass or more and 4% by mass or less. In this case, in addition the good high-temperature overcharge life and the good capacity recoverability after overdischarge or deep discharge, the amount of decrease in the electrolyte solution can be reduced.

[0016]

<Lead-acid battery>

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

[0017]

(Negative electrode plate)

The negative electrode plate includes a negative current collector and a negative composite. The negative composite is held by the negative current collector.

[0018]

(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.

[0019]

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.

[0020]

(Negative composite)

The negative composite contains lead and carbon black.

[0021]

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. Some or all of the lead in the negative composite may be present as lead sulfate or the like.

[0022]

The carbon black is present in the negative composite as particles containing carbon as the main component. The upper limit of the DBP oil absorption of the carbon black contained in the negative composite is 170 mL/100 g and may be preferably 160 mL/100 g, more preferably 150 mL/100 g, and even more preferably 140 mL/100 g. Setting the DBP oil absorption of the carbon black to the upper limit or less makes the high-temperature overcharge life longer, whereby the amount of decrease in the electrolyte solution tends to be reduced. The lower limit of DBP oil absorption of carbon black is, for example, 50 mL/100 g and may be preferably 80 mL/100 g, more preferably 120 mL/100 g, and even more preferably 140 mL/100 g. Setting the DBP oil absorption of the carbon black to the lower limit or more leads to an increase in the conductivity of the carbon black, whereby the capacity recoverability after overdischarge or deep discharge, the charge acceptability, and the like tend to be improved.

[0023]

The lower limit of the content of the carbon black in the negative composite relative to lead (100% by mass) may be preferably 0.01% by mass, more preferably 0.05% by mass, even more preferably 0.1% by mass, and still more preferably 0.2% by mass. Setting the content of the carbon black to the lower limit or more leads to an increase in the conductivity of the

negative composite due to the carbon black, whereby the capacity recoverability after overdischarge or deep discharge and the charge acceptability tend to be improved. The upper limit of the content of carbon black relative to lead (100% by mass) may be preferably 0.6% by mass, more preferably 0.5% by mass, and even more preferably 0.4% by mass, 0.3% by mass, or 0.2% by mass. Setting the content of the carbon black to the upper limit or less leads to a more sufficient reduction in the amount of overcharge during charge in a high-temperature environment, whereby the high-temperature overcharge life tends to be further improved.

[0024]

The carbon black is not particularly limited as long as having a DBP oil absorption of 170 mL/100 g or less, and various carbon blacks are used. Examples of the carbon black include furnace black, channel black, thermal black, acetylene black, and ketjen black. These may be used alone or in a combination of two or more.

[0025]

The DBP oil absorption of the carbon black can be adjusted to a desired value by mixing two or more kinds of commercially available carbon black each having a different DBP oil absorption or by some other way.

[0026]

The negative composite preferably further contains barium sulfate. With the barium sulfate contained, the growth of coarse lead sulfate crystals can be reduced to improve the overcharge life, the capacity recoverability after overdischarge or deep discharge, the charge acceptability, and the like.

[0027]

The lower limit of the content of the barium sulfate in the negative composite relative to lead (100% by mass) is preferably 0.5% by mass, more preferably 1% by mass, still more preferably 1.5% by mass, and still more preferably 2% by mass. Setting the content of the barium sulfate to the lower limit or more enables more sufficient production of the above-described effect of the barium sulfate. The upper limit of the content of the barium sulfate relative to lead (100% by mass) may be preferably 10% by mass, more preferably 5% by mass, still more preferably 4% by mass, and still more preferably 3% by mass. By setting the content of the barium sulfate to the upper limit or less, the amount of decrease in the electrolyte solution tends to be reduced.

[0028]

Barium sulfate is usually present as particles in the negative composite. The lower limit of the average primary particle size of the barium sulfate is, for example, 0.1 μm , and preferably 0.2 μm . The upper limit of the average primary particle size is 1 μm , and is preferably 0.5 μm . The use of the barium sulfate having such a particle size enables more sufficient production of the above-described effect produced due to the barium sulfate being contained. Note that the average primary particle size of the barium sulfate is assumed to be a value obtained by arbitrarily selecting 20 primary particles of barium sulfate in an enlarged photograph of the negative composite and averaging the particle sizes of the selected particles. The particle size is the diameter of the corresponding circle having the same area as the projected area of the primary particles of the barium sulfate visible in the magnified photograph.

