



(22) Date de dépôt/Filing Date: 1999/11/26
(41) Mise à la disp. pub./Open to Public Insp.: 2000/05/30
(45) Date de délivrance/Issue Date: 2013/07/09
(62) Demande originale/Original Application: 2 290 655
(30) Priorités/Priorities: 1998/11/30 (JP340325/1998);
1999/03/19 (JP74702/1999); 1999/03/23 (JP77943/1999);
1999/07/06 (JP191844/1999)

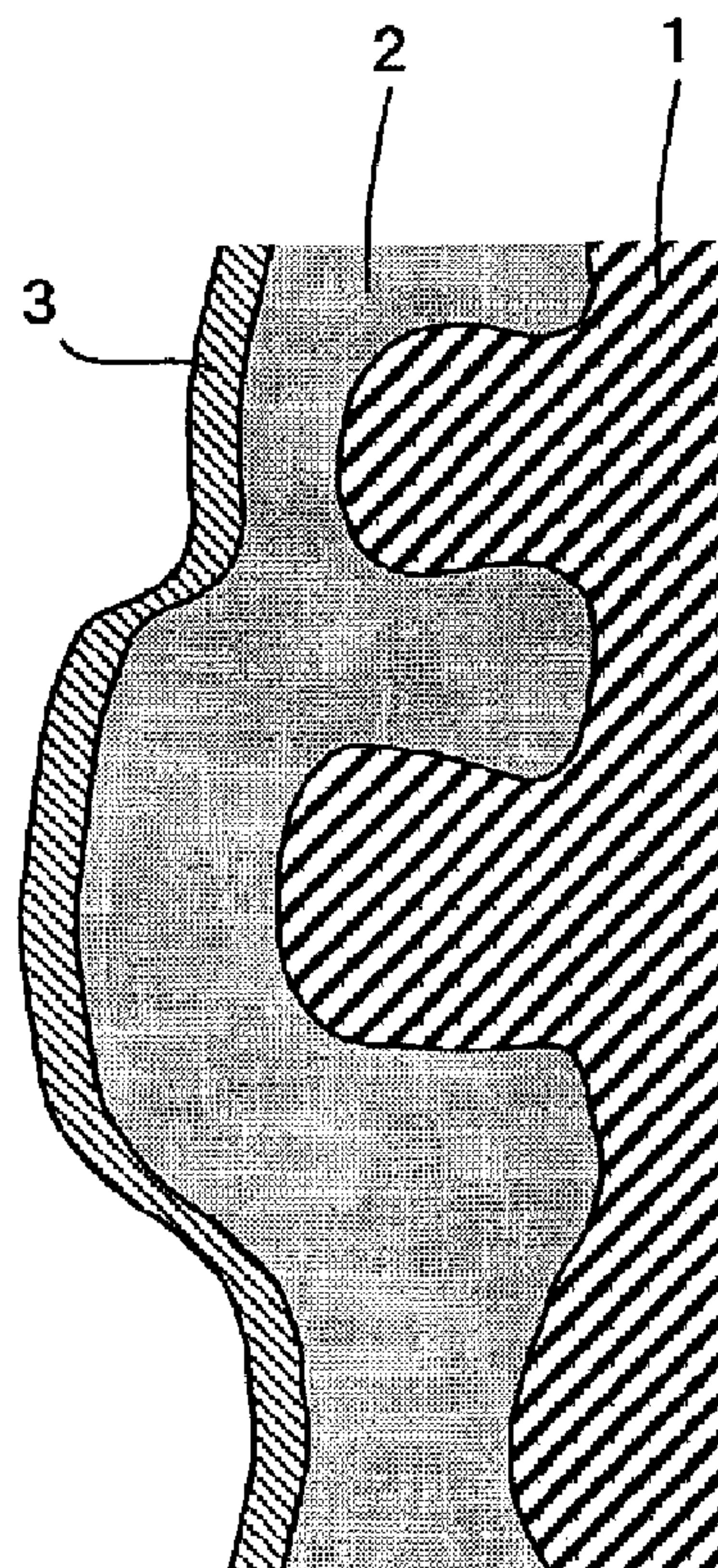
(51) Cl.Int./Int.Cl. *H01M 4/32* (2006.01),
H01M 10/02 (2006.01)

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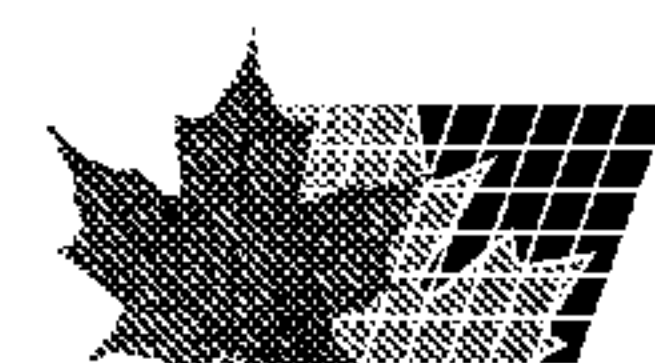
(74) Agent: MARKS & CLERK

(54) Titre : ELECTRODES EN NICKEL POUR PILE ALCALINE SECONDAIRE ET BATTERIE ALCALINE SECONDAIRE
(54) Title: NICKEL ELECTRODES FOR ALKALINE SECONDARY BATTERY AND ALKALINE SECONDARY BATTERIES



(57) Abrégé/Abstract:

A sintered nickel electrode, which employs a porous sintered nickel substrate obtained by sintering and is fabricated by chemically impregnating the porous sintered nickel substrate with an active material, for an alkaline secondary battery is provided. The sintered nickel electrode comprises a porous sintered nickel substrate; a nickel hydroxide-based active material layer provided on the porous sintered nickel substrate; and a first layer which is provided on the active material layer and is based on a complex compound of nickel and cobalt, calcium, strontium, scandium, yttrium, lanthanide, bismuth, magnesium or barium. A positive electrode is also provided.



ABSTRACT

A sintered nickel electrode, which employs a porous sintered nickel substrate obtained by sintering and is fabricated by chemically impregnating the porous sintered nickel substrate with an active material, for an alkaline secondary battery is provided. The sintered nickel electrode comprises a porous sintered nickel substrate; a nickel hydroxide-based active material layer provided on the porous sintered nickel substrate; and a first layer which is provided on the active material layer and is based on a complex compound of nickel and cobalt, calcium, strontium, scandium, yttrium, lanthanide, bismuth, magnesium or barium. A positive electrode is also provided.

NICKEL ELECTRODES FOR ALKALINE SECONDARY BATTERY
AND ALKALINE SECONDARY BATTERIES

This is a divisional application of Canadian Patent Application Serial No. 2,290,655 filed on November 26, 1999.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to nickel electrodes for alkaline secondary battery wherein a porous sintered nickel substrate is loaded with a nickel hydroxide-based active material, and alkaline secondary batteries employing the same as the positive electrode therefor. The invention is directed to the improvement of the nickel electrode for alkaline secondary battery for suppression of self discharge associated with oxygen evolution during storage of the charged alkaline secondary battery under high temperature conditions and for increase in the high-current discharge capacity of the electrode. It should be understood that the expression "the invention" and the like encompasses the subject matter of both the parent and the divisional applications.

Description of the Related Art

The conventional alkaline secondary batteries such as nickel-hydrogen secondary batteries, nickel-cadmium secondary batteries and the like, have employed sintered nickel electrodes or non-sintered nickel electrodes as the positive electrode therefor.

The non-sintered nickel electrode is fabricated by directly loading a nickel hydroxide-based active material

paste into a porous conductive body, such as a nickel substrate foam. Although this electrode is easy to fabricate, there is a disadvantage of poor charge/discharge characteristics at high current.

On the other hand, the sintered nickel electrode employs a porous sintered nickel substrate obtained by sintering and is fabricated by chemically impregnating the porous sintered nickel substrate with a salt as the active material. The sintered nickel substrate presents higher conductivity. In addition, the electrode is excellent in the charge/discharge characteristics at high current because of good adhesion of the active material to the porous sintered nickel substrate. On this account, the alkaline secondary batteries with the sintered nickel electrodes are favorably used in electric power tools requiring high current discharge.

Unfortunately, the sintered nickel electrode has a lower loading ratio of the active material than the non-sintered nickel electrode and therefore, must be improved in the utilization of the active material therefor. In addition, repeated charges/discharges of the alkaline secondary battery with the sintered nickel electrode result in brittleness of the sintered nickel substrate. Thus, the sintered nickel electrode is susceptible to improvement in the charge/discharge cycle characteristics.

In this connection, proposals have been made in the art as follows. For instance, Japanese Unexamined Patent Publication No.1(1989)-200555 discloses a process aimed at the increase in the conductivity of the active material for improved utilization thereof, the process comprising the steps of laying a cobalt hydroxide layer on a surface of the active material loaded into the porous sintered substrate, and oxidizing the cobalt hydroxide layer by heat treatment in the presence of oxygen and an alkaline solution. Further, Japanese Unexamined Patent Publication No.63(1985)-216268 discloses a process aimed at the suppression of corrosion of the sintered nickel substrate during the loading of the active material and the improvement in the charge/discharge cycle characteristics of the alkaline secondary battery, the process comprising the steps of laying a cobalt hydroxide layer on a surface of a porous sintered nickel substrate, heating the substrate in the presence of oxygen and an alkaline solution, and then loading the nickel hydroxide-based active material into the sintered nickel substrate.

Unfortunately, where the sintered nickel electrode of Japanese Unexamined Patent Publication No.1-200555 is used as the positive electrode of the alkaline secondary battery, the alkaline secondary battery still suffers the occurrence of self discharge due to the oxygen evolution in

the sintered nickel electrode when the charged battery is stored at high temperatures of about 50°C over an extended period of time. Thus, the alkaline secondary battery is reduced in capacity.

Where the sintered nickel electrode of Japanese Unexamined Patent Publication No.63-216268(Japanese Examined Patent Publication No.5(1993)-50099) is used as the positive electrode of the alkaline secondary battery, as well, the oxygen evolution occurs in the alkaline secondary battery charged at high temperatures of about 50°C before the positive electrode is charged to full. As a result, the battery is decreased in charge efficiency.

Further, Japanese Unexamined Patent Publication No.48(1973)-50233 has proposed a sintered nickel electrode employing a positive-electrode active material incorporating yttrium hydroxide for improvement in the utilization thereof under high temperature conditions. Alternatively, Japanese Unexamined Patent Publication No.5(1993)-28992 discloses an alkaline secondary battery employing a nickel oxide-based active material with a compound, such as yttrium, indium, antimony and the like, added thereto for accomplishing improvement in the utilization of the active material under high temperature conditions.

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In those batteries of the above official gazettes, however, the compounds such as of yttrium or the like, are simply added to the active materials and thus the active materials or the sintered nickel substrates are not sufficiently covered with the compounds such as of yttrium of the like. This detrimentally allows for contact between the electrolyte and the active material and/or the sintered nickel substrate. Hence, there still exists the problem of the oxygen evolution in the nickel electrode under high temperature conditions and of the underutilization of the active material.

In a previous published PCT application WO 99/043035, the present inventors have proposed a nickel electrode for alkaline secondary battery wherein a coating layer is laid on a surface portion of the nickel hydroxide-based active material loaded into the sintered nickel substrate, and is based on a hydroxide of at least one element selected from the group consisting of calcium, strontium, scandium, yttrium, lanthanide and bismuth, as well as a nickel electrode for alkaline secondary battery wherein an intermediate layer is interposed between the sintered nickel substrate and the above active material, and is based on a hydroxide of at least one element selected from the group consisting of calcium, strontium, scandium, yttrium, lanthanide and bismuth.

