

Description

BACKGROUND OF THE INVENTION

5 The present invention relates to a sealed alkaline storage battery using a negative electrode of a hydrogen absorbing alloy capable of electrochemically absorbing/desorbing hydrogen acting as an active material.

Recently, hydrogen absorbing alloys capable of electro-chemically absorbing/desorbing hydrogen acting as an active material have attracted attention for use as a negative electrode material having high
10 energy density. High-capacity sealed storage batteries such as a sealed nickel-hydrogen storage battery and a closed manganese dioxide-hydrogen storage battery have been developed by combining this type negative electrodes and available positive electrodes such as a nickel positive electrode and a manganese dioxide positive electrode. In the past, this type negative electrodes for use in the sealed nickel-hydrogen storage battery and methods of producing this type negative electrodes have been proposed as follows.

15 (1) A method of producing a negative electrode comprising filling a nickel porous matter having a three-dimensional structure with hydrogen absorbing alloy powder together with an alkali-resisting binding agent (Japanese Patent Unexamined Publication No. 53-38631).

(2) A method of producing a negative electrode comprising the steps of; applying hydrogen absorbing alloy powder to a supporting metal; and sintering the alloy powder in an atmosphere of an inert gas
20 (Japanese Patent Unexamined Publication No. 62-278754).

(3) A method of producing a negative electrode comprising the steps of; kneading hydrogen absorbing alloy powder and polytetrafluoroethylene (hereinafter referred to as "PTFE") powder or its aqueous solution dispersion while applying shearing stress thereto; pressing the kneaded matter to prepare a sheet; and sticking the sheet to a nickel net or the like (Japanese Patent Unexamined Publication No. 60-
25 136162).

(4) A method in which at least one portion of a negative electrode formed of a hydrogen absorbing alloy is provided with a hydrophobic layer (Japanese Patent Unexamined Publication No. 61-118963).

The negative electrodes produced by the aforementioned methods have a disadvantage in that short-time (about an hour) charging required in portable apparatus and the like is difficult or in that the reliability
30 of the battery may deteriorate with repetition of charging/discharging though short-time (rapid) charging may be made in the early stage where the battery is just constructed. When the prior art negative electrodes formed by the above methods (1) and (2) are subject to relatively slow charging with respect to which the time required for perfect charging is within a range of from about 4.5 hours to about 16 hours, there arises no problem particularly awaiting solution. When the prior art negative electrodes produced by the above
35 methods (1) and (2) are subject to rapid charging, however, the internal gas pressure of the battery increases in an overcharging period so that a safety vent (which is, in general, actuated by the battery inner pressure of 10 to 15 kg/cm² in the same manner as an ordinary nickel-cadmium battery) is actuated so that the alkaline electrolyte of the battery leaks to constitute an obstacle to various battery characteristics and safety. Accordingly, in the prior art negative electrodes produced by the above methods (1) and (2), short-
40 time charging is impossible.

In the prior art negative electrode produced by the above method (3), the respective sheets composed of fiber-like fluororesin and hydrogen absorbing alloy powder are located on the opposite sides of the nickel net respectively. In the configuration of the negative electrode, the fiber-like fluororesin gives suitable hydrophobic property to the surfaces of the hydrogen absorbing alloy powders to improve gas absorption
45 ability in an overcharging period to thereby make it possible to perform short-time charging in the early stage where the battery is just constructed. It is however very difficult to prepare reproducibly similar sheets by the aforementioned steps of; kneading hydrogen absorbing alloy powder and PTFE powder while applying shearing stress thereto; and pressing the mulled matter. Accordingly, the internal gas pressure of the battery in a short-time charging period varies widely and sometimes exceeds 20 kg/cm². Furthermore,
50 the negative electrode is inferior in mechanical strength because the sheet formed by tangling the alloy particles with the fluororesin fibers is stuck to the nickel net. Accordingly, the alloy and the fluororesin are subject to expansion/contraction due to repetition of charging/discharging and changes in temperature, resulting in deterioration in the negative electrode. Accordingly, the prior art negative electrode produced by the above method (3) has a problem in that the reliability of the battery deteriorates with repetition of
55 charging/discharging.

The proposal by the above method (4) is that a hydrophobic layer is provided in a portion of a negative electrode to thereby improve gas absorption capacity in an overcharging period. Although short-time charging is possible in this case, there arises a problem in that the hydrophobic layer provided in the

negative electrode is made to come off by the expansion/contraction of the alloy due to repetition of charge/discharge or by a gas generated, so that the internal gas pressure of the battery increases with repetition of charging/discharging cycles.

According to EP 0 386 305, particularly example 19, a hydrophobic substance, i. e. FEP, is applied on the surface of the foamed nickel matrix after said foamed nickel matrix was filled with a paste containing PVA, i. e. a hydrophilic substance. Thus, the hydrophobic substance FEP is applied on the surface of said nickel matrix and, therefore, on the surface portion of the negative electrode. The priority date of the aforesaid patent application is February 23, 1989.

According to JP-A-58 46 830, the anode, is prepared by filling a porous H-absorbing sheet with an active material and by immersing the filled sheet in a dispersion of a fluoropolymer

JP-A-62 139 255 teaches a similar disclosure to that of JP-A-58 46 830.

JP-A-58 201 271 discloses means for acceleration oxygen gas absorption. To this end, polytetrafluorethylene is sprayed in "the required part" of the nickel metal.

15 OBJECTS AND SUMMARY OF THE INVENTION

It is therefore an object of the present invention to solve the aforementioned problems in the prior art.

That is to say the object of the invention is to provide a highly reliable sealed alkaline storage battery in which the battery internal gas pressure never rises over the actuation pressure of a safety vent even if short-time charging is performed, and never rises even if charging/discharging cycles are repeated.

The above object is achieved by a sealed alkaline storage battery according to Claim 1 and a method of producing a negative electrode of a sealed alkaline storage battery according to Claim 14, respectively.

Preferred embodiments are claimed in the subclaims.

25 DESCRIPTION OF THE DRAWINGS

Fig. 1A is a schematic sectional view of a supporter of a three-dimensional structure having hydrophobic property, in which PTFE is fixed to a surface portion of a skeleton of a sponge-like nickel porous matter, as an embodiment of the present invention;

Fig. 1B is a typical enlarged view of the support depicted in Fig. 1A;

Fig. 2 is a sectional view of a negative electrode prepared by filling the supporter of a three-dimensional structure support having hydrophobic property with hydrogen absorbing alloy powder;

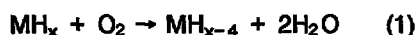
Fig. 3 is a sectional view of a negative electrode in which a layer of PTFE is provided in the surface portion thereof;

Fig. 4 is a schematic sectional view of a sealed nickel-hydrogen storage battery having a capacity of 1000 mAh; and

Fig. 5 is a graph view showing the relation between the charge rate and the internal gas pressure of the battery.