[0029]

It is possible to contain, in the negative composite, other additives, such as a carbonaceous material other than the carbon black and lignin, when necessary.

[0030]

(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.

[0031]

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 an element including the non-chemically converted negative electrode plate in a state where the element is immersed in an 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.

[0032]

(Positive electrode plate)

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

[0033]

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.

[0034]

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.

[0035]

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.

[0036]

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.

[0037]

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.

[0038]

(Electrolyte solution)

The electrolyte solution is an aqueous solution containing sulfuric acid. The electrolyte solution contains sodium ions. The upper limit of the content of the sodium ions in the electrolyte solution is 30 mmol/L and may be preferably 20 mmol/L, and more preferably 15 mmol/L or 10 mmol/L.

Setting the content of the sodium ions to the upper limit or less enables an improvement in the overcharge life. There is also a tendency that the decreased amount of the electrolyte solution is reduced and the charge acceptability is improved. On the other hand, the content of the sodium ions in the electrolyte solution may be more than 0 mmol/L, and the lower limit of the content is preferably 0.1 mmol/L, more preferably 1 mmol/L, and still more preferably 3 mmol/L. Setting the content of the sodium ions to the lower limit or more makes the capacity recoverability after overdischarge or deep discharge more sufficient.

[0039]

The sodium ions can be contained in the electrolyte solution by adding the sodium ions to the electrolyte solution as a salt such as sodium sulfate, sodium carbonate, or sodium bicarbonate.

[0040]

The electrolyte solution may further contain metal ions other than sodium ions. However, as the upper limit of the total content of the metal ions other than sodium ions in the electrolyte solution, 70 mmol/L may be preferred, 50 mmol/L may be more preferred, and 20 mmol/L may be further preferred.

[0041]

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, 1.25 g/cm³ and preferably 1.28 g/cm³. On the other hand, the upper limit of the specific gravity is, for example, 1.35 g/cm³, and preferably 1.32 g/cm³.

[0042]

(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.

[0043]

(Applications)

The lead-acid battery has a long high-temperature overcharge life and has sufficient capacity recoverability after overdischarge or deep discharge. 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 that is repeatedly charged and discharged many times

and required to have a sufficient overcharge life, capacity recoverability, and the like.

[0044]

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.

[0045]

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.

[0046]

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

[0047]

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

[0048]

<Example 1>

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

Carbon black having a DBP oil absorption of 100 mL/100 g, barium sulfate having an average primary particle size of 0.3 μm , and lignin having

a mass average molecular weight of 6000 were mixed as additives with a lead powder containing lead monoxide as the main component in a predetermined ratio. Water and 50% dilute sulfuric acid were further added to this mixture in a predetermined ratio, followed by kneading, 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.

[0049]

The carbon black was blended with the negative composite paste so that the content of the carbon black in the negative composite of the lead-acid battery fully charged after chemical conversion was 0.3% by mass. The barium sulfate was blended with the negative composite paste so that the content of the barium sulfate in the negative composite of the lead-acid battery fully charged after chemical conversion was 2.1% by mass.

[0050]

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

A lead powder, which is a raw material and contains lead monoxide as the main component, was mixed with water and 50% dilute sulfuric acid in a predetermined ratio 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 in accordance with the conventional method to obtain a non-chemically converted positive electrode plate.

[0051]

(3) Preparation of the electrolyte solution

Sulfuric acid and a mixture of sodium sulfate and sodium carbonate were added to water to prepare an electrolyte solution having a content of sodium ions of 5 mmol/L.

[0052]

(4) Production of lead-acid battery

Each non-chemically converted negative electrode plate was housed into a bag-shaped separator formed using a polyethylene microporous film, and the plates with the same electrode of seven non-chemically converted negative electrode plates and six non-chemically converted positive electrode plates were welded together to form an element. The element was housed into a polypropylene container and welded in series, the electrolyte solution was injected, and chemical conversion was performed in the container to assemble a flooded-type lead-acid battery of Example 1.