Where such a nickel electrode for alkaline secondary battery is used as the positive electrode for alkaline secondary battery, the self discharge due to the oxygen evolution in the nickel electrode is suppressed during the long term storage of the charged alkaline secondary battery under high temperature conditions. Thus are provided the alkaline secondary batteries excellent in high temperature storability.

Recently, however, there is an additional desire for a further increased discharge capacity at high current in order to cope with the aforementioned favorable use of the alkaline secondary batteries in the electric power tools.

SUMMARY OF THE INVENTION

An object of the invention is to improve the nickel electrode for alkaline secondary battery comprising a porous sintered nickel substrate loaded with a nickel hydroxide-based active material, for suppression of the self discharge of the alkaline secondary battery employing this nickel electrode as the positive electrode and for enhancement of the storability of the battery stored under high temperature conditions.

Another object of the invention is to improve the alkaline secondary battery employing the above nickel electrode as the positive electrode in the high density

current charge/discharge characteristics (high-rate characteristics).

According to a first aspect of the invention, a nickel electrode for alkaline secondary battery including a porous sintered nickel substrate loaded with a nickel hydroxide-based active material, the nickel electrode comprises a first coating layer of cobalt compound laid on a surface portion of the active material loaded into the sintered nickel substrate; and a second coating layer laid on the first coating layer and based on a compound of at least one element selected from the group consisting of nickel, magnesium, calcium, barium, strontium, scandium, yttrium, lanthanide and bismuth.

The lanthanide in the second coating layer of the nickel electrode for alkaline secondary battery according to the first aspect hereof may be composed of at least one element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium and ytterbium.

According to a second aspect of the invention, a nickel electrode for alkaline secondary battery including a porous sintered nickel substrate loaded with a nickel hydroxide-based active material, the nickel electrode comprises a first coating layer of cobalt compound laid on a surface portion of the active material loaded into the

sintered nickel substrate, and a second coating layer laid on the first coating layer and based on a complex compound of cobalt and at least one element selected from the group consisting of nickel, magnesium, calcium, barium, strontium, scandium, yttrium, lanthanide and bismuth.

The lanthanide in the second coating layer of the nickel electrode for alkaline secondary battery according to the second aspect hereof may be composed of at least one element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium and ytterbium.

Where an alkaline secondary battery is fabricated using the nickel electrode of the first or second aspect hereof as the positive electrode therefor, the first and second coating layers on the surface portion of the active material loaded into the porous sintered nickel substrate serve to prevent the electrolyte from coming into contact with the active material and the sintered nickel substrate. Additionally, the cobalt compound in the first coating layer increases conductivity, thus contributing to an increased discharge capacity. On the other hand, because of the compound of nickel, magnesium and/or the like or the complex compound of cobalt and magnesium and/or the like forming the second coating layer, the oxygen evolution is suppressed and hence, the self discharge is prevented.

during storage of the charged battery under high temperature conditions. This results in the improvement of the high temperature storability.

In the nickel electrode for alkaline secondary battery of the first and second aspects hereof, the second coating layer may preferably employ such a compound of nickel, magnesium and/or the like or such a complex compound of cobalt and magnesium and/or the like as that which is relatively stably present in the alkaline secondary battery. For this reason, the above compound or complex compound is preferably composed of a hydroxide, an oxide or a mixture of these.

If, in the second coating layers of the nickel electrodes of the first and second aspects hereof, the compound of nickel, magnesium and/or the like or the complex compound of cobalt and nickel, magnesium and/or the like contains the above element(s) (including cobalt) in insufficient concentrations, the alkaline secondary battery is not sufficiently improved in the high temperature storability. On the other hand, if the element(s) are contained in excessive concentrations, the alkaline secondary battery cannot attain a sufficient battery capacity because the loading ratio of the active material in the nickel electrode is decreased. Accordingly, the compound or complex compound of the second coating layer

preferably contains the above element(s) (including cobalt) in the range of 0.05 to 5 wt% based on the total weight of the active material, and first and second coating layers.

The nickel electrode for alkaline secondary battery of the first aspect hereof may be fabricated by the steps of: dipping the sintered substrate loaded with the nickel hydroxide-based active material in a solution of cobalt salt and then dipping this sintered substrate in an aqueous alkaline solution thereby forming the first coating layer of cobalt compound on the active-material surface portion; and dipping the sintered substrate in a solution containing a salt of at least one element selected from the group consisting of nickel, magnesium, calcium, barium, strontium, scandium, yttrium, lanthanide and bismuth and then dipping the sintered substrate in the aqueous alkaline solution thereby forming the second coating layer on the first coating layer.

The nickel electrode for alkaline secondary battery of the second aspect hereof may be fabricated by the steps of: dipping the sintered substrate loaded with the nickel hydroxide-based active material in a solution of cobalt salt and then dipping this sintered substrate in the aqueous alkaline solution thereby forming the first coating layer of the cobalt compound on the active-material surface portion; and dipping the sintered substrate in a solution

containing a cobalt salt and a salt of at least one element selected from the group consisting of nickel, magnesium, calcium, barium, strontium, scandium, yttrium, lanthanide and bismuth and then dipping the sintered substrate in the aqueous alkaline solution thereby forming the second coating layer on the first coating layer.

According to a third aspect of the invention, a nickel electrode for alkaline secondary battery including a porous sintered nickel substrate loaded with a nickel hydroxide-based active material, the nickel electrode comprises a layer laid between a surface portion of the active material loaded into the sintered nickel substrate and/or the sintered nickel substrate, and the active material, the layer based on a complex compound of nickel and at least one element selected from the group consisting of cobalt, calcium, strontium, scandium, yttrium, lanthanide, bismuth, magnesium and barium.

The lanthanide in the above layer may be composed of at least one element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, europium and ytterbium.

Where an alkaline secondary battery is fabricated using the nickel electrode of the third aspect hereof as the positive electrode therefor, the above layer between the surface portion of the active material loaded into the

porous sintered nickel substrate and/or the sintered nickel substrate, and the active material prevents the electrolyte from coming into contact with the active material and sintered nickel substrate.

In the nickel electrode for alkaline secondary battery of the third aspect hereof, the layer between the active-material surface portion and/or the sintered nickel substrate, and the active material contains the complex compound of nickel and the aforesaid element(s) and therefore, the nickel compound of this layer promotes the charge/discharge reactions thereby improving the alkaline secondary battery in the high-current discharge capacity. In addition, the compound of the aforesaid element(s), such as cobalt and calcium and the like, suppresses the oxygen evolution during storage of the charged battery under high temperature conditions and hence, the self discharge is prevented. This results in the enhanced high temperature storability.

In the nickel electrode for alkaline secondary battery of the third aspect hereof, the above layer may preferably employ such a complex compound as that which is relatively stably present in the alkaline secondary battery. For this reason, the above complex compound is preferably composed of a hydroxide, an oxide or a mixture of these.

In the layer based on the complex compound of nickel and the aforesaid element(s) and laid between the surface portion of the active material loaded into the sintered nickel substrate and/or the sintered nickel substrate, and the active material, if the aforesaid complex compound is contained in insufficient concentrations, inabilities to adequately suppress the reaction between the electrolyte and the active material and the like and to adequately improve the high temperature storability of the alkaline secondary battery result. On the other hand, if the complex compound is contained in excessive concentrations, the alkaline secondary battery cannot attain a sufficient capacity because the loading ratio of the active material in the nickel electrode is decreased. Accordingly, a mixing ratio of the complex compound in the aforesaid layer is preferably in the range of 0.5 to 5 wt% based on the total weight of all the loaded materials which include the nickel hydroxide-based active material. Further, the above layer preferably contains the compound of the element(s) selected from the group consisting of cobalt, calcium, strontium, scandium, yttrium, lanthanide, bismuth, magnesium and barium in a total weight percentage of 0.3 to 3 wt% based on the total weight of all the loaded materials which include the nickel hydroxide-based active material loaded into the sintered nickel substrate.

According to a fourth aspect of the invention, a nickel electrode for alkaline secondary battery including a porous sintered nickel electrode loaded with a nickel hydroxide-based active material, the nickel electrode comprises a first coating layer which is laid on a surface portion of the active material loaded into the sintered nickel substrate and is based on a compound of at least one element selected from the group consisting of magnesium, calcium, barium, strontium, scandium, yttrium, lanthanide and bismuth, and a second coating layer of cobalt compound laid on the first coating layer.

According to a fifth aspect of the invention, a nickel electrode for alkaline secondary battery including a porous sintered nickel substrate loaded with a nickel hydroxide-based active material, the nickel electrode comprises a first coating layer which is laid on a surface portion of the active material loaded into the sintered nickel substrate and is based on a complex compound of cobalt and at least one element selected from the group consisting of magnesium, calcium, barium, strontium, scandium, yttrium, lanthanide and bismuth, and a second coating layer of cobalt compound laid on the first coating layer.

The lanthanide in the first coating layer of the nickel electrodes for alkaline secondary battery according

to the fourth and fifth aspects hereof may be composed of at least one element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, europium and ytterbium.

Where an alkaline secondary battery is fabricated using the nickel electrode of the fourth or fifth aspect hereof as the positive electrode therefor, the first and second coating layers laid on the surface portion of the active material loaded into the porous sintered nickel substrate prevent the electrolyte from coming into contact with the active material and sintered nickel substrate. Additionally, because of the compound of magnesium, calcium and/or the like or the complex compound of cobalt and magnesium, calcium and/or the like in the first coating layer, the oxygen evolution is suppressed and hence, the self discharge is prevented during storage of the charged battery under high temperature conditions. This results in the improvement in the high temperature storability. At the same time, the cobalt compound in the second coating layer increases conductivity, allowing for discharge at high voltage. Particularly, as suggested by the nickel electrode of the fifth aspect hereof, the first coating layer, which is based on the complex compound of cobalt and magnesium, calcium and/or the like, is further improved in conductivity, thus contributing to an even greater high

temperature storability and allowing for discharge at an even higher voltage.

In the nickel electrodes for alkaline secondary battery of the fourth and fifth aspects hereof, the first coating layer may preferably employ such a compound of magnesium, calcium and the like or such a complex compound of cobalt and magnesium, calcium and/or the like as that which is relatively stably present in the alkaline secondary battery. For this reason, the above compound or complex compound is preferably composed of a hydroxide, an oxide or a mixture of these.

In the nickel electrodes of the fourth and fifth aspects hereof, if the first coating layer contains the compound of magnesium, calcium or the like, or the complex compound of cobalt and magnesium, calcium and/or the like in insufficient concentrations, inabilities to adequately suppress the reaction between the electrolyte and the active material and to sufficiently improve the high temperature storability result. On the other hand, if the compound or complex compound is contained in excessive concentrations, the battery cannot attain a sufficient battery capacity because the loading ratio of the active material in the nickel electrode is decreased.

Accordingly, a mixing ratio of the compound or complex compound in the first coating layer is preferably in the

range of 0.5 to 5 wt% based on the total weight of the active material, and first and second coating layers.