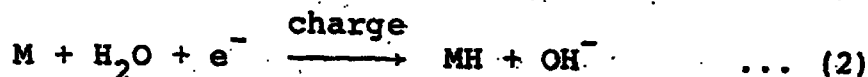
40 DETAILED DESCRIPTION OF THE INVENTION

The principle of sealed cell construction in a nickel-hydrogen storage battery is the same as that in a nickel-cadmium battery which has been proposed by Neumann. Also in the nickel-hydrogen storage battery, the maximum charge capacity of the negative electrode is established to be larger than the maximum charge capacity of the positive electrode. That is to say, the negative electrode is not perfectly charged even in the condition that the positive electrode has been perfectly charged. Accordingly, a hydrogen gas is prevented from being generated from the negative electrode in an overcharging period. At the same time, an oxygen gas generated from the positive electrode is reduced on the negative electrode by the reaction represented by the following formula (1) to keep the closing state of the battery.

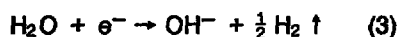


In the formula (1) M represents a hydrogen absorbing alloy.

However, in the case where the negative electrode using a hydrogen absorbing alloy is charged, the hydrogen absorbing reaction and the hydrogen generation reaction respectively represented by the following formula (2) and (3) occur in the last stage of the charging period. The reaction of the formula (3) occurs more easily as the battery is charged more rapidly.

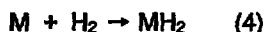


In the formula (2) M represents a hydrogen absorbing alloy.



Accordingly, the increase of the internal gas pressure of the sealed nickel-hydrogen storage battery in the overcharging period is caused by both an oxygen gas generated from the positive electrode and a hydrogen gas generated from the negative electrode. In this battery system, the reaction of oxygen gas reduction represented by the formula (1) progresses relatively rapidly even in the case where the battery is subject to rapid charging. Accordingly, the increase of the battery internal pressure caused by an oxygen gas is not important in this battery system. On the other hand, in the case where the negative electrode is prepared by an ordinary producing method, a hydrogen gas generated in accordance with the formula (3) is difficult to absorb. Accordingly, the increase of the battery internal pressure caused by a hydrogen gas becomes severer as the battery is charged more rapidly.

According to the present invention, a supporter of a three-dimensional structure having hydrophobic property is used in the negative electrode, so that when the negative electrode is assembled, hydrophobic property is given to the surfaces of hydrogen absorbing alloy particles which are in contact with the supporter. Accordingly, a hydrogen gas generated by the reaction represented by the formula (3) is absorbed smoothly into the alloy powders being not in contact with the electrolytic solution, by the gas phase reaction represented by the following formula (4) to thereby suppress increase of the battery internal gas pressure, because the hydrogen absorbing alloy of the negative electrode has a sufficient absorption capacity.



In the formula (4) M represents a hydrogen absorbing alloy.

If a portion having a hydrophobic layer is further provided on the surface portion of the negative electrode, the reaction of the formula (4) progresses so more rapidly that the battery inner pressure is little increased in a rapid charging period.

According to the aforementioned construction of the negative electrode, the hydrogen absorbing alloy particles are kept in the three-dimensional porous matter having hydrophobic property to improve the mechanical strength thereof to thereby prevent lowering of hydrophobic property caused by repetition of charging/discharging. Further, the negative electrode is not affected by expansion/contraction of the hydrogen absorbing alloy, so that the internal gas pressure of the battery is little increased regardless of repetition of charging/discharging cycles.

Also in the case where the nickel porous matter having a three-dimensional structure is filled with paste mainly containing hydrogen absorbing alloy powder in accordance with the negative electrode producing method of the present invention, the fluororesin is not easily disconnected from the nickel porous matter because the fluororesin is fixed to the skeletal portion of the nickel porous matter. Accordingly, sufficient hydrophobic property can be given to the surfaces of the hydrogen absorbing alloy particles. Further, because the fluororesin is fixed to the nickel porous matter having a three-dimensional structure, the fluororesin is not easily disconnected from the skeleton of the nickel porous matter regardless of expansion of the negative electrode caused by repetition of charging/discharging, so that stable internal gas pressure of the battery can be obtained.

EMBODIMENTS

Example 1

Now, the present invention will be described in conjunction with various examples. Figs. 1A and 1B show a supporter of a three-dimensional structure having hydrophobic property as an embodiment of the present invention. Fig. 1A is a sectional view of the supporter, and Fig. 1B is a typical enlarged view of the supporter. In Figs. 1A and 1B, the reference numeral 1 designates a fluororesin, 2 a skeleton formed of