[0053]

<Examples 2 to 26 and Comparative Examples 1 to 25>

Lead-acid batteries of Example 2 to 26 and Comparative Examples 1 to 25 were assembled similarly to Example 1, except that the DBP oil absorption of the carbon black used and the contents of the carbon black, barium sulfate, and sodium ions were set as shown in Table 1. Note that the DBP oil absorption of the carbon black was adjusted by using carbon black having different DBP oil absorptions singly or more than one kind of commercially available carbon blacks in a mixed manner.

[0054]

[Evaluation]

<Overcharge life>

A high-temperature overcharge life test was conducted on each lead-acid battery in accordance with JIS-D-5301 (2006). However, for a light load life test, in order to adjust the degradation mode of the lead-acid battery to actual conditions in the market, the discharge time for discharge at 25A was changed from 240 seconds to 60 seconds. Specifically, the test was conducted in the following procedure.

- 1) In an atmosphere of 75°C, discharge at 25 A for 60 seconds and charge at 14.8 V for 600 seconds were repeated for 480 cycles.
- 2) After being left in the atmosphere of 75°C for 56 hours, the battery was discharged by a cold cranking current for 30 seconds.
- 3) The weight of the lead-acid battery was measured in the atmosphere of 75°C, water addition was performed up to the upper limit line of the electrolyte solution, and the weight was measured again.
- 4) The battery was left in the atmosphere of 75°C for 24 hours.
- 5) 1) to 4) above were repeated until the discharge voltage during the discharge by the cold cranking current in 3) above fell below 7.2V. The number of repetitions of 1) to 4) above when the discharge voltage fell below 7.2 V was taken as an index for the high-temperature overcharge life.

[0055]

<Decreased amount of liquid>

In the high-temperature overcharge life test described above, the accumulated amount of water added from the start of the test to the end of the life was taken as the decreased amount of liquid.

[0056]

<Charge acceptability>

A charge acceptability test was conducted on each lead-acid battery in accordance with JIS-D-5301 (2006). Specifically, the test was conducted in the following procedure.

1) Discharge was performed at 7.2 A for 2.5 hours in an atmosphere of 25°C.

2) After being left in an atmosphere of 0°C for 12 hours, the battery was charged at 14.4 V for ten minutes, and a value of charge current ten minutes after the start of charge was taken as an index for charge acceptability.

[0057]

<Capacity recoverability after overdischarge>

A test for capacity recoverability after overdischarge was conducted on each lead-acid battery in the following procedure.

1) Discharge was performed in an atmosphere of 25°C until the discharge voltage at 7.2 A became 10.5 V.

2) A load of 10 w was set in an atmosphere of 40°C, and the battery was left for 14 days.

3) The load was removed, and the battery was left for an additional 14 days.

4) In an atmosphere of 25°C, the battery was charged at 15.0 V for four hours.

5) After being left in an atmosphere of -15°C for 16 hours, discharge was performed by a high-rate discharge current until the discharge voltage became 6.0 V. The duration of the discharge by the high-rate discharge

current was taken as an index for capacity recoverability after overdischarge.

[0058]

Each evaluation result is shown in Table 1. Each evaluation result is shown as a relative value with Comparative Example 22 as a reference (100%).

[0059]

[Table 1]