In the nickel electrodes of the fourth and fifth aspects hereof, if the second coating layer contains the cobalt compound in insufficient concentrations, the nickel electrode for alkaline secondary battery is not sufficiently improved in conductivity and an inability to discharge at high voltage results. On the other hand, if the compound is contained in excessive concentrations, the battery cannot attain a sufficient battery capacity because the loading ratio of the active material in the nickel electrode is decreased. Accordingly, a mixing ratio of the cobalt compound in the second coating layer is preferably in the range of 0.5 to 5 wt% based on the total weight of the active material, and first and second coating layers.

According to a sixth aspect of the invention, a nickel electrode for alkaline secondary battery including a porous sintered nickel substrate loaded with a nickel hydroxide-based active material, the nickel electrode comprises a layer which is laid between a surface portion of the active material on the porous sintered nickel substrate and/or the sintered nickel substrate, and the active material, and which is based on a complex compound of at least one element selected from the group consisting of cobalt and nickel, and at least one element selected

from the group consisting of manganese, aluminum, iron, copper and silver.

Where an alkaline secondary battery is fabricated using the nickel electrode of the sixth aspect hereof as the positive electrode therefor, the aforesaid layer, which is laid between the surface portion of the active material loaded into the porous sintered nickel substrate and/or the sintered nickel substrate, and the active material, prevents the electrolyte from coming into contact with the active material and sintered nickel substrate.

In the nickel electrode for alkaline secondary battery according to the sixth aspect hereof, the layer between the surface portion of the active material and/or the sintered nickel substrate and the active material employs the complex compound of at least one element selected from the group of cobalt and nickel and at least one element selected from the group of manganese, aluminum, iron, copper and silver, such that the self discharge due to the oxygen evolution is prevented during storage of the charged electrode under high temperature conditions. Thus, the alkaline secondary battery is improved in the high temperature storability. In addition, the electrode with this complex compound provides smoother charge/discharge reactions than the conventional sintered nickel electrode formed with a manganese hydroxide layer over its surface,

thus allowing for the discharge at high voltage.

Furthermore, the complex compound also suppresses the expansion of the nickel electrode for alkaline secondary battery thereby improving the charge/discharge cycle characteristics of the battery.

In the nickel electrode for alkaline secondary battery of the sixth aspect hereof, the above layer may preferably employ such a complex compound as that which is relatively stably present in the alkaline secondary battery. For this reason, the above complex compound is preferably composed of a hydroxide, an oxide or a mixture of these.

In the layer which is laid between the surface portion of the active material loaded into the sintered nickel substrate and/or the sintered nickel substrate, and the active material and which is based on the above complex compound, if the layer contains the complex compound in insufficient concentrations, inabilities to adequately suppress the reaction between the electrolyte and the active material and the like and to sufficiently improve the alkaline secondary battery in the high temperature storability result. If, on the other hand, the layer contains the complex compound in excessive concentrations, the battery cannot attain a sufficient battery capacity because the loading ratio of the active material in the

nickel electrode for alkaline secondary battery is decreased. Besides, the alkaline secondary battery is lowered in the charge/discharge cycle characteristics because of decreased discharge voltage. Accordingly, a mixing ratio of the complex compound in the above layer is preferably in the range of 0.5 to 5 wt% based on the total weight of all the loaded materials which include the nickel hydroxide-based active material. Further, the above layer preferably contains the compound of the element(s) selected from the group of manganese, aluminum, iron, copper and silver in a total weight percentage of 0.3 to 3 wt% based on the total weight of all the loaded materials which include the nickel hydroxide-based active material loaded into the sintered nickel substrate.

According to a seventh aspect of the invention, a nickel electrode for alkaline secondary battery including a porous sintered nickel substrate loaded with a nickel hydroxide-based active material, the nickel electrode comprises a coating layer which is laid on a surface portion of the active material loaded into the sintered nickel substrate and which contains a complex compound of at least one element selected from the group consisting of yttrium and ytterbium and at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver.

According to an eighth aspect of the invention, a nickel electrode for alkaline secondary battery including a porous sintered nickel substrate loaded with a nickel hydroxide-based active material, the nickel electrode comprises a coating layer which is laid on a surface portion of the active material loaded into the sintered nickel substrate and which contains a complex compound of at least one element selected from the group consisting of yttrium and ytterbium, at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver, and at least one element selected from the group consisting of cobalt and nickel.

Where an alkaline secondary battery is fabricated using the nickel electrode for alkaline secondary battery of the seventh or eighth aspect hereof as the positive electrode therefor, the above coating layer on the surface portion of the active material loaded into the porous sintered nickel substrate prevents the electrolyte from coming into contact with the active material and sintered nickel substrate, thereby suppressing the self discharge.

In the nickel electrodes for alkaline secondary battery according to the seventh and eighth aspects hereof, the coating layers employ the aforesaid complex compound, yttrium and/or ytterbium of which is more effective to suppress the oxygen evolution and hence the self discharge

in the charged electrode stored under high temperature conditions, as compared with the conventional sintered nickel electrode formed with the manganese hydroxide layer over its surface. Thus, the alkaline secondary battery is improved in the high temperature storability and the charge efficiency at high temperatures. The complex compounds also provide smooth charge/discharge reactions, allowing for discharge at high voltage. In addition, the expansion of the nickel electrode for alkaline secondary battery is prevented and thus, the alkaline secondary battery is improved in the charge/discharge cycle characteristics.

In the nickel electrode for alkaline secondary battery of the eight aspect hereof, the complex compound of the coating layer further contains at least one element selected from the group of cobalt and nickel so that the coating layer is improved in the conductivity and the battery reactions. This allows for high voltage discharge and contributes to the improvement of the charge/discharge cycle characteristics.

In the nickel electrodes for alkaline secondary battery of the seventh and eighth aspects hereof, the above coating layers may preferably employ such a complex compound as that which is relatively stably present in the alkaline secondary battery. For this reason, the above

complex compound is preferably composed of a hydroxide, an oxide or a mixture of these.

In the nickel electrodes for alkaline secondary battery according to the seventh and eighth aspects hereof, if the coating layers contain the above complex compounds in insufficient concentrations, the coating layers are incapable of adequately suppressing the reactions between the electrolyte and the active material and of sufficiently improving the alkaline secondary batteries in the high temperature storability. If, on the other hand, the coating layers contain the complex compounds in excessive concentrations, the battery cannot attain a sufficient battery capacity because the loading ratio of the active material in the nickel electrode for alkaline secondary battery is decreased. In addition, the alkaline secondary battery is lowered in the discharge voltage and suffers the expansion of the nickel electrode thereof which results from the increase in an undischarged portion of the electrode. This leads to lowered charge/discharge cycle characteristics of the battery. Accordingly, a mixing ratio of the complex compound in the coating layer is preferably in the range of 0.5 to 5 wt% based on the total weight of the active material and coating layer.

If the above complex compound contains the compound of the element(s) selected from the group of manganese,

aluminum, iron, copper and silver in insufficient concentrations, the alkaline secondary battery is lowered in the high temperature storability and cycle characteristics. If, on the other hand, the complex compound contains such a compound in excessive concentrations, the alkaline secondary battery is lowered in the working voltage and the charge efficiency at high temperatures. Hence, the complex compound preferably contains the compound of the element(s) selected from the group of manganese, aluminum, iron, copper and silver in a total weight percentage of 0.3 to 3 wt% and more preferably 2 to 3 wt% based on the total weight of the active material and coating layer.

If the complex compound contains the compound of the element(s) selected from the group of yttrium and ytterbium in insufficient concentrations, the alkaline secondary battery is lowered in the working voltage and the charge efficiency at high temperatures. If, on the other hand, the complex compound contains such a compound in excessive concentrations, the alkaline secondary battery is lowered in the high temperature storability and cycle characteristics. Hence, the complex compound preferably contains the compound of the element(s) selected from the group of yttrium and ytterbium in a total weight percentage

of 0.3 to 3 wt% and more preferably 2 to 3 wt% based on the total weight of the active material and coating layer.

Incidentally, it is preferred that zinc, cadmium, magnesium, cobalt, manganese or the like is incorporated into the nickel hydroxide-based active material as solid solution for the prevention of the expansion of the nickel electrode during the charge/discharge processes of the alkaline secondary battery employing any of the nickel electrodes of the first to eighth aspects hereof.

According to an embodiment of the present invention, there is provided a sintered nickel electrode, which employs a porous sintered nickel substrate obtained by sintering and is fabricated by chemically impregnating the porous sintered nickel substrate with an active material, for alkaline secondary battery, comprising:

- a porous sintered nickel substrate;

- a nickel hydroxide-based active material layer provided on the porous sintered nickel substrate; and

- a coating layer which is provided on the active material layer and is based on a complex compound of nickel and cobalt, calcium, strontium, scandium, yttrium, lanthanide, bismuth, magnesium or barium.

These and other objects, advantages and features of the invention will become apparent from the following description thereof taken in conjunction with the accompanying drawings which illustrate specific embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a schematic sectional view showing an exemplary nickel electrode for alkaline secondary battery according to the invention wherein a first coating layer and a second coating layer are sequentially laid on a surface portion of an active material loaded into a porous sintered nickel substrate;

Fig.2 is a schematic sectional view showing another exemplary nickel electrode for alkaline secondary battery according to the invention wherein a coating layer is laid

on the surface portion of the active material loaded into the porous sintered nickel substrate; and

Fig.3 is a schematic sectional view showing still another exemplary nickel electrode for alkaline secondary battery according to the invention wherein an intermediate layer is laid between the porous sintered nickel substrate and the active material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now, nickel electrodes for alkaline secondary battery and alkaline secondary batteries employing the same according to the preferred embodiments of the invention will hereinbelow be described in detail while comparative examples will be cited to demonstrate advantages of the nickel electrodes for alkaline secondary battery and the alkaline secondary batteries employing the same according to the preferred embodiments hereof. It should be appreciated that the nickel electrodes for alkaline secondary battery and the alkaline secondary batteries of the invention are not limited to the following examples but variations and modifications thereto may be made within the scope and spirit of the invention.

(Examples A1 to A15)

In fabrication of nickel electrodes for alkaline secondary battery of Examples A1 to A15, there was used a

porous sintered nickel substrate prepared in the following manner.

The porous sintered nickel substrate was prepared by the steps of: forming a nickel slurry by kneading carbonyl nickel powder and a binder; spreading the slurry on a 50 μ m-thick punched foil; allowing the slurry to dry; and sintering the slurry in a reducing atmosphere. The resultant porous sintered nickel substrate had a porosity of 85% and a thickness of 0.65 mm.

Subsequently, a nickel hydroxide-based active material was loaded into the sintered nickel substrate using six impregnation cycles, where each cycle comprised the steps of: dipping the sintered nickel substrate into an aqueous solution mixture of nickel nitrate and cobalt nitrate (specific gravity:1.75, atomic ratio between nickel and cobalt:10:1) thereby impregnating the sintered nickel substrate with the aqueous solution mixture of nickel nitrate and cobalt nitrate; and dipping the sintered nickel substrate into a 25% NaOH aqueous solution thereby allowing hydroxides of nickel and cobalt to deposit onto the sintered nickel substrate.

Next, as shown in Fig.1, a first coating layer 3a and a second coating layer 3b were sequentially laid on the active material 2 thus loaded into the sintered nickel substrate 1. Although the figure illustrates the active

material layer 2, first coating layer 3a and second coating layer 3b uniformly overlaid on one another on the sintered nickel substrate 1, it is to be noted that the active material layer 2, first coating layer 3a and second coating layer 3b each may be partially broken or may not be observed as a totally independent layer.