nickel, and 3 a supporter having a three-dimensional structure. The supporter of a three-dimensional structure having hydrophobic property was prepared as follows. An available sponge-like nickel porous matter (30 mg/cm^2 by weight per apparent unit area) having a porosity of 95% was dipped into an aqueous solution dispersion of fluororesin powder (PTFE) to deposit the fluororesin on the skeletal portion of the nickel porous matter. Then, the fluororesin in an amount of 7.5% by weight was fixed to the skeletal portion of the nickel porous matter by heat treatment in the atmosphere of 300°C to thereby prepare a support of a three-dimensional structure having a hydrophobic portion. Figs. 2 and 3 are sectional views showing examples of negative electrodes constructed by using the support having hydrophobic property. Fig. 4 is a schematic view of an AA-size sealed nickel-hydrogen storage battery constructed by using these negative electrodes. The negative electrodes as shown in Figs. 2 and 3 were respectively prepared as follows. Hydrogen absorbing alloy powder 5 using $\text{MmNi}_{3.8}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.5}$ with a theoretical capacity of 250 mAh/g and an average particle size of $12 \mu\text{m}$ and water were mixed to prepare paste having a water content of about 20%. The aforementioned porous matter of a three-dimensional structure (thickness; 1.2 mm) having hydrophobic property was filled with the paste. After drying the paste, the porous matter was pressed into a thickness of 0.5 mm and cut into a size of $39 \text{ mm} \times 80 \text{ mm}$, thereby preparing a negative electrode A having a porosity of 31% as shown in Fig. 2. On the other hand, a further negative electrode was prepared in the same manner as the negative electrode A. PTFE powder was deposited on the surface of the negative electrode by using a spray coating instrument equipped with static generator. Then, the PTFE powder was fixed to the surface portion of the negative electrode by pressing. Then, the resulting negative electrode was cut into the same size as that of the negative electrode A, thereby preparing a negative electrode B as shown in Fig. 3. Consequently, the negative electrode B was coated with a PTFE powder layer 6 in an amount of 0.48 mg/cm^2 . As a comparative example, a negative electrode C was prepared in the same manner as the negative electrode A, except that the supporter of the negative electrode C was formed of a sponge-like nickel porous matter having a porosity of 95% without fluororesin deposited thereon. Then, by using the negative electrodes thus prepared, ten cells of AA-size sealed nickel-hydrogen storage batteries limited by the positive electrode capacity of 1000 mAh were respectively prepared to have a spiral structure constituted by a negative electrode 7, a known foamed metal type nickel positive electrode 8 and a separator 9 prepared by sulfonated polypropylene non-woven fabric and disposed between the negative electrode 7 and the positive electrode 8 as shown in Fig. 4. The condition of the battery design was that the chargeable capacity of the negative electrode was established to be from 1.3 times to 1.4 times as much as that of the positive electrode. A KOH aqueous solution having specific gravity of 1.30 and saturated with $\text{LiOH} \cdot \text{H}_2\text{O}$ was poured into the respective battery cases 10 by an amount of 2.2 cm^3 . The reference numeral 11 designates a gasket for insulating the edge of a sealing plate 14 and a positive electrode terminal cap 15 from the battery case 10. The reference numeral 12 designates an insulating plate for insulating the inner bottom portion of the battery case from the lower portion of the spiral electrodes. The reference numeral 16 designates a positive electrode lead for electrically connecting the nickel positive electrode to the sealing plate. Although the safety vent is, in general, operated by pressure of 10 to 15 kg/cm^2 , the safety vent 13 in this embodiment is established to be operated by pressure of not less than 30 kg/cm^2 for the purpose of measuring the internal gas pressure of the battery. The internal gas pressure of the battery was measured as follows. After assembled, the battery was charged with 0.1 cmA for 15 hours in an atmosphere of 20°C , and then discharged with 0.2 cmA to 1.0 V . Then, a $1 \text{ mm} \phi$ hole was formed in the bottom portion of the battery case 10. The battery was fixed to an apparatus provided with a pressure sensor. The internal gas pressure of the battery was measured with the pressure sensor at the point of time when the battery was charged by 150% with the charge rate changed to various values. Fig. 5 shows the relation between the charge rate and the internal gas pressure of the battery with respect to the batteries respectively constituted by using the negative electrodes A, B and C. In Fig. 5 the symbols A, B and C show characteristics of the batteries using the negative electrodes A, B and C, respectively. In the comparative example C, the internal gas pressure of the battery was within a range of from 22 to 27 kg/cm^2 when the battery was rapidly charged at 1 cmA . Accordingly, in an actual battery having a safety vent which is actuated to open by pressure of 10 to 15 kg/cm^2 , rapid charging is impossible. Compared with the battery using the negative electrode C, the batteries using the negative electrodes A and B were excellent in characteristics as shown by the symbols A and B in Fig. 5. In short, the internal gas pressure of the battery A was within a range of from 5 to 6.4 kg/cm^2 when the battery was charged at 1 cmA , and the internal gas pressure of the battery B was within a range of from 3 to 4 kg/cm^2 when the battery was charged at 1 cmA . Furthermore, in the cases of the batteries A and B, the battery internal pressure was little increased regardless of repetition of charging/discharging 500 times. Consequently, the batteries A and B showed excellent characteristics, respectively.

Although this example has shown the case where the fluororesin is disposed in the skeletal surface portion of the sponge-like nickel porous matter as a supporter of a three-dimension structure having hydrophobic property, the same effect can be attained as long as said supporter of said negative electrode is formed of fabric selected from woven or non-woven fabric formed of a hydrophobic resin having continuous space in its three-dimensional structure, a foam resin formed by giving hydrophobic property to a hydrophilic resin, and a fiber resin. If the porosity of the nickel porous matter having a three-dimensional structure is not more than 90%, the capacity density of the negative electrode is lowered so that battery internal pressure increases when the battery is constructed under the conditions as described above. Accordingly, it is preferable that the porosity is not less than 80%.

Further, if the weight per apparent unit area of the nickel porous matter becomes not less than 60 mg/cm², the porosity of the negative electrode prepared by filling the porous matter with the hydrogen absorbing alloy by a pre-determined amount becomes not more than 28% to thereby increase battery internal pressure. If the weight becomes not more than 20 mg/cm², on the contrary, mechanical strength of the nickel porous matter is lowered to make it difficult to fill the porous matter with the hydrogen absorbing alloy. If the porosity of the negative electrode becomes not more than 28%, the hydrogen gas absorbing reaction area thereof is lowered so that battery internal pressure increases. If porosity becomes not less than 38%, on the contrary, the capacity density of the negative electrode is lowered to make it impossible to construct a sealed battery of positive electrode capacity limitation. Porosity should be at least 28%.

Hydrophobic material in the skeletal surface portion of the nickel porous matter should be given by an amount within a range of from 2 to 36% by weight relative to the total weight of said porous matter.

Example 2

An available sponge-like nickel porous matter having a porosity of 95% was dipped into an aqueous solution dispersion containing 70 part by weight of PTFE powder and 30 part by weight of palladium black powder capable of catalyzing the decomposition ($H_2 \rightarrow 2H$) of hydrogen gas, to deposit the PTFE powder and the palladium black powder on the skeletal portion of the nickel porous matter in the ratio 70:30. Then the porous matter was heated at 300°C to prepare a support of a three-dimensional structure having a mixture of PTFE and palladium black at its skeletal portion. A negative electrode D was prepared by using the supporter in the same manner as in the Example 1. Then, a mixture of PTFE and palladium black in the ratio 70:30 was applied to the surface of the negative electrode D to prepare a negative electrode E having a layer of the mixture of PTFE and catalyst at its surface portion in the same manner as in the Example 1. Said application may be carried out by smearing or dipping. On the other hand, a sponge-like nickel porous matter was dipped into an aqueous solution dispersion containing 70 part by weight of PTFE powder and 30 part by weight of acetylene black powder having electron conductivity, thereby depositing the mixture of PTFE powder and acetylene black powder on the skeletal portion of the nickel porous matter. Then, the porous matter was treated in an atmosphere of 300°C to prepare a support of a three-dimensional structure having the mixture of PTFE and acetylene black at its skeletal portion. A negative electrode F was prepared by using this supporter in the same manner as in the Example 1. Then, a mixture of PTFE and palladium black in the weight ratio 70:30 was applied to the surface of the negative electrode F to prepare a negative electrode G having a layer of the mixture of PTFE and electron conductive matter at its surface portion in the same manner as in the Example 1. By using the negative electrodes (D, E, F and G), various batteries were prepared in the same manner as in the Example 1. The values of battery internal pressure of the batteries at the point of time when the respective battery was charged by 150% with 1 cmA are shown in Table 1. The results of the batteries A, B and C in the Example 1 are also shown in the Table 1.