	Negative composite			Electrolyte solution	Evaluation					
	Carbon black		Barium sulfate	Sodium ions	Overcharge life [%]	Decreased liquid amount [%]	Charge acceptability [%]	Capacity recoverability after overdischarge [%]		
	DBP oil absorption [mL/100 mg]	Content [mass%]	Content [mass%]	Content [mass%]						
Comparative Example 1	100	0.3	2.1	0	175	56	84	74		
Example 1			2.1	5	161	62	80	85		
Example 2			2.1	15	145	69	78	87		
Example 3			2.1	20	131	77	76	88		
Comparative Example 2			2.1	45	94	102	72	91		
Comparative Example 3			2.1	70	82	117	70	94		
Comparative Example 4	130	0.3	2.1	0	171	58	91	77		
Example 4			2.1	5	160	63	88	89		
Example 5			2.1	15	144	69	86	90		
Example 6			2.1	20	130	77	85	92		
Comparative Example 5			2.1	45	92	105	83	95		
Comparative Example 6			2.1	70	80	120	81	88		
Example 7		0.05	2.1	15	167	66	79	91		
Comparative Example 7		0.1	2.1	0	179	61	88	79		
Example 8			2.1	5	165	66	86	91		
Example 9			2.1	15	149	73	84	93		
Example 10			2.1	20	134	81	83	95		
Comparative Example 8			2.1	45	93	113	81	98		
Comparative Example 9			2.1	70	81	129	79	101		
Comparative Example 10		0.3	1.0	0	149	51	94	80		
Comparative Example 11			2.1	0	172	59	97	81		
Comparative Example 12			3.5	0	185	63	101	83		
Example 11			1.0	5	138	55	92	92		
Example 12			2.1	5	159	63	95	93		
Example 13	3.5		5	171	68	99	96			
Example 14	1.0		15	124	61	91	94			
Example 15	2.1		15	143	70	94	95			
Example 16	3.5		15	154	76	96	98			
Example 17	5.0		15	166	91	99	102			
Example 18	1.0		20	112	68	89	95			
Example 19	2.1		20	129	78	92	97			
Example 20	3.5		20	139	84	95	98			
Comparative Example 13			0.3	2.1	45	89	109	90	100	
Comparative Example 14				2.1	70	77	124	88	103	
Example 21		0.5		2.1	5	144	57	105	98	
Example 22				2.1	15	130	64	103	100	
Example 23				2.1	20	116	70	101	102	
Comparative Example 15				2.1	45	81	99	98	104	
Comparative Example 16				2.1	70	70	113	97	108	
Comparative Example 17		160		0.3	2.1	0	170	59	99	83
Example 24					2.1	5	158	63	96	95
Example 25					2.1	15	142	70	94	97
Example 26					2.1	20	123	81	92	99
Comparative Example 18					2.1	45	84	116	91	102
Comparative Example 19					2.1	70	73	132	89	105
Comparative Example 20		175		0.3	2.1	0	105	93	105	74
Comparative Example 21					2.1	5	103	97	102	98
Comparative Example 22	2.1		15		100	100	100	100		
Comparative Example 23	2.1		20		92	109	98	102		
Comparative Example 24	2.1		45		74	133	96	105		
Comparative Example 25	2.1		70		64	152	94	108		

[0060]

As shown in Table 1, as compared to Comparative Example 22, the

lead-acid batteries of Examples 1 to 26 all have an overcharge life of 110% or more and a capacity recoverability after overdischarge of 85% or more, resulting in a long overcharge life at high temperature and sufficient capacity recoverability after overdischarge. On the other hand, the lead-acid batteries of Comparative Examples 2, 3, 5, 6, 8, 9, 13 to 16, and 18 to 25, in which the content of sodium ions in the electrolyte solution was more than 30 mmol/L or the DBP oil absorption of carbon black was more than 170 mL/100 g, resulted in a short overcharge life. Further, the lead-acid batteries of Comparative Examples 1, 4, 7, 10 to 12, 17, and 20 using the electrolyte solution containing no sodium ion resulted in poor capacity recoverability after overdischarge.

INDUSTRIAL APPLICABILITY

[0061]

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

[0062]

- 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 lead-acid battery comprising:
 - a negative electrode having a negative composite that contains lead and carbon black; and
 - an electrolyte solution containing sodium ions,
 - wherein the carbon black has a di-butyl phthalate (DBP) oil absorption of 170 mL/100 g or less, and
 - a content of the sodium ions in the electrolyte solution is more than 0 mmol/L and 30 mmol/L or less.
2. The lead-acid battery according to claim 1, wherein a content of the carbon black relative to the lead is 0.01% by mass or more and 0.6% by mass or less.
3. The lead-acid battery according to claim 2, wherein the content of the carbon black relative to the lead is 0.1% by mass or more and 0.4% by mass or less.
4. The lead-acid battery according to any one of claims 1 to 3, wherein
 - the negative composite further contains barium sulfate, and
 - a content of the barium sulfate relative to the lead is 0.5% by mass or more and 10% by mass or less.
5. The lead-acid battery according to claim 4, wherein the content

of the barium sulfate relative to the lead is 2% by mass or more and 10% by mass or less.

6. The lead-acid battery according to claim 4, wherein the content of the barium sulfate relative to the lead is 0.5% by mass or more and 4% by mass or less.