The first coating layer 3a of cobalt hydroxide was laid on the active material loaded into the sintered nickel substrate by the steps of: dipping the sintered nickel substrate with the active material into an aqueous solution of 3 wt% cobalt nitrate; and dipping the substrate into the 25% NaOH aqueous solution at 80°C.

There were prepared aqueous solutions of 3 wt% nitrates for Examples A1 to A15. Specifically, there were used nickel (Ni) nitrate for Example A1; magnesium (Mg) nitrate for Example A2; calcium (Ca) nitrate for Example A3; barium (Ba) nitrate for Example A4; strontium (Sr) nitrate for Example A5; scandium (Sc) nitrate for Example A6; yttrium (Y) nitrate for Example A7; lanthanide (La) nitrate for Example A8; cerium (Ce) nitrate for Example A9; praseodymium (Pr) nitrate for Example A10; neodymium (Nd) nitrate for Example A11; samarium (Sm) nitrate for Example A12; europium (Eu) nitrate for Example A13; ytterbium (Yb) nitrate for Example A14; and bismuth (Bi) nitrate for Example A15.

The sintered nickel substrate formed with the first coating layer was dipped into each of the above aqueous nitrate solutions and then dipped into the 25% NaOH aqueous solution at 80°C. Thus, the respective second coating layers of hydroxides of the elements listed in Table 1 as below were laid on the surface of the first coating layer.

The resultant first and second coating layers substantially had a constant weight per unit area of 5 to 6 mg/cm² regardless of the element types. The weight of the first or second coating layer accounted for 2.9 to 3 wt% based on the total weight of all the loaded materials of the first and second coating layers, and active material.

The weight percentage of each element of the above second coating layers was determined based on the total weight of all the loaded materials of the first and second coating layers, and active material. The resultant weight percentages of the elements were in the range of 1.3 to 2.4 wt%, as shown in Table 1.

The following procedure was taken to fabricate respective alkaline secondary batteries of Examples A1 to A15 having a battery capacity of about 1.0 Ah, using the respective nickel electrodes for alkaline secondary battery as the positive electrode therefor and a hydrogen-absorbing alloy represented by a composition formula of $\text{Mm}_{1.0}\text{Ni}_{3.2}\text{Co}_{1.0}\text{Al}_{0.2}\text{Mn}_{0.6}$ as the negative electrode. The

procedure comprised the steps of: inserting a separator of polyolefin nonwoven fabric between the positive and negative electrodes and winding them into a roll shape; placing the roll into a battery can; filling the battery can with 6-normal solution of potassium hydroxide as the electrolyte; and sealing the battery can.

(Comparative Examples a1 to a15)

In fabrication of nickel electrodes for alkaline secondary battery of Comparative Examples a1 to a15, the formation of the first coating layer of cobalt hydroxide was dispensed with and only the second coating layers were laid on the active material loaded into the sintered nickel substrate in correspondence with those of Examples A1 to A15.

Alkaline secondary batteries of Comparative Examples a1 to a15 were fabricated the same way as Examples A1 to A15 correspondingly using the resultant nickel electrodes as the positive electrode therefor.

The resultant alkaline secondary batteries of Examples A1 to A15 and Comparative Examples a1 to a15 were cycled at room temperatures through 10 cycles with 16 hr charge using a 100 mA current and discharge to a voltage of 1.0 V using a 100 mA current.

On the 10th cycle, the discharge capacity Q_{10} of each battery was determined and the results are listed in Tables

1 and 2 as below. After the 11th charge cycle, the batteries were subject to storage at 50°C for two weeks. Subsequently, the batteries were placed under room temperatures again and discharged at 100 mA to 1.0 V so as to determine the discharge capacities Q_{11} at cycle 11. The discharge capacity Q_{10} at cycle 10 was compared with the discharge capacity Q_{11} at cycle 11 so as to determine the high temperature storability based on the following equation:

$$\text{High-temperature storability(\%)} = (Q_{11}/Q_{10}) \times 100$$

The results are listed in Tables 1 and 2 as below.

Table 1

	element of first coating layer	second coating layer		Q ₁₀ (mAh)	high- temperature storability (%)
		element	weight percentage (wt%)		
example A1	Co	Ni	1.9	1150	77
example A2	Co	Mg	1.3	1170	72
example A3	Co	Ca	1.6	1230	79
example A4	Co	Ba	2.4	1120	73
example A5	Co	Sr	2.2	1110	74
example A6	Co	Sc	1.4	1100	79
example A7	Co	Y	1.9	1250	80
example A8	Co	La	2.2	1140	74
example A9	Co	Ce	2.2	1100	77
example A10	Co	Pr	2.2	1090	73
example A11	Co	Nd	2.2	1100	72
example A12	Co	Sm	2.2	1090	74
example A13	Co	Eu	2.2	1090	76
example A14	Co	Yb	2.3	1200	79
example A15	Co	Bi	2.4	1210	78

Table 2

	coating layer		Q ₁₀ (mAh)	high- temperature storability (%)
	element	weight percentage (wt%)		
comparative example a1	Ni	2.0	1000	62
Comparative example a2	Mg	1.3	1000	57
Comparative example a3	Ca	1.7	1050	64
Comparative example a4	Ba	2.5	1000	57
Comparative example a5	Sr	2.2	1000	58
Comparative example a6	Sc	1.5	1000	64
Comparative example a7	Y	2.0	1060	66
Comparative example a8	La	2.3	1000	58
Comparative example a9	Ce	2.3	1000	62
Comparative example a10	Pr	2.3	1000	59
Comparative example a11	Nd	2.3	1000	58
Comparative example a12	Sm	2.3	1000	59
Comparative example a13	Eu	2.3	1000	61
Comparative example a14	Yb	2.4	1030	63
Comparative example a15	Bi	2.5	1040	62

As apparent from Tables 1 and 2, the alkaline secondary batteries of Examples A1 to A15 are all improved

in the discharge capacity and high temperature storability on the 10th cycle as compared with the alkaline secondary batteries of Comparative Examples a1 to a15 which are free from the first coating layer of cobalt hydroxide, the batteries of Examples A1 to A15 each having the first coating layer of cobalt hydroxide formed on the active material loaded into the sintered nickel substrate and the second coating layer which is laid on the first coating layer and based on a hydroxide of an element selected from the group consisting of nickel, magnesium, calcium, barium, strontium, scandium, yttrium, lanthanide and bismuth.

(Examples A16 to A30)

In fabrication of nickel electrodes of Examples A16 to A30, the same procedure as in Examples A1 to A15 was taken to form the first coating layer of cobalt hydroxide on the active material loaded into the sintered nickel substrate.

Preparatory to the formation of the second coating layer over the first coating layer, aqueous solutions of 3 wt% nitrates were prepared which each contained cobalt nitrate and a nitrate of a different element in a weight ratio of 1:1.

As the nitrate of the different element, nickel nitrate was used in Example A16; magnesium nitrate in Example A17; calcium nitrate in Example A18; barium nitrate

in Example A19; strontium nitrate in Example A20; scandium nitrate in Example A21; yttrium nitrate in Example A22; lanthanum nitrate in Example A23; cerium nitrate in Example A24; praseodymium nitrate in Example A25; neodymium nitrate in Example A26; samarium nitrate in Example A27; europium nitrate in Example A28; ytterbium nitrate in Example A29; and bismuth nitrate in Example A30.

The sintered nickel substrate with the first coating layer was dipped into each of the above nitrate solutions, and then dipped into the 25% NaOH aqueous solution at 80°C thereby to form the respective second coating layers based on nitrates of two elements as listed in Table 3 as below.

The resultant second coating layers substantially had a constant weight per unit area of 5 to 6 mg/cm² regardless of the different element types. The weight of the second coating layer accounted for 3 wt% based on the total weight of all the loaded materials of the first and second coating layers, and active material.

The weight percentage of cobalt and the different element in each second coating layer was determined based on the total weight of all the loaded materials of the first and second coating layers, and active material. The results were in the range of 1.6 to 2.2 wt% as shown in Table 3 as below.

Subsequently, alkaline secondary batteries of Examples A16 to A30 were fabricated using the respective nickel electrodes for alkaline secondary battery as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Examples a16 to a30)

In fabrication of nickel electrodes of Comparative Examples a16 to a30, the formation of the first coating layer of cobalt hydroxide was dispensed with and only the second coating layers were laid on the active material loaded into the sintered nickel substrate in correspondence with those of Examples A16 to A30, as shown in Table 4.

Alkaline secondary batteries of Comparative Examples a16 to a30 were fabricated using the resultant nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example a31)

In fabrication of a nickel electrode of Comparative Example a31, the active material was loaded into the sintered nickel substrate the same way as in Examples A1 to A15 and the formation of any coating layer thereon was dispensed with.

An alkaline secondary battery of Comparative Example a31 was fabricated using the resultant nickel electrode as

the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example a32)

In fabrication of a nickel electrode of Comparative Example a32, the active material was loaded into the sintered nickel substrate the same way as in Examples A1 to A15 and only the coating layer of cobalt hydroxide was laid thereon.

An alkaline secondary battery of Comparative Example a32 was fabricated using the resultant nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to 15.

Similarly to Examples A1 to A15 and Comparative Examples a1 to a15, the discharge capacity Q_{10} at cycle 10 and the high temperature storability were determined for the respective alkaline secondary batteries of Examples A16 to A30 and Comparative Examples a16 to a32. The results are listed in Tables 3 and 4 as below.

Table 3

	element of first coating layer	second coating layer		Q_{10} (mAh)	high- temperature storability (%)
		element	weight percentage (wt%)		
example A16	Co	Co+Ni	1.9	1190	79
example A17	Co	Co+Mg	1.6	1200	74
example A18	Co	Co+Ca	1.8	1260	82
example A19	Co	Co+Ba	2.2	1150	75
example A20	Co	Co+Sr	2.0	1140	76
example A21	Co	Co+Sc	1.7	1140	81
example A22	Co	Co+Y	1.9	1280	82
example A23	Co	Co+La	2.0	1160	76
example A24	Co	Co+Ce	2.1	1130	79
example A25	Co	Co+Pr	2.1	1120	75
example A26	Co	Co+Nd	2.1	1130	74
example A27	Co	Co+Sm	2.1	1120	76
example A28	Co	Co+Eu	2.1	1110	78
example A29	Co	Co+Yb	2.1	1230	82
example A30	Co	Co+Bi	2.2	1240	81

Table 4

	coating layer		Q ₁₀ (mAh)	high- temperature storability (%)
	element	weight percentage (wt%)		
comparative example a16	Co+Ni	2.0	1020	64
comparative example a17	Co+Mg	1.6	1020	60
Comparative example a18	Co+Ca	1.8	1080	68
Comparative example a19	Co+Ba	2.2	1000	61
Comparative example a20	Co+Sr	2.1	1000	61
Comparative example a21	Co+Sc	1.7	1000	67
Comparative example a22	Co+Y	2.0	1080	68
Comparative example a23	Co+La	2.1	1010	61
Comparative example a24	Co+Ce	2.1	1000	64
Comparative example a25	Co+Pr	2.1	1000	62
Comparative example a26	Co+Nd	2.1	1000	62
Comparative example a27	Co+Sm	2.1	1000	63
Comparative example a28	Co+Eu	2.1	1000	64
Comparative example a29	Co+Yb	2.2	1060	66
Comparative example a30	Co+Bi	2.2	1080	67
Comparative example a31	-	-	900	49
Comparative example a32	Co	1.9	1000	52

As apparent from Tables 3 and 4, the alkaline secondary batteries of Examples A16 to A30, wherein the first coating layer of cobalt hydroxide is laid on the active material loaded into the sintered nickel substrate and the second coating layer of the complex hydroxide of cobalt and an element selected from the group of nickel, magnesium, calcium, barium, strontium, scandium, yttrium, lanthanide and bismuth was laid on the first coating layer, have greater discharge capacities at cycle 10 and high temperature storabilities than those of Comparative Examples a15 to a30 free from the first coating layer of cobalt compound, that of Comparative Example a31 without any coating layer, and that of Comparative Example a32 without the second coating layer of the complex hydroxide. (Examples A7.1 to A7.10)

The following procedure was taken to fabricate nickel electrodes of Examples A7.1 to A7.10. The active material was loaded into the sintered nickel substrate the same way as in Examples A1 to A15. Then, first coating layers differing in the concentration of cobalt were formed on the active material using aqueous solutions varied in the concentration of cobalt nitrate as shown in Table 5 as below. The second coating layer of yttrium hydroxide was formed on each of the first coating layers the same way as in Example A7.