Table 1

Battery	Negative Electrode	Internal Gas Pressure	Capacity Ratio
A	A	5 ~ 6.4 kg/cm ²	74 ~ 76%
B	B	3 ~ 4 kg/cm ²	72 ~ 75%
C	C	22 ~ 27 kg/cm ²	80 ~ 83%
D	D	4 ~ 5.2 kg/cm ²	79 ~ 82%
E	E	2 ~ 2.8 kg/cm ²	80 ~ 83%
F	F	5 ~ 7 kg/cm ²	79 ~ 82%
G	G	3 ~ 5 kg/cm ²	79 ~ 83%

Further, the discharge characteristic in each of the batteries using the negative electrodes A to G was examined. In the Table 1, the discharge characteristic is expressed as capacity ratio [capacity ratio = (the capacity when discharged with 3 cmA)/(the capacity when discharged with 0.2 cmA) x 100%] of the capacity when each battery was discharged with 3 cmA to 1.0 V to the capacity when discharged with 0.2 cmA to 1.0 V after charged in an atmosphere of 20 °C. The larger the value of the capacity ratio, the more excellent the discharge characteristic. The values of internal gas pressure of the respective batteries using the negative electrodes D and E were within a range of from 4 to 5.2 kg/cm² and within a range of from 2 to 2.8 kg/cm², respectively. In the cases of the negative electrodes D and E, the battery internal pressure was reduced because of the presence of palladium black capable of catalyzing the decomposition of a hydrogen gas, compared with the cases of the negative electrodes A and B. In short, the batteries using the negative electrodes D and E showed excellent characteristics. The values of internal gas pressure of the batteries F and G using the sponge-like nickel porous matter having the mixture of acetylene black and PTFE at its skeletal portion were excellent similarly to the values of internal gas pressure of the batteries A and B. On the contrary, the discharge characteristic of the battery C using the negative electrode C as a comparative example was so good that the capacity ratio was from 80 to 83%. The capacity ratio of the batteries using the negative electrodes A and B were within a range of from 74 to 76% and within a range of from 72 to 75%, respectively, the values being slightly lower than the value in the case of the negative electrode C. This is because the surface portion of the nickel porous matter having electron conductivity was coated with PTFE having little electron conductivity. In other words, this is because the contacting area between the hydrogen absorbing alloy powder and the skeleton of nickel decreased. On the other hand, the discharge characteristics of the batteries F and G using the supporter having the mixture of PTFE and acetylene black at its skeletal portion were within a range of from 79 to 82% and within a range of from 79 to 83%, respectively, the values being excellent similarly to the value in the case of the battery C. Also the discharge characteristics of the batteries D and E showed values similar to the value in the case of the battery C. This is because acetylene black having electron conductivity and palladium black having both catalytic property and electron conductivity existed in the surface portion of the skeleton of nickel.

Although this example has shown the case where palladium black is used as a material capable of catalyzing the decomposition of a hydrogen gas, the same effect can be attained even in the case where another catalyst, such as platinum, platinum carrying carbon, palladium carrying carbon or the like, is used. Although this example has shown the case where acetylene black is used as a material having electron conductivity, the same effect can be attained even in the case where another material having electron conductivity, such as nickel powder, carbon black or the like, is used. Further, the portion having hydrophobic property may be formed of a mixture of PTFE, a catalytic material and a conductive material.

Example 3

A supporter formed of a sponge-like nickel porous matter having hydrophobic property in the same manner as in the Example 1 was filled with paste prepared by mixing hydrogen absorbing alloy powder having a mean particle diameter of 12 μ m and represented by the formula $MmNi_{0.8}Mn_{0.4}Al_{0.3}Co_{0.5}$ and a polyvinyl alcohol aqueous solution as a hydrophilic material. While the polyvinyl alcohol concentration of the aqueous solution was changed, negative electrodes H, I, J and K were prepared in the same manner as the negative electrode A in the Example 1. The negative electrodes H, I, J and K contained polyvinyl alcohol by

amounts of 0.02 wt%, 0.18 wt%, 0.25 wt% and 0.3 wt%, respectively. Then, a PTFE layer was formed on each of the negative electrodes prepared in the same manner as the negative electrodes H, I, J and K, thereby preparing negative electrodes L, M, N and O. By using these negative electrodes, various batteries were prepared in the same manner as in the Example 1 (except that the safety vent in each of the batteries was set to be actuated to open by pressure of 12 kg/cm²). The internal gas pressure and charge/discharge cycle life were examined. The cycle life test was conducted under the condition that the battery was charged with 1 cmA for 1.5 hours in an atmosphere of 20°C and then discharged with 1 cmA till the terminal voltage reached 1.0 V. The discharge capacity in each cycle was examined in the cycle life test. The measurement condition of battery internal pressure was the same as in the Example 1. The internal gas pressure of the batteries using various negative electrodes and the cycle number when the discharge capacity was reduced by 10% relative to the initial capacity are shown in Table 2. Further, the characteristics of the batteries using the negative electrodes A and B containing no polyvinyl alcohol are also shown in the Table 2. The internal pressure in each of the batteries H, I, J, L, M and N using negative electrodes containing polyvinyl alcohol by the amounts of 0.02 wt%, 0.18 wt% and 0.25 wt% was excellent similarly to that in each of the batteries A and B using negative electrodes containing no polyvinyl alcohol. However, the internal pressure in each of the batteries K and O using negative electrodes containing polyvinyl alcohol by an amount of 0.3 wt% was increased compared with that in each of the batteries A and B. Accordingly, it is preferable that the negative electrode contains polyvinyl alcohol by an amount of not more than 0.25 wt%. On the other hand, the cycle life in each of the batteries H, I, J, L, M and N was improved compared with that in each of the batteries A and B. This is because hydrophilic polyvinyl alcohol existing in the negative electrode keeps the electrolyte in the negative electrode regardless of expansion of the position electrode caused by repetition of charge/discharge cycles. On the other hand, the cycle life in each of the batteries K and L was short. This is because the surfaces of the alloy particles are covered with polyvinyl alcohol to thereby reduce the hydrogen absorbing capacity and increase the battery internal pressure, so that the safety vent is actuated to thereby reduce the discharge capacity. Accordingly, it is preferable that the negative electrode contains polyvinyl alcohol by an amount within a range of from 0.02 to 0.25 wt%.

Although this example has shown the case where polyvinyl alcohol is used as a hydrophilic material, the same effect can be attained even in the case where another hydrophilic material, such as carboxymethylcellulose, methylcellulose or the like, is used.