The weight percentage of cobalt in the respective first coating layers was determined based on the total weight of all the loaded materials of the first and second coating layers, and active material. The results are listed in Table 5.

Alkaline secondary batteries of Examples A7.1 to A7.10 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples A1 to A15 and Comparative Examples a1 to a15, the discharge capacity Q_{10} at cycle 10 and the high temperature storability were determined for the respective alkaline secondary batteries of Examples A7.1 to A7.10. The results are listed in Table 5 as below.

Table 5

	content of Co nitrate (wt%)	content of cobalt (wt%)	Q_{10} (mAh)	high- temperature storability (%)
example A7.1	0.03	0.01	1140	77
example A7.2	0.05	0.02	1150	78
example A7.3	0.1	0.05	1200	79
example A7.4	0.2	0.1	1210	80
example A7.5	2	1	1230	80
example A7.6	3	1.8	1250	80
example A7.7	5	3	1240	80
example A7.8	8	5	1220	79
example A7.9	10	7	1150	78
example A7.10	15	10	1140	77

As apparent from Table 5, the discharge capacity at cycle 10 and the high temperature storability are improved in the batteries wherein the first coating layer contains cobalt in concentrations of 0.05 to 5 wt% based on the total weight of the active material, and first and second coating layers.

(Examples A7.11 to A7.20)

In fabrication of nickel electrodes of Examples A7.11 to A7.20, the same procedure as in Examples A1 to A15

was taken to form the first coating layer on the active material loaded into the sintered nickel substrate. Then, second coating layers differing in the concentration of yttrium were laid on the first coating layers using aqueous solutions varied in the concentration of yttrium nitrate as listed in Table 6 as below.

The weight percentage of yttrium in each second coating layer was determined based on the total weight of all the loaded materials of the first and second coating layers, and active material. The results are listed in Table 6.

Alkaline secondary batteries of Examples A7.11 to A7.20 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples A1 to A15 and Comparative Examples a1 to a15, the discharge capacity Q_{10} at cycle 10 and the high temperature storability were determined for the respective alkaline secondary batteries of Examples A7.11 to A7.20. The results are listed in Table 6 as below.

Table 6

	content of Y nitrate (wt%)	content of Y (wt%)	Q ₁₀ (mAh)	high- temperature storability (%)
example A7.11	0.03	0.01	1220	69
example A7.12	0.04	0.02	1230	72
example A7.13	0.1	0.05	1240	77
example A7.14	0.2	0.1	1240	78
example A7.15	2	1	1250	79
example A7.16	3	1.9	1250	80
example A7.17	5	3	1230	81
example A7.18	8	5	1200	81
example A7.19	11	7	1150	81
example A7.20	14	10	1100	81

As apparent from Table 6, the high temperature storability is lowered where the second coating layer contains yttrium in concentrations of less than 0.05 wt% based on the total weight of all the loaded materials of the active material, and first and second coating layers. Where the second coating layer contains yttrium in concentrations of more than 5 wt%, the discharge capacity at cycle 10 is lowered. Therefore, it is desirable that the second coating layer contains yttrium in the weight

percentage of 0.05 to 5 wt% based on the total weight of all the loaded materials of the active material, and first and second coating layers.

(Examples B1 to B14)

In Examples B1 to B14, as well, the same procedure as in Examples A1 to A15 was taken to load the nickel hydroxide-based active material into the porous sintered nickel substrate.

Then, as shown in Fig.2, the coating layer 3 of a complex hydroxide of nickel and an element selected from the group consisting of cobalt, calcium, strontium, scandium, yttrium, lanthanide, bismuth, magnesium and barium was laid on the nickel hydroxide-based active material 2 loaded into the sintered nickel substrate 1. Although the figure illustrates the coating layer 3 of the complex hydroxide of the aforesaid elements uniformly formed on the nickel hydroxide-based active material 2, it is to be noted that the active material layer 2 and the coating layer 3 each may be partially broken or may not be observed as a totally independent layer.

In formation of the coating layer of the above complex hydroxide on the active material loaded into the sintered nickel substrate, a solution mixture of nitrates of nickel (Ni) and each of the above elements was used. Specifically, there were used cobalt (Co) nitrate in

Example B1; calcium (Ca) nitrate in Example B2; strontium (Sr) nitrate in Example B3; scandium (Sc) nitrate in Example B4; yttrium (Y) nitrate in Example B5; lanthanum (La) nitrate in Example B6; cerium (Ce) nitrate in Example B7; praseodymium (Pr) nitrate in Example B8; neodymium (Nd) nitrate in Example B9; europium (Eu) nitrate in Example B10; ytterbium (Yb) nitrate in Example B11; bismuth (Bi) nitrate in Example B12; magnesium (Mg) nitrate in Example B13; and barium (Ba) nitrate in Example B14.

There was prepared a 3 wt% nitrate aqueous solution containing nitrates of nickel and each of the above elements in the weight ratio of 1:1. The sintered nickel substrate loaded with the nickel hydroxide-based active material was dipped into the aqueous solution. Then, the substrate was dipped into the 25% NaOH aqueous solution at 80°C and thus, each coating layer of the complex hydroxide of two elements, as listed in Table 7, was formed on the active material loaded into the sintered nickel substrate. The resultant coating layers substantially had a constant weight per unit area of 5 to 6 mg/cm² regardless of the different element types. Each complex hydroxide accounted for about 3 wt% based on the total weight of all the loaded materials of the coating layer and active material.

Alkaline secondary batteries of Examples B1 to B14 were fabricated using the respective nickel electrodes as

the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example b1)

Comparative Example b1 employed a nickel electrode with the sintered nickel substrate loaded with only the nickel hydroxide-based active material. An alkaline secondary battery was fabricated using this nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example b2)

In Comparative Example b2, a nickel electrode having a cobalt hydroxide layer laid on the nickel hydroxide-based active material was fabricated by the steps of loading the active material into the sintered nickel substrate; dipping the sintered nickel substrate into an aqueous solution of 3 wt% cobalt nitrate; dipping the substrate into an NaOH aqueous solution thereby allowing cobalt hydroxide to deposit onto the active material loaded into the sintered nickel substrate; and allowing the substrate to dry. An alkaline secondary battery of Comparative Example b2 was fabricated using the resultant nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example b3)

In Comparative Example b3, cobalt hydroxide was allowed to deposit onto the nickel hydroxide-based active material loaded into the sintered nickel substrate the same way as in Comparative Example b2. Then, the substrate wetted with the NaOH aqueous solution was heated at 80°C in the atmosphere or in the presence of oxygen for oxidizing the above cobalt hydroxide. Thus was obtained a nickel electrode wherein a coating layer of oxidized cobalt hydroxide was formed on the active material. The resultant nickel electrode is equivalent to the nickel electrode for alkaline secondary battery disclosed in Japanese Unexamined Patent Publication No.1(1989)-200555.

An alkaline secondary battery of Comparative Example b3 was fabricated using this nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Examples b4 to b16)

In Comparative Examples b4 to b16, nickel electrodes were fabricated by the steps of loading the nickel hydroxide-based active material into the sintered nickel substrate and forming, on the active material, respective coating layers of hydroxides of different elements as listed in Table 8 as below.

The coating layers of hydroxides of different elements listed in Table 8 were each formed on the active

material by the steps of preparing an aqueous solution containing 3 wt% nitrate of each of the elements; dipping the sintered nickel substrate loaded with the nickel hydroxide-based active material into the aqueous solution of nitrate of each element the same way as in Examples B1 to B14; and dipping the substrate into the 25% NaOH aqueous solution at 80°C.

Alkaline secondary batteries of Comparative Examples b4 to b16 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

The resultant alkaline secondary batteries of Examples B1 to B14 and Comparative Examples b1 to b16 were cycled at room temperatures through 10 cycles with 16 hr charge using a 100 mA current and discharge to a voltage of 1.0 V using a 100 mA current.

On the 10th cycle, the discharge capacity Q_{10} of each battery was determined. After the 11th charge cycle, the batteries were subject to storage at 50°C for two weeks. Subsequently, the batteries were placed under room temperatures again and discharged at 100 mA to 1.0 V so as to determine the discharge capacity Q_{11} at cycle 11. The high temperature storability was determined based on the following equation:

$$\text{High-temperature storability(\%)} = (Q_{11}/Q_{10}) \times 100$$

The results are listed in Tables 7 and 8 as below.

Additionally, the alkaline secondary batteries were cycled through 10 charge/discharge cycles and charged at a high charge current of 1000 mA for 1.2 hours.

Subsequently, the alkaline secondary batteries were discharged to 1.0 V at a high discharge current of 1000 mA so as to determine the discharge capacities of the batteries subjected to such a high current charge/discharge process. The results are listed as the high-rate discharge capacity in Tables 7 and 8 as below.

Table 7

	element of complex hydroxide in coating layer	high- temperature storability (%)	high-rate discharge capacity (mAh)
example B1	Ni+Co	66	1040
example B2	Ni+Ca	66	1040
example B3	Ni+Sr	61	990
example B4	Ni+Sc	66	1050
example B5	Ni+Y	70	1050
example B6	Ni+La	62	990
example B7	Ni+Ce	64	990
example B8	Ni+Pr	61	990
example B9	Ni+Nd	60	990
example B10	Ni+Eu	63	990
example B11	Ni+Yb	66	1010
example B12	Ni+Bi	65	1040
example B13	Ni+Mg	60	990
example B14	Ni+Ba	60	990
comparative example b1	-	49	890
Comparative example b2	Co	52	960
Comparative example b3	Co (heat treatment)	54	970

Table 8

	element of hydroxide in coating layer	high- temperature storability (%)	high-rate discharge capacity (mAh)
comparative example b4	Ca	64	940
Comparative example b5	Sr	58	900
Comparative example b6	Sc	64	900
Comparative example b7	Y	66	950
Comparative example b8	La	58	900
Comparative example b9	Ce	62	900
Comparative example b10	Pr	59	900
Comparative example b11	Nd	58	900
Comparative example b12	Eu	61	900
Comparative example b13	Yb	63	920
Comparative example b14	Bi	62	940
Comparative example b15	Mg	57	930
Comparative example b16	Ba	57	940

As apparent from Table 7, the alkaline secondary batteries of Examples B1 to B14 employing the nickel electrodes, wherein the coating layer of complex hydroxide of Ni and an element selected from the group of Co, Ca, Sr, Sc, Y, La, Ce, Pr, Nd, Eu, Yb, Bi, Mg and Ba is formed on

the nickel hydroxide-based active material loaded into the sintered nickel substrate, accomplish notable improvement in the high temperature storability and increase in the high-rate discharge capacity, as compared with that of Comparative Example b1 employing the nickel electrode free from the coating layer, that of Comparative Example b2 employing the nickel electrode with the coating layer of cobalt hydroxide which is not heat treated, and that of Comparative Example b3 employing the nickel electrode with the coating layer of cobalt hydroxide which is heat treated.