Table 2

Battery	Negative Electrode	Concentration of hydrophilic polyvinyl alcohol in negative electrode	Internal Gas pressure	Cycle Life
A	A	0 wt%	5 ~ 6.4 kg/cm ²	450 ~ 500 cycles
B	B	0 wt%	3 ~ 4 kg/cm ²	450 ~ 500 cycles
H	H	0.02 wt%	5 ~ 6.4 kg/cm ²	480 ~ 520 cycles
I	I	0.18 wt%	5 ~ 6.4 kg/cm ²	500 ~ 550 cycles
J	J	0.25 wt%	5.5 ~ 7 kg/cm ²	500 ~ 550 cycles
K	K	0.3 wt%	9 ~ 12 kg/cm ²	200 ~ 300 cycles
L	L	0.02 wt%	3 ~ 4 kg/cm ²	480 ~ 520 cycles
M	M	0.18 wt%	3 ~ 4 kg/cm ²	500 ~ 550 cycles
N	N	0.25 wt%	3.5 ~ 5 kg/cm ²	500 ~ 550 cycles
O	O	0.3 wt%	8 ~ 12 kg/cm ²	200 ~ 300 cycles

Example 4

Negative electrodes P, Q, R, S, T and U were prepared in the same manner as the negative electrode B in the Example 1 while the quantity of PTFE to be applied to the surface thereof was changed variously. By using the negative electrodes P, Q, R, S, T and U, various batteries were prepared in the same manner

as in the Example 1. The internal gas pressure in each of the batteries was examined. The results of examination are shown in Table 3.

Table 3

Battery	Negative Electrode	Surface Coating Amount of PTFE	Internal Gas Pressure
P	P	0.1 mg/cm ²	5 ~ 6 Kg/cm ²
Q	Q	0.15 mg/cm ²	4 ~ 5 Kg/cm ²
R	R	0.5 mg/cm ²	3 ~ 4 Kg/cm ²
S	S	1.0 mg/cm ²	3 ~ 4 Kg/cm ²
T	T	1.5 mg/cm ²	4 ~ 5 Kg/cm ²
U	U	2.0 mg/cm ²	7 ~ 9 Kg/cm ²

The internal pressure in each of the batteries Q, R, S and T using the negative electrodes respectively coated with PTFE by amounts of 0.15 mg/cm², 0.5 mg/cm², 1.0 mg/cm² and 1.5 mg/cm² was not more than 5 kg/cm² and was very excellent. On the other hand, the internal gas pressure of the battery P using the negative electrode coated with PTFE by an amount of 0.1 mg/cm² was similar to that of the battery A in the Example 1. In the battery P, there was no effect by the coating of PTFE on the surface of the negative electrode. The internal gas pressure of the battery U using the negative electrode coated with PTFE by an amount of 2.0 mg/cm² was increased to be within a range of from 7 to 9 kg/cm². This is because the hydrophobic resin in the surface of the negative electrode increases to suppress absorption of the electrolyte into the negative electrode to thereby deteriorate charge efficiency of the negative electrode. Accordingly, it is preferable that the quantity of PTFE deposited on the surface portion of the negative electrode is within a range of from 0.15 to 1.5 mg/cm².

Example 5

Various negative electrodes V, W, X and Y were prepared in the same manner as the negative electrode A in the Example 1, except that the temperature for heat treatment after deposition of PTFE was changed variously to 150 °C, 200 °C, 400 °C and 450 °C. By using the negative electrodes thus prepared, various batteries were prepared. The battery internal pressure and cycle life (under the condition that the operation pressure of the safety vent used in the cycle life test was 12 kg/cm²) were examined in the same manner as in the Examples 1 and 3. The results of examination are shown in Table 4. The characteristics of the battery using the negative electrode A in the Example 1 were also shown in the Table 4.

Table 4

Battery	Negative Electrode	Heat-treatment Temperature	Internal Gas Pressure	Cycle Life
V	V	150 °C	10~12 Kg/cm ²	200~250 cycles
W	W	200 °C	5~ 6.4 Kg/cm ²	450~480 cycles
A	A	300 °C	5~ 6.4 Kg/cm ²	450~500 cycles
X	X	400 °C	5~ 6.4 Kg/cm ²	480~530 cycles
Y	Y	450 °C	10~12 Kg/cm ²	250~300 cycles

Each of the batteries W, A and X using the supports prepared by the steps of depositing PTFE on the skeletal portion of the sponge-like nickel porous matter, and heat-treating the porous matter at a temperature of 200 to 400 °C, was excellent in battery internal pressure and cycle life. On the other hand, the internal gas pressure of the battery V using the supporter subjected to rapid charging was found to be within a range from 10 to 12 kg/cm². Further, the cycle life of the battery V was within a range of from 200

to 250 cycles. Consequently, the characteristics of the battery V were deteriorated. This is because PTFE could not be sufficiently fixed to the skeletal surface portion of the nickel porous matter when the temperature for heat treatment was 150°C, so that PTFE was dropped out of the skeleton during the impregnating of the porous matter with the paste or with repetition of charge/discharge cycles to thereby reduce hydrophobic property of the negative electrode. On the contrary, when the temperature for heat treatment reached 450°C as shown in the battery Y, PTFE was partly decomposed to thereby reduce hydrophobic property of the negative electrode and shorten the cycle life. Accordingly, it is preferable that the temperature for heat treatment is to be within a range of from 200 to 400°C.

Next, a negative electrode Z in which PTFE was coated on the surface of the negative electrode but not fixed by pressing was prepared in the same manner as the negative electrode B in the Example 1. By using the negative electrode Z, a battery was prepared in the same manner as in the Example 1. The internal gas pressure and cycle life of the battery thus prepared were examined. The internal gas pressure of the battery using the negative electrode Z was within a range of from 3 to 4 kg/cm² and was excellent similarly to that of the battery B in the Example 1. However, the internal gas pressure of the battery was increased with repetition of charge/discharge cycles. When charge/discharge was repeated by 400 cycles, the internal gas pressure of the battery became not less than 12 kg/cm² to operate the safety vent to make a gas and the electrolyte escape to thereby reduce the discharge capacity. This is because PTFE was not sufficiently fixed to the surface portion of the negative electrode so that PTFE was dropped out of the surface portion of the negative electrode with repetition of charge/discharge cycles.

As described above, according to the present invention, in a sealed alkaline storage battery comprising a positive electrode constituted mainly by a metal oxide, a negative electrode constituted mainly by a hydrogen absorbing alloy capable of absorbing/desorbing hydrogen acting as an active material and a supporter for supporting said alloy, an alkaline electrolyte, and a separator, an effect to enable rapid charging (1 cmA) to be performed can be obtained by making the supporter to have a three-dimensional structure having hydrophobic property. Further, an effect to enable more rapid charging (2 cmA) to be performed can be obtained by providing a portion having hydrophobic property on a surface portion of the negative electrode.

Further, in the method of producing a negative electrode for the above-mentioned sealed alkaline storage battery, it is possible to obtain an effect that a sealed alkaline storage battery capable of being subject to rapid charging and excellent in cycle life against repetition charge/discharge can be produced by employing the steps of: depositing a fluororesin on a skeletal portion of a nickel porous matter having a three-dimensional structure; fixing the fluororesin to the skeletal portion of the nickel porous matter by heat treatment at a temperature lower than the temperature of decomposition of the fluororesin to thereby prepare a support having a hydrophobic portion; and preparing a negative electrode through filling the supporter with paste mainly containing a hydrogen absorbing alloy, drying the paste and then pressing/cutting the support into predetermined thickness and size.