As indicated by Tables 7 and 8, a significant difference of the high temperature storability is not found in the comparison between the batteries of Examples B1 to B14 and those of Comparative Examples b4 to b16 employing the nickel electrodes, wherein the coating layer of hydroxide of an element selected from the group of Ca, Sr, Sc, Y, La, Ce, Pr, Nd, Eu, Yb, Bi, Mg and Ba is formed on the nickel hydroxide-based active material loaded into the sintered nickel substrate. However, the batteries of Examples B1 to B14 present greater high-rate discharge capacities.

(Examples B5.1 to B5.9)

In Examples B5.1 to B5.9, the nickel hydroxide-based active material was loaded into the sintered nickel

substrate and similarly to Example B5, the aqueous solution containing nickel nitrate and yttrium nitrate in the weight ratio of 1:1 was used for forming respective coating layers on the active material.

Specifically, Examples B5.1 to B5.9 varied the combined weight percentage of nitrates of nickel (Ni) and yttrium (Y) in the aqueous nitrate solution within the range of 0.1 to 7 wt%. Using such aqueous nitrate solutions, the respective coating layers of complex hydroxides of nickel and yttrium were formed on the active material.

The weight percentage of the complex hydroxide of nickel and yttrium was determined for the respective coating layers based on the total weight of all the loaded materials of the coating layer and active material. The results are listed in Table 9 as below.

Alkaline secondary batteries of Examples B5.1 to B5.9 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

The high temperature storability and high-rate discharge capacity were determined for the respective alkaline secondary batteries of these examples the same way as in Examples B1 to B14 and Comparative examples b1 to

b16. The results along with that of Example B5 are listed in Table 9.

Table 9

	complex hydroxide in coating layer		high- temperature storability (%)	high-rate discharge capacity (mAh)
	element	weight percentage (wt%)		
example B5.1	Ni+Y	0.1	59	1030
example B5.2	Ni+Y	0.3	63	1030
example B5.3	Ni+Y	0.5	67	1040
example B5.4	Ni+Y	1	68	1040
example B5.5	Ni+Y	2	69	1040
example B5	Ni+Y	3	70	1050
example B5.6	Ni+Y	4	70	1050
example B5.7	Ni+Y	5	71	1040
example B5.8	Ni+Y	6	71	1010
example B5.9	Ni+Y	7	71	980

As apparent from this table, the high temperature storability and the high-rate discharge capacity are improved with the coating layer which is formed on the nickel hydroxide-based active material loaded into the sintered nickel substrate, and which contains the complex

hydroxide of nickel and yttrium in the weight percentage of 0.5 to 5 wt% based on the total weight of all the loaded materials of the coating layer and active material.

Although Examples B5, B5.1 to B5.9 cite the coating layers formed on the active material loaded into the sintered nickel substrate and based on the complex hydroxide of nickel and yttrium, substantially the same results may be attained by the coating layer of complex hydroxide of nickel and an element selected from the group consisting of cobalt, calcium, strontium, scandium, lanthanide, bismuth, magnesium and barium.

(Examples B5.11 to B5.19)

In Examples B5.11 to B5.19, the nickel hydroxide-based active material was loaded into the sintered nickel substrate and similarly to Example B5, nickel (Ni) nitrate and yttrium (Y) nitrate were used for forming respective coating layers on the active material.

In these examples, there were prepared respective aqueous nitrate solutions containing nickel nitrate and yttrium nitrate in weight ratios listed in Table 10 as below and in the total weight percentage of 5 wt%. Using such aqueous nitrate solutions, the respective coating layers of the complex hydroxide of nickel and yttrium were formed on the active material. Table 10 lists the weight percentages of yttrium hydroxide in the resultant coating

layers based on the total weight of all the loaded materials of the coating layer and active material.

Alkaline secondary batteries of Examples B5.11 to B5.19 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples B1 to B14 and Comparative Examples b1 to b16, the high temperature storability and the high-rate discharge capacity were determined for the respective alkaline secondary batteries of these examples. The results along with that of Example B5.7 are listed in Table 10 as below.

Table 10

	Ni nitrate: Y nitrate (weight percentage)	content of Y nitrate (wt%)	high- temperature storability (%)	high-rate discharge capacity (mAh)
example B5.11	9.77:0.23	0.1	61	1030
example B5.12	9.55:0.45	0.2	65	1030
example B5.13	9.38:0.62	0.3	69	1040
example B5.14	7.8:2.2	1.0	70	1040
example B5.15	6.1:3.9	1.8	71	1040
example B5.7	1:1	2.3	71	1040
example B5.16	4.3:5.7	2.7	71	1040
example B5.17	3.7:6.3	3.0	72	1040
example B5.18	3.3:6.7	3.2	72	1010
example B5.19	2.9:7.1	3.4	72	980

As apparent from this table, the high temperature storability and the high-rate discharge capacity are improved with the coating layer which is formed from the complex hydroxide of nickel and yttrium on the active material loaded into the sintered nickel substrate, and which contains yttrium hydroxide in the weight percentage of 0.3 to 3 wt% based on the total weight of all the loaded materials of the coating layer and active material.

Although Examples B5.7, B5.11 to B5.19 cite the coating

layers formed on the active material loaded into the sintered nickel substrate and based on the complex hydroxide of nickel and yttrium, substantially the same results may be attained by the coating layer of complex hydroxide of nickel and an element selected from the group consisting of cobalt, calcium, strontium, scandium, lanthanide, bismuth, magnesium and barium.

(Examples C1 to C14)

Examples C1 to C14 employed the sintered nickel substrate prepared the same way as in Examples A1 to A15.

As shown in Fig.3, formed on the sintered nickel substrate 1 is an intermediate layer 4 based on a complex hydroxide of nickel and an element selected from the group consisting of cobalt, calcium, strontium, scandium, yttrium, lanthanide, bismuth, magnesium and barium. Then, the nickel hydroxide-based active material 3 was loaded into the sintered nickel substrate 1 formed with the intermediate layer 4. Although the figure illustrates the intermediate layer 4 and the active material layer 2 uniformly formed on the sintered nickel substrate 1, it is to be noted that the intermediate layer 4 and the active material layer 2 each may be partially broken or may not be observed as a totally independent layer.

The intermediate layer of the above complex hydroxide was formed on the sintered nickel substrate using

a solution mixture containing nickel (Ni) nitrate and the nitrate of the above element. Specifically, there were used cobalt (Co) nitrate in Example C1; calcium (Ca) nitrate in Example C2; strontium (Sr) nitrate in Example C3; scandium (Sc) nitrate in Example C4; yttrium (Y) nitrate in Example C5; lanthanum (La) nitrate in Example C6; cerium (Ce) nitrate in Example C7; praseodymium (Pr) nitrate in Example C8; neodymium (Nd) nitrate in Example C9; europium (Eu) nitrate in Example C10; ytterbium (Yb) nitrate in Example C11; bismuth (Bi) nitrate in Example C12; magnesium (Mg) nitrate in Example C13; and barium (Ba) nitrate in Example C14.

There was prepared a 10 wt% nitrate aqueous solution containing nickel nitrate and the nitrate of each of the above elements in the weight ratio of 1:1. The sintered nickel substrate was dipped into each of the aqueous solutions and then dipped into the 25% NaOH aqueous solution at 80°C, thereby to form, on the sintered nickel substrate, each intermediate layer of the complex hydroxide of two elements as listed in Table 10. The presence of the respective intermediate layers was confirmed by X-ray diffraction analysis. The resultant intermediate layers of the complex hydroxides on the sintered nickel substrate substantially had a constant weight per unit area of 8 to 10 mg/cm².

Subsequently, the nickel hydroxide-based active material was loaded into the respective sintered nickel substrates formed with the intermediate layers using 6 impregnation cycles, where each impregnation cycle comprised the steps of dipping the sintered nickel substrate into an aqueous solution mixture of nickel nitrate and cobalt nitrate (specific gravity:1.75, atomic ratio between nickel and cobalt:10:1) for impregnation of the sintered nickel substrate with the solution mixture; and dipping the substrate into the 25% NaOH aqueous solution thereby allowing these hydroxides to deposit onto the sintered nickel substrate formed with the intermediate layer. Thus were fabricated respective nickel electrodes for alkaline secondary battery. Incidentally, each of the intermediate layers contained the complex hydroxide in concentrations of about 5 wt% based on the total weight of all the loaded materials of the active material and intermediate layer.

Alkaline secondary batteries of Examples C1 to C14 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example c1)

Comparative Example c1 employed the sintered nickel substrate prepared the same way as in Examples A1 to A15.

An intermediate layer was formed by the steps of dipping the sintered nickel substrate into an aqueous solution of 3 wt% cobalt nitrate; dipping the substrate into the NaOH aqueous solution thereby allowing cobalt hydroxide to deposit onto the sintered nickel substrate; and heating the substrate wetted with the NaOH aqueous solution at 80°C in the atmosphere or in the presence of oxygen, thereby oxidizing the above cobalt hydroxide. Subsequently, the same procedure as in Examples C1 to C14 was taken to load the nickel hydroxide-based active material into the sintered nickel substrate formed with the intermediate layer. Thus was fabricated a nickel electrode for alkaline secondary battery. The resultant nickel electrode is equivalent to the nickel electrode for alkaline secondary battery disclosed in Japanese Unexamined Patent Publication No.63-216268.

An alkaline secondary battery of Comparative Example c1 was fabricated using the resultant nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples B1 to B14 and Comparative Examples b1 to b16, the high temperature storability and the high-rate discharge capacity were determined for the respective alkaline secondary batteries of Examples C1 to

C14 and Comparative Example c1. The results are listed in Table 11.

Table 11

	element of complex hydroxide in intermediate layer	high- temperature storability (%)	high-rate discharge capacity (mAh)
example C1	Ni+Co	64	1020
example C2	Ni+Ca	64	1020
example C3	Ni+Sr	58	970
example C4	Ni+Sc	64	1030
example C5	Ni+Y	68	1030
example C6	Ni+La	60	970
example C7	Ni+Ce	61	970
example C8	Ni+Pr	58	970
example C9	Ni+Nd	58	970
example C10	Ni+Eu	60	970
example C11	Ni+Yb	64	990
example C12	Ni+Bi	63	1020
example C13	Ni+Mg	58	970
example C14	Ni+Ba	57	970
comparative example c1	Co (heat treatment)	51	940

As apparent from this table, the alkaline secondary batteries of Examples C1 to C14 employing the nickel electrodes, wherein the intermediate layer of the complex hydroxide of Ni and one element selected from the group of Co, Ca, Sr, Sc, Y, La, Ce, Pr, Nd, Eu, Yb, Bi, Mg and Ba is formed on the sintered nickel substrate and the nickel hydroxide-based active material is loaded into the sintered nickel substrate formed with the intermediate layer, accomplish notable improvement in the high temperature storability and greater high-rate discharge capacity, as compared with the battery of Comparative Example c1 employing the nickel electrode including the intermediate layer of the heat-treated cobalt hydroxide.

(Examples C5.1 to C5.9)

Examples C5.1 to C5.9 employed the porous sintered nickel substrate prepared the same way as in Examples A1 to A15. Similarly to Example C5, intermediate layers were formed on the sintered nickel substrate using the aqueous nitrate solution containing nickel (Ni) nitrate and yttrium (Y) nitrate in the weight ratio of 1:1.

In Examples C5.1 to C5.9, the intermediate layers of the complex hydroxide of Ni and Y were each formed on the sintered nickel substrate using the aqueous nitrate solutions varied in the combined weight percentage of nickel nitrate and yttrium nitrate within the range of 0.2

to 14 wt%. Subsequently, the same procedure as in Examples C1 to C14 was taken to load the nickel hydroxide-based active material into the resultant intermediate layer and to fabricate respective nickel electrodes for alkaline secondary battery.

The weight percentage of the complex hydroxide of nickel (Ni) and yttrium (Y) was determined for the respective intermediate layers based on the total weight of all the loaded materials of the intermediate layer and active material. The results are listed in Table 12 as below.

Alkaline secondary batteries of Examples C5.1 to C5.9 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples B1 to B14 and Comparative Examples b1 to b16, the high temperature storability and the high-rate discharge capacity were determined for the respective alkaline secondary batteries of these examples. The results along with that of Example C5 are listed in Table 12 as below.

Table 12

	complex hydroxide in intermediate layer		high- temperature storability (%)	high-rate discharge capacity (mAh)
	element	weight percentage (wt%)		
example C5.1	Ni+Y	0.1	56	1030
example C5.2	Ni+Y	0.3	60	1030
example C5.3	Ni+Y	0.5	64	1040
example C5.4	Ni+Y	1	65	1040
example C5.5	Ni+Y	2	66	1040
example C5.6	Ni+Y	3	66	1040
example C5.7	Ni+Y	4	67	1040
example C5	Ni+Y	5	68	1030
example C5.8	Ni+Y	6	68	1010
example C5.9	Ni+Y	7	68	980

As apparent from this table, the high temperature storability and the high-rate discharge capacity are improved with the intermediate layer which is formed between the sintered nickel substrate and the active material, and which contains the complex hydroxide of nickel and yttrium in the weight percentage of 0.5 to 5 wt% based on the total weight of all the loaded materials of

the intermediate layer and active material. Although Examples C5, C5.1 to C5.9 cite the intermediate layers formed between the sintered nickel substrate and the active material and based on the complex hydroxide of nickel and yttrium, substantially the same results may be attained by the intermediate layer based on the complex hydroxide of nickel and an element selected from the group consisting of cobalt, calcium, strontium, scandium, lanthanide, bismuth, magnesium and barium.

(Examples C5.11 to C5.19)

Examples C5.11 to C5.19 employed the porous sintered nickel substrate prepared the same way as in Examples A1 to A15. Similarly to Example C5, intermediate layers were formed on the sintered nickel substrate using nickel (Ni) nitrate and yttrium (Y) nitrate.

In Examples C5.11 to C5.19, the intermediate layers of the complex hydroxide of Ni and Y were each formed on the sintered nickel substrate using aqueous nitrate solutions varied in the weight ratio of nickel nitrate and yttrium nitrate as listed in Table 13 as below and containing these nitrates in 10 wt%. Subsequently, the same procedure as in Examples C1 to C14 was taken to load the nickel hydroxide-based active material into the sintered nickel substrate formed with the intermediate layer and to fabricate respective nickel electrodes for

alkaline battery. The weight percentage of yttrium hydroxide was determined for the respective intermediate layers based on the total weight of all the loaded materials of the resultant intermediate layer and active material. The results are listed in Table 13 as below.

Alkaline secondary batteries of Examples C5.11 to C5.19 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples B1 to B14 and Comparative Examples b1 to b16, the high temperature storability and the high-rate discharge capacity were determined for the respective alkaline secondary batteries of these examples. The results along with that of Example C5 are listed in Table 13 as below.

Table 13

	Ni nitrate: Y nitrate (weight percentage)	content of Y nitrate (wt%)	high- temperature storability (%)	high-rate discharge capacity (mAh)
example C5.11	9.77:0.23	0.1	57	1030
example C5.12	9.55:0.45	0.2	62	1030
example C5.13	9.38:0.62	0.3	66	1040
example C5.14	7.8:2.2	1.0	67	1040
example C5.15	6.1:3.9	1.8	68	1040
example C5	1:1	2.3	68	1030
example C5.16	4.3:5.7	2.7	68	1030
example C5.17	3.7:6.3	3.0	69	1030
example C5.18	3.3:6.7	3.2	69	1000
example C5.19	2.9:7.1	3.4	69	970

As apparent from the table, the high temperature storability and the high-rate discharge capacity are improved with the intermediate layer which is formed from the complex hydroxide of nickel and yttrium between the sintered nickel substrate and the active material and which contains yttrium hydroxide in the weight percentage of 0.3 to 3 wt% based on the total weight of all the loaded materials of the intermediate layer and active material. Although Examples C5, C5.11 to C5.19 cite the intermediate

layers formed between the sintered nickel substrate and the active material and based on the complex hydroxide of nickel and yttrium, substantially the same results may be attained by the intermediate layer based on the complex hydroxide of nickel and an element selected from the group consisting of cobalt, calcium, strontium, scandium, lanthanide, bismuth, magnesium and barium.

In the foregoing, Example B cites the coating layer which is formed on the surface portion of the active material on the porous sintered nickel substrate and which contains the complex hydroxide of nickel and cobalt or the like, whereas Example C cites the intermediate layer which is formed between the porous sintered nickel substrate and the active material and which contains the complex hydroxide of nickel and cobalt or the like. An alternative configuration may be made such that the intermediate layer based on the complex hydroxide of nickel and cobalt or the like is formed between the porous sintered nickel substrate and the active material, and the coating layer based on the complex hydroxide of nickel and cobalt or the like is formed on the surface portion of the active material on the sintered nickel substrate.

(Examples D1 to D13)

In Examples D1 to D13, the same procedure as in Examples A1 to A15 was taken to load the nickel hydroxide-

based active material into the porous sintered nickel substrate.

Then, as shown in Fig.1, the first coating layer 3a and the second coating layer 3b were sequentially laid on the active material 2 loaded into the sintered nickel substrate 1. Although the figure illustrates the active material layer 2, first coating layer 3a and second coating layer 3b uniformly overlaid on one another on the sintered nickel substrate 1, it is to be noted that the active material layer 2, first coating layer 3a and second coating layer 3b each may be partially broken or may not be observed as a totally independent layer.

In formation of first coating layers on the active material loaded into the sintered nickel substrate, aqueous solutions of 3 wt% nitrate were prepared. Specifically, there were used magnesium (Mg) nitrate in Example D1; calcium (Ca) nitrate in Example D2; barium (Ba) nitrate in Example D3; strontium (Sr) nitrate in Example D4; scandium (Sc) nitrate in Example D5; yttrium (Y) nitrate in Example D6; lanthanum (La) nitrate in Example D7; cerium (Ce) nitrate in Example D8; praseodymium (Pr) nitrate in Example D9; neodymium (Nd) nitrate in Example D10; europium (Eu) nitrate in Example D11; ytterbium (Yb) nitrate in Example D12; and bismuth (Bi) nitrate in Example D13.

Next, the sintered nickel substrate loaded with the active material was dipped into each of the above aqueous nitrate solutions, and then dipped into the 25% NaOH aqueous solution at 80°C. Thus, the first coating layer of the hydroxide of each element listed in Table 14 as below was formed on the active material loaded into the sintered nickel substrate.

The second coating layer of cobalt hydroxide was formed on the respective first coating layers by the steps of dipping the sintered nickel substrate formed with the first coating layer into an aqueous solution of 3 wt% cobalt nitrate, and dipping the substrate into the 25% NaOH aqueous solution at 80°C. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

Where the first coating layer based on the hydroxide of each of the above elements was formed on the active material in this manner, the respective first coating layers substantially had a constant weight per unit area of 5 to 6 mg/cm². Further, each first coating layer contained hydroxide of the above element in the weight percentage of 2.9 wt% based on the total weight of all the loaded materials of the first and second coating layers and active material, as shown in Table 14.

The second coating layers formed from cobalt hydroxide on the first coating layers substantially had a constant weight per unit area of 5 to 6 mg/cm². The second coating layers contained cobalt hydroxide in the weight percentage of 3.0 wt% based on the total weight of all the loaded materials of the first and second coating layers and active material, as shown in Table 14.

Alkaline secondary batteries of Examples D1 to D13 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example d1)

Comparative example d1 employed a nickel electrode for alkaline secondary battery wherein only the nickel hydroxide-based active material was loaded into the porous sintered nickel substrate and the coating layer on the active material was dispensed with.

An alkaline secondary battery of Comparative Example d1 was fabricated using this nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example d2)

In Comparative Example d2, a nickel electrode with the first coating layer of cobalt hydroxide formed on the active material was fabricated using the same procedure as

in Examples D1 to D13, the procedure comprising the steps of loading the nickel hydroxide-based active material into the sintered nickel substrate, dipping the substrate into the aqueous solution of 3 wt% cobalt nitrate, dipping the substrate into the NaOH aqueous solution thereby allowing cobalt hydroxide to deposit onto the active material loaded into the sintered nickel substrate, and allowing the substrate to dry. Incidentally, the first coating layer contained cobalt hydroxide in the weight percentage of about 3.1 wt% based on the total weight of all the loaded materials of the first coating layer and active material.

An alkaline secondary battery of Comparative Example d2 was fabricated using the resultant nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Examples d3 to d15)

In Comparative Examples d3 to d15, the nickel hydroxide-based active material was loaded into the sintered nickel substrate and then only the first coating layer based on the hydroxide of each element listed in Table 14 as below was formed on the active material.

The first coating layer of the hydroxide of each element listed in Table 14 was formed on the active material using the same procedure as in Examples D1 to D13, the procedure comprising the steps of preparing the aqueous

solution of 3 wt% nitrate of each of the elements, dipping the sintered nickel substrate loaded with the active material into each of the aqueous nitrate solutions, and dipping the substrate into the 25% NaOH aqueous solution at 80°C. Thus were fabricated nickel electrodes of these comparative examples. The first coating layers each contained the hydroxide of each element in the weight percentage of about 3.0 wt% based on the total weight of all the loaded materials of the first coating layer and active material.

Alkaline secondary batteries of Comparative Examples d3 to d15 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

The resultant alkaline secondary batteries of Examples D1 to D13 and Comparative Examples d1 to d15 were cycled at room temperatures through 10 cycles with 16 hr charge using a 100 mA current and discharge to a voltage of 1.0 V using a 200 mA current.

On the 10th cycle, the discharge capacity Q_{10} of each battery was determined. After the 11th charge cycle, the batteries were subject to storage at 50°C for two weeks. Subsequently, the batteries were placed under room temperatures again and discharged to 1.0 V so as to determine the discharge capacity Q_{11} at cycle 11. The high

temperature storability was determined based on the following equation:

$$\text{High-temperature storability(\%)} = (Q_{11}/Q_{10}) \times 100$$

The results are listed in Tables 14 and 15 as below.

Additionally, the alkaline secondary batteries were cycled through 10 charge/discharge cycles and then, charged at a high charge current of 1000 mA for 16 hours.