Claims

1. A sealed alkaline storage battery comprising:
a positive electrode including a metal oxide as a main constituent material thereof; a negative electrode (4) including, as main constituent material thereof, a hydrogen absorbing alloy (5) capable of absorbing/desorbing hydrogen acting as an active material and a porous supporter (2) for supporting said alloy; an alkaline electrolyte; and a separator; characterised in that those pores containing said hydrogen absorbing alloy (5) have hydrophobic property.
2. A sealed alkaline storage battery according to Claim 1, in which said supporter is formed of a nickel porous matter having a three-dimensional structure with a porosity of 80%, said nickel porous matter containing a hydrophobic material at a skeletal surface portion thereof.
3. A sealed alkaline storage battery according to Claim 1 or 2, in which said supporter has a hydrophobic portion composed of a mixture of a hydrophobic material and a material capable of catalyzing the decomposition of a hydrogen gas.
4. A sealed alkaline storage battery according to Claims 1 or 2, in which said supporter has a hydrophobic portion composed of a mixture of hydrophobic material and an electron conductive material.



to 250 cycles. Consequently, the characteristics of the battery V were deteriorated. This is because PTFE could not be sufficiently fixed to the skeletal surface portion of the nickel porous matter when the temperature for heat treatment was 150°C, so that PTFE was dropped out of the skeleton during the impregnating of the porous matter with the paste or with repetition of charge/discharge cycles to thereby
 5 reduce hydrophobic property of the negative electrode. On the contrary, when the temperature for heat treatment reached 450°C as shown in the battery Y, PTFE was partly decomposed to thereby reduce hydrophobic property of the negative electrode and shorten the cycle life. Accordingly, it is preferable that the temperature for heat treatment is to be within a range of from 200 to 400°C.

Next, a negative electrode Z in which PTFE was coated on the surface of the negative electrode but not
 10 fixed by pressing was prepared in the same manner as the negative electrode B in the Example 1. By using the negative electrode Z, a battery was prepared in the same manner as in the Example 1. The internal gas pressure and cycle life of the battery thus prepared were examined. The internal gas pressure of the battery using the negative electrode Z was within a range of from 3 to 4 kg/cm² and was excellent similarly to that of the battery B in the Example 1. However, the internal gas pressure of the battery was increased with
 15 repetition of charge/discharge cycles. When charge/discharge was repeated by 400 cycles, the internal gas pressure of the battery became not less than 12 kg/cm² to operate the safety vent to make a gas and the electrolyte escape to thereby reduce the discharge capacity. This is because PTFE was not sufficiently fixed to the surface portion of the negative electrode so that PTFE was dropped out of the surface portion of the negative electrode with repetition of charge/discharge cycles.

As described above, according to the present invention, in a sealed alkaline storage battery comprising
 20 a positive electrode constituted mainly by a metal oxide, a negative electrode constituted mainly by a hydrogen absorbing alloy capable of absorbing/desorbing hydrogen acting as an active material and a supporter for supporting said alloy, an alkaline electrolyte, and a separator, an effect to enable rapid charging (1 cmA) to be performed can be obtained by making the supporter to have a three-dimensional
 25 structure having hydrophobic property. Further, an effect to enable more rapid charging (2 cmA) to be performed can be obtained by providing a portion having hydrophobic property on a surface portion of the negative electrode.

Further, in the method of producing a negative electrode for the above-mentioned sealed alkaline storage battery, it is possible to obtain an effect that a sealed alkaline storage battery capable of being
 30 subject to rapid charging and excellent in cycle life against repetition charge/discharge can be produced by employing the steps of: depositing a fluororesin on a skeletal portion of a nickel porous matter having a three-dimensional structure; fixing the fluororesin to the skeletal portion of the nickel porous matter by heat treatment at a temperature lower than the temperature of decomposition of the fluororesin to thereby
 35 prepare a support having a hydrophobic portion; and preparing a negative electrode through filling the supporter with paste mainly containing a hydrogen absorbing alloy, drying the paste and then pressing/cutting the support into predetermined thickness and size.

Claims

- 40 1. A sealed alkaline storage battery comprising:
 a positive electrode including a metal oxide as a main constituent material thereof; a negative electrode (4) including, as main constituent material thereof, a hydrogen absorbing alloy (5) capable of absorbing/desorbing hydrogen acting as an active material and a porous supporter (2) for supporting said alloy; an alkaline electrolyte; and a separator; characterised in that those pores containing said
 45 hydrogen absorbing alloy (5) have hydrophobic property.
2. A sealed alkaline storage battery according to Claim 1, in which said supporter is formed of a nickel porous matter having a three-dimensional structure with a porosity of 80%, said nickel porous matter containing a hydrophobic material at a skeletal surface portion thereof.
- 50 3. A sealed alkaline storage battery according to Claim 1 or 2, in which said supporter has a hydrophobic portion composed of a mixture of a hydrophobic material and a material capable of catalyzing the decomposition of a hydrogen gas.
- 55 4. A sealed alkaline storage battery according to Claims 1 or 2, in which said supporter has a hydrophobic portion composed of a mixture of hydrophobic material and an electron conductive material.



5. A sealed alkaline storage battery according to anyone of Claims 1 to 4, in which said negative electrode includes a hydrophilic material by an amount within a range of from 0.02 to 0.25% by weight.
6. A sealed alkaline storage battery according to Claim 1, in which said supporter of said negative electrode is formed of fabric selected from woven or non-woven fabric formed of a hydrophobic resin having continuous space in its three-dimensional structure, a foam resin formed by giving hydrophobic property to a hydrophilic resin, and a fiber resin.
7. A sealed alkaline storage battery according to anyone of Claims 1 to 6, in which said negative electrode using the supporter of a three-dimensional structure having hydrophobic property has a porosity within a range of from 28 to 38%.
8. A sealed alkaline storage battery according to anyone of Claims 1 to 7, in which said metal oxide included in said positive electrode as its main constituent material is a nickel oxide.
9. A sealed alkaline storage battery according to anyone of Claims 1 to 7, in which said metal oxide included in said positive electrode as its main constituent material is a manganese oxide.
10. A sealed alkaline storage battery according to Claim 2, in which said nickel porous matter having a three-dimensional structure has a weight per apparent unit area within a range of from 20 to 60 mg/cm².
11. A sealed alkaline storage battery according to Claim 2, in which said hydrophobic material in said skeletal surface portion of said nickel porous matter is given by an amount within a range of from 2 to 36% by weight relative to the total weight of said porous matter.
12. A sealed alkaline storage battery according to any preceding claim, in which a portion having hydrophobic property is provided on said negative electrode at its surface portion.
13. A sealed alkaline storage battery according to Claim 12, in which a hydrophobic material is deposited on the surface portion of said negative electrode by a mean amount within a range of from 0.15 mg/cm² to 1.5 mg/cm².
14. A method of producing a negative electrode of a sealed alkaline storage battery comprising a positive electrode including a metal oxide as a main constituent material thereof, a negative electrode including, as main constituent materials thereof, a hydrogen absorbing alloy capable of absorbing/desorbing hydrogen acting as an active material and a supporter for supporting said alloy, an alkaline electrolyte, and a separator, said method comprising the steps of; depositing a fluororesin on a skeletal portion of a nickel porous matter having a three-dimensional structure; fixing said fluororesin to said skeletal portion of said nickel porous matter by heat treatment at a temperature lower than the temperature of decomposition of said fluororesin to thereby prepare a support having a hydrophobic portion; and preparing a negative electrode through filling said supporter with paste mainly containing a hydrogen absorbing alloy, drying said paste and then pressing/cutting said supporter into predetermined thickness and size.
15. A method of producing a negative electrode of a sealed alkaline storage battery according to Claim 14, further comprising the steps of; depositing fluororesin powder on a negative electrode surface portion through selected one of smearing and dipping after filling a supporter having hydrophobic property with paste mainly containing a hydrogen absorbing alloy, drying said support and then pressing said support into predetermined thickness; and fixing said fluororesin powder to said negative electrode surface portion.
16. A method of producing a negative electrode of a sealed alkaline storage battery according to Claim 14 or 15, in which said heat treatment is carried out at a temperature within a range of from 200 to 400 °C.

55 Patentansprüche

1. Abgedichtete alkalische Sammlerbatterie, aufweisend:
eine positive Elektrode, die als ihr Hauptbestandteilmaterial ein Metalloxid beinhaltet; eine negative



Elektrode (4), die als ihr Hauptbestandteilmaterial eine wasserstoffabsorbierende Legierung (5), die Wasserabsorbieren/Desorbieren kann, als ein aktives Material dienend, und einen porösen Träger (2) zum Tragen der Legierung beinhaltet; einen alkalischen Elektrolyten; und einen Scheider, dadurch gekennzeichnet, daß diejenigen Poren, die die wasserstoffabsorbierende Legierung (5) beinhalten, hydrophobe Eigenschaft haben.

2. Abgedichtete alkalische Sammlerbatterie nach Anspruch 1, bei der der Träger aus einer porösen Nickelsubstanz mit einer dreidimensionalen Struktur mit einer Porösität von 80% gebildet ist, wobei die poröse Nickelsubstanz ein hydrophobes Material an einem Skelettoberflächenteil davon beinhaltet.
3. Abgedichtete alkalische Sammlerbatterie nach Anspruch 1 oder 2, bei der der Träger einen hydrophoben Teil hat, der sich aus einer Mischung aus einem hydrophoben Material und einem Material zusammensetzt, das die Zersetzung eines Wasserstoffgases katalysieren kann.
4. Abgedichtete alkalische Sammlerbatterie nach Anspruch 1 oder 2, bei der der Träger einen hydrophoben Teil hat, der sich aus einer Mischung aus hydrophobem Material und einem Elektronen leitenden Material zusammensetzt.
5. Abgedichtete alkalische Sammlerbatterie nach einem der Ansprüche 1 bis 4, bei der die negative Elektrode ein hydrophiles Material in einer Menge innerhalb eines Bereiches von 0,02 bis 0,25 Gew.% beinhaltet.
6. Abgedichtete alkalische Sammlerbatterie nach Anspruch 1, bei der der Träger der negativen Elektrode aus einem Gewebe gebildet ist, das ausgewählt ist aus gewobenem oder nicht gewobenem Gewebe, das gebildet ist aus einem hydrophoben Harz mit kontinuierlichem Raum in seiner dreidimensionalen Struktur, einem Schaumharz, der dadurch gebildet ist, daß einem hydrophilen Harz hydrophobe Eigenschaft gegeben wird, und einem Fiberharz.
7. Abgedichtete alkalische Sammlerbatterie nach einem der Ansprüche 1 bis 6, bei der die den Träger einer dreidimensionalen Struktur mit hydrophober Eigenschaft verwendende negative Elektrode eine Porösität innerhalb eines Bereiches von 28 bis 38 % hat.
8. Abgedichtete alkalische Sammlerbatterie nach einem der Ansprüche 1 bis 7, bei der das Metalloxid in der positiven Elektrode als ihr Hauptbestandteilmaterial ein Nickeloxid ist.
9. Abgedichtete alkalische Sammlerbatterie nach einem der Ansprüche 1 bis 7, bei der das Metalloxid in der positiven Elektrode als ihr Hauptbestandteilmaterial ein Manganoxid ist.
10. Abgedichtete alkalische Sammlerbatterie nach Anspruch 2, bei der die poröse Nickelsubstanz mit einer dreidimensionalen Struktur ein Gewicht pro wirksamer Flächeneinheit innerhalb eines Bereiches von 20 bis 60 mg/cm² hat.
11. Abgedichtete alkalische Sammlerbatterie nach Anspruch 2, bei der das hydrophobe Material in dem Skelettoberflächenteil der porösen Nickelsubstanz in einer Menge innerhalb eines Bereiches von 2 bis 36 Gew.-% bezogen auf das Gesamtgewicht der porösen Substanz gegeben ist.
12. Abgedichtete alkalische Sammlerbatterie nach einem der vorangehenden Ansprüche, bei der ein Teil mit hydrophober Eigenschaft auf der negativen Elektrode an ihrem Oberflächenteil vorgesehen ist.
13. Abgedichtete alkalische Sammlerbatterie nach Anspruch 12, bei der ein hydrophobes Material auf dem Oberflächenteil der negativen Elektrode mit einer mittleren Menge innerhalb eines Bereiches von 0,15 mg/cm² bis 1,5 mg/cm² aufgebracht ist.
14. Verfahren zum Herstellen einer negativen Elektrode einer abgedichteten alkalischen Sammlerbatterie mit einer positiven Elektrode, die ein Metalloxid als ihr Hauptbestandteilmaterial beinhaltet, einer negativen Elektrode, die als ihr Hauptbestandteilmaterial eine wasserstoffabsorbierende Legierung, die Wasserstoff absorbieren/desorbieren kann, als ein aktives Material dienend, und einen Träger zum Tragen der Legierung beinhaltet, mit einem alkalischen Elektrolyten und mit einem Scheider, wobei das



Verfahren folgende Schritte beinhaltet: Auftragen eines Fluorharzes auf einen Skeletteil einer porösen Nickelsubstanz mit einer dreidimensionalen Struktur; Fixieren des Fluorharzes an dem Skeletteil der porösen Nickelsubstanz durch Wärmebehandlung bei einer Temperatur unterhalb der Temperatur der Zersetzung des Fluorharzes, um dadurch einen Träger mit einem hydrophoben Teil zu schaffen; und Herstellen einer negativen Elektrode durch Füllen des Trägers mit einer Paste, die hauptsächlich eine wasserstoffabsorbierende Legierung beinhaltet, Trocknen der Paste und sodann Pressen/Schneiden des Trägers in vorbestimmte Dicke und Größe.

15. Verfahren zum Herstellen einer negativen Elektrode einer abgedichteten alkalischen Sammlerbatterie nach Anspruch 14, ferner folgende Schritte beinhaltend: Aufbringen von Fluorharzpulver auf einen Oberflächenteil der negativen Elektrode entweder durch Auftragen oder durch Eintauchen nach dem Füllen eines Trägers mit hydrophober Eigenschaft mit Paste, die hauptsächlich eine wasserstoffabsorbierende Legierung beinhaltet, Trocknen des Trägers und sodann Pressen des Trägers auf eine vorbestimmte Stärke; und Fixieren des Fluorharzpulvers an dem Oberflächenteil der negativen Elektrode.
16. Verfahren zum Herstellen einer negativen Elektrode einer abgedichteten alkalischen Sammlerbatterie nach Anspruch 14 oder 15, bei dem die Wärmebehandlung bei einer Temperatur in dem Bereich von 200 bis 400 °C ausgeführt wird.

Revendications

1. Accumulateur alcalin étanche comprenant : une électrode positive contenant un oxyde métallique comme matière constitutive principale de celle-ci; une électrode négative (4) contenant comme matière constitutive principale de celle-ci, un alliage (5) absorbant l'hydrogène capable d'absorber/désorber l'hydrogène agissant en tant que matière active et un support poreux (2) pour supporter ledit alliage; un électrolyte alcalin; et un séparateur, caractérisé en ce que ces pores contenant ledit alliage (5) absorbant l'hydrogène ont une propriété hydrophobe.
2. Accumulateur alcalin étanche selon la revendication 1, dans lequel ledit support est formé d'une matière poreuse à base de nickel ayant une structure tridimensionnelle avec une porosité de 80%, ladite matière poreuse à base de nickel contenant une matière hydrophobe sur une fraction de la surface de son squelette.
3. Accumulateur alcalin étanche selon la revendication 1 ou 2, dans lequel ledit support a une fraction hydrophobe composée d'un mélange d'une matière hydrophobe et d'une matière capable de catalyser la décomposition d'un gaz hydrogène.
4. Accumulateur alcalin étanche selon la revendication 1 ou 2, dans lequel ledit support a une fraction hydrophobe composée d'un mélange de matière hydrophobe et d'une matière conductrice d'électrons.
5. Accumulateur alcalin étanche selon l'une quelconque des revendications 1 à 4, dans lequel ladite électrode négative contient une matière hydrophile en une quantité comprise entre 0,02 et 0,25% en poids.
6. Accumulateur alcalin étanche selon la revendication 1, dans lequel ledit support de ladite électrode négative est formé de toile choisie parmi une toile tissée ou non tissée formée en une résine hydrophobe et présentant une continuité dans sa structure tridimensionnelle, d'une résine de mousse formée en donnant une propriété hydrophobe à une résine hydrophile, et d'une résine de fibres.
7. Accumulateur alcalin étanche selon l'une quelconque des revendications 1 à 6, dans lequel ladite électrode négative utilisant le support de structure tridimensionnelle ayant une propriété hydrophobe a une porosité comprise entre 28 et 38%.
8. Accumulateur alcalin étanche selon l'une quelconque des revendications 1 à 7, dans lequel ledit oxyde métallique contenu dans ladite électrode positive en tant que sa matière constitutive principale est un oxyde de nickel.



9. Accumulateur alcalin étanche selon l'une quelconque des revendications 1 à 7, dans lequel ledit oxyde métallique contenu dans ladite électrode positive en tant que sa matière constitutive principale est un oxyde de manganèse.

10. Accumulateur alcalin étanche selon la revendication 2, dans lequel ladite matière poreuse à base de nickel ayant une structure tridimensionnelle présente un poids surfacique apparent compris entre 20 et 60 mg/cm².

11. Accumulateur alcalin étanche selon la revendication 2, dans lequel ladite matière hydrophobe dans ladite fraction de la surface du squelette de ladite matière poreuse à base de nickel est apportée en une quantité comprise entre 2 et 36% en poids par rapport au poids total de ladite matière poreuse.

12. Accumulateur alcalin étanche selon l'une quelconque des revendications précédentes, dans lequel une fraction ayant une propriété hydrophobe est apportée sur ladite électrode négative, sur sa fraction de surface.

13. Accumulateur alcalin étanche selon la revendication 12, dans lequel une matière hydrophobe est déposée à la fraction de surface de ladite électrode négative en une quantité moyenne comprise entre 0,15 mg/cm² et 1,5 mg/cm².

14. Procédé de préparation d'une électrode négative d'un accumulateur alcalin étanche comprenant une électrode positive contenant un oxyde métallique en tant que sa matière constitutive principale, une électrode négative contenant en tant que ses matières constitutives principales, un alliage absorbant l'hydrogène capable d'absorber/désorber l'hydrogène en tant que matière active et un support pour supporter ledit alliage, un électrolyte alcalin, et un séparateur, ledit procédé comprenant les étapes consistant à; déposer une résine fluorée sur une fraction du squelette d'une matière poreuse à base de nickel ayant une structure tridimensionnelle; fixer ladite résine fluorée sur ladite fraction du squelette de ladite matière poreuse à base de nickel par traitement thermique à une température inférieure à la température de décomposition de ladite résine fluorée, pour préparer ainsi un support ayant une fraction hydrophobe; et préparer une électrode négative par imprégnation dudit support avec de la pâte contenant principalement un alliage absorbant l'hydrogène, et sécher ladite pâte puis comprimer/couper ledit support en épaisseur et taille prédéterminées.

15. Procédé de préparation d'une électrode négative d'un accumulateur alcalin étanche selon la revendication 14, comprenant de plus les étapes consistant à; déposer de la poudre de résine fluorée sur une fraction de surface de l'électrode négative selon l'une des opérations consistant à enduire ou immerger un support ayant une propriété hydrophobe, après l'avoir imprégné avec de la pâte contenant principalement un alliage absorbant l'hydrogène, sécher ledit support puis comprimer ledit support en une épaisseur prédéterminée; et fixer ladite poudre de résine fluorée sur ladite fraction de surface de l'électrode négative.

16. Procédé de préparation d'une électrode négative d'un accumulateur alcalin étanche selon la revendication 14 ou 15, dans lequel ledit traitement thermique est effectué à une température comprise entre 200 et 400 °C.