Subsequently, the alkaline secondary batteries were discharged to 1.0 V at a high discharge current of 1000 mA so as to determine the battery voltage, as the working voltage, at midpoint of the period during which the voltage fell to the above cutoff voltage. The results are listed in Tables 14 and 15 as below.

Table 14

	hydroxide in first coating layer		weight percentage of cobalt hydroxide in second coating layer (wt%)	high-temperature storability (%)	working voltage (V)
	element	weight percentage (wt%)			
example D1	Mg	2.9	3.0	62	1.210
example D2	Ca	2.9	3.0	71	1.212
example D3	Ba	2.9	3.0	64	1.214
example D4	Sr	2.9	3.0	64	1.211
example D5	Sc	2.9	3.0	69	1.214
example D6	Y	2.9	3.0	71	1.221
example D7	La	2.9	3.0	64	1.216
example D8	Ce	2.9	3.0	68	1.216
example D9	Pr	2.9	3.0	62	1.214
example D10	Nd	2.9	3.0	61	1.213
example D11	Eu	2.9	3.0	67	1.211
example D12	Yb	2.9	3.0	71	1.218
example D13	Bi	2.9	3.0	70	1.216
comparative example d1	-	-	-	49	1.200
comparative example d2	Co	3.1	-	52	1.204

Table 15

	hydroxide in first coating layer		weight percentage of cobalt hydroxide in second coating layer (wt%)	high-temperature storability (%)	working voltage (V)
	element	weight percentage (wt%)			
comparative example d3	Mg	3.0	-	57	1.205
Comparative example d4	Ca	3.0	-	64	1.205
Comparative example d5	Ba	3.0	-	57	1.206
Comparative example d6	Sr	3.0	-	58	1.205
Comparative example d7	Sc	3.0	-	64	1.206
Comparative example d8	Y	3.0	-	66	1.207
Comparative example d9	La	3.0	-	58	1.207
Comparative example d10	Ce	3.0	-	62	1.206
Comparative example d11	Pr	3.0	-	59	1.205
Comparative example d12	Nd	3.0	-	58	1.205
Comparative example d13	Eu	3.0	-	61	1.205
Comparative example d14	Yb	3.0	-	63	1.207
Comparative example d15	Bi	3.0	-	62	1.207

As apparent from Table 14, the alkaline secondary batteries of Examples D1 to D13 employing the nickel electrodes, wherein the first coating layer of the

hydroxide of an element selected from the group of Mg, Ca, Ba, Sr, Sc, Y, La, Ce, Pr, Nd, Eu, Yb and Bi is formed on the nickel hydroxide-based active material loaded into the sintered nickel substrate and the second coating layer of cobalt hydroxide is laid on the first coating layer, attain notable improvement in the high temperature storability and greater working voltages, as compared with that of Comparative Example d1 employing the nickel electrode without any layer on the active material, and that of Comparative Example d2 employing the nickel electrode including only the first coating layer of cobalt hydroxide on the active material.

As indicated by Tables 14 and 15, a significant difference of the high temperature storability is not found in the comparison between the batteries employing the nickel electrodes of Examples D1 to D13 and the batteries employing the nickel electrodes of Comparative Examples d3 to d15, wherein only the first coating layer of hydroxide of an element selected from the group of Mg, Ca, Ba, Sr, Sc, Y, La, Ce, Pr, Nd, Eu, Yb and Bi is formed on the nickel hydroxide-based active material loaded into the sintered nickel substrate. However, the batteries of Examples D1 to D13 present greater working voltages. (Examples D6.1 to D6.9)

In Examples D6.1 to D6.9, the nickel hydroxide-based active material was loaded into the sintered nickel substrate the same way as in Examples D1 to D13 and then, first coating layers were formed on the active material loaded into the sintered nickel substrate using similar aqueous solutions of yttrium (Y) nitrate to that used in Example D6.

In Examples D6.1 to D6.9, the aqueous solution of yttrium nitrate was varied in the concentration of yttrium nitrate within the range of 0.1 to 7.2 wt%. Using such aqueous solutions, the first coating layers varied in the concentration of yttrium hydroxide were formed on the active material. Subsequently, the same procedure as in Example D6 was taken to form the second coating layer of cobalt hydroxide on the respective first coating layers, thereby to fabricate nickel electrodes for alkaline secondary battery of these examples.

As to the resultant nickel electrodes for alkaline secondary battery, the weight percentages of yttrium hydroxide in the first coating layer and of cobalt hydroxide in the second coating layer were respectively determined based on the total weight of all the loaded materials of the first and second coating layers, and active material. The results are listed in Table 16 as below.

Alkaline secondary batteries of Examples D6.1 to D6.9 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples D1 to D13 and Comparative examples d1 to d15, the high temperature storability and the working voltage were determined for the respective alkaline secondary batteries of Examples D6.1 to D6.9. The results along with that of Example D6 are listed in Table 16 as below.

Table 16

	hydroxide in first coating layer		weight percentage of cobalt hydroxide in second coating layer (wt%)	high-temperature storability (%)	working voltage (V)
	element	weight percentage (wt%)			
example D6.1	Y	0.1	3.1	60	1.221
example D6.2	Y	0.3	3.1	64	1.221
example D6.2	Y	0.5	3.1	67	1.222
example D6.4	Y	1.0	3.1	68	1.222
example D6.5	Y	2.0	3.0	69	1.222
example D6	Y	2.9	3.0	71	1.221
example D6.6	Y	4.0	3.0	72	1.220
example D6.7	Y	5.0	2.9	72	1.219
example D6.8	Y	6.0	2.9	72	1.216
example D6.9	Y	7.0	2.9	72	1.212

As apparent from the table, the high temperature storability and the working voltage are improved with the combination of the first coating layer which is formed on the active material loaded into the sintered nickel substrate and contains yttrium hydroxide in the weight percentage of 0.5 to 5 wt% based on the total weight of all the loaded materials of the first and second coating layers

and active material, and the second coating layer of cobalt hydroxide laid on the first coating layer. Although Examples D6, D6.1 to D6.9 cite the first coating layers of yttrium hydroxide formed on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the first coating layer based on the hydroxide of an element selected from the group consisting of Mg, Ca, Ba, Sr, Sc, La, Ce, Pr, Nd, Eu, Yb and Bi.

(Examples D6.10 to D6.18)

In Examples D6.10 to D6.18, the nickel hydroxide-based active material was loaded into the sintered nickel substrate the same way as in Examples D1 to D13 and then, the first coating layer of yttrium hydroxide was formed on the active material loaded into the sintered nickel substrate the same way as in Example D6.

In Examples D6.10 to D6.18, the aqueous solution of cobalt nitrate was varied in the concentration of cobalt nitrate within the range of 0.1 to 7 wt%. Using such aqueous solutions, second coating layers varied in the concentration of cobalt hydroxide were each formed on the first coating layer. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

As to the resultant nickel electrodes for alkaline secondary battery, the weight percentages of yttrium hydroxide in the first coating layer and of cobalt hydroxide in the second coating layer were respectively determined based on the total weight of all the loaded materials of the first and second coating layers, and active material. The results are listed in Table 17 as below.

Alkaline secondary batteries of Examples D6.10 to D6.18 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples D1 to D13 and Comparative examples d1 to d15, the high temperature storability and the working voltage were determined for the respective alkaline secondary batteries of Examples D6.10 to D6.18. The results along with that of Example D6 are listed in Table 17 as below.

Table 17

	hydroxide in first coating layer		weight percentage of cobalt hydroxide in second coating layer (wt%)	high-temperature storability (%)	working voltage (V)
	element	weight percentage (wt%)			
example D6.10	Y	3.0	0.1	72	1.209
example D6.11	Y	3.0	0.3	72	1.214
example D6.12	Y	3.0	0.5	72	1.218
example D6.13	Y	3.0	1.0	72	1.219
example D6.14	Y	2.9	2.0	71	1.220
example D6	Y	2.9	3.0	71	1.221
example D6.15	Y	2.9	4.0	70	1.221
example D6.16	Y	2.8	5.0	69	1.222
example D6.17	Y	2.8	6.0	66	1.222
example D6.18	Y	2.8	7.0	62	1.222

As apparent from the table, the high temperature storability and the working voltage are improved with the combination of the first coating layer of yttrium hydroxide formed on the active material loaded into the sintered nickel substrate, and the second coating layer of cobalt hydroxide which is laid on the first coating layer and contains cobalt hydroxide in the weight percentage of 0.5

to 5 wt% based on the total weight of all the loaded materials of the first and second coating layers, and active material. Although Examples D6, D6.1 to D6.9 cite the first coating layer formed from yttrium hydroxide on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the first coating layer based on the hydroxide of an element selected from the group consisting of Mg, Ca, Ba, Sr, Sc, La, Ce, Pr, Nd, Eu, Yb and Bi.

(Examples E1 to E13)

In Examples E1 to E13, the same procedure as in Examples D1 to D13 was taken to load the nickel hydroxide-based active material into the sintered nickel substrate and then, to form, on the active material, first coating layers which are each based on a complex hydroxide of cobalt (Co) and an element selected from the group consisting of Mg, Ca, Ba, Sr, Sc, Y, La, Ce, Pr, Nd, Eu, Yb and Bi.

In formation of the first coating layer of the above complex hydroxide on the active material loaded into the sintered nickel substrate, a solution mixture of nitrates of cobalt (Co) and each of the above elements was used. Specifically, there were used magnesium (Mg) nitrate in Example E1; calcium (Ca) nitrate in Example E2; barium (Ba) nitrate in Example E3; strontium (Sr) nitrate in Example

E4; scandium (Sc) nitrate in Example E5; yttrium (Y) nitrate in Example E6; lanthanum (La) nitrate in Example E7; cerium (Ce) nitrate in Example E8; praseodymium (Pr) nitrate in Example E9; neodymium (Nd) nitrate in Example E10; europium (Eu) nitrate in Example E11; ytterbium (Yb) nitrate in Example E12; and bismuth (Bi) nitrate in Example E13.

There were prepared 3 wt% nitrate aqueous solutions which each contained cobalt nitrate and the nitrate of the above element in the weight ratio of 1:1. The first coating layers each based on the complex hydroxide of two elements listed in Table 18 as below were formed on the active material by the steps of dipping the sintered nickel substrate into each of the above solutions, and dipping the substrate into the 25% NaOH aqueous solution at 80°C. Subsequently, the same procedure as in Examples D1 to D13 was taken to form the second coating layer of cobalt hydroxide on the respective first coating layers. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

The first coating layers contained the respective complex hydroxides in the weight percentage of 2.9 wt% based on the total weight of all the loaded materials of the first and second coating layers, and active material, as shown in Table 18. On the other hand, the second

coating layer contained cobalt hydroxide in the weight percentage of 3.0 wt% as shown in Table 18.

Alkaline secondary batteries of Examples E1 to E13 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples D1 to D13 and Comparative examples d1 to d15, the high temperature storability and the working voltage were determined for the respective alkaline secondary batteries of Examples E1 to E13. The results are listed in Table 18 as below.

Table 18

	hydroxide in first coating layer		weight percentage of cobalt hydroxide in second coating layer (wt%)	high-temperature storability (%)	working voltage (V)
	element	weight percentage (wt%)			
example E1	Co+Mg	2.9	3.0	64	1.220
example E2	Co+Ca	2.9	3.0	73	1.222
example E3	Co+Ba	2.9	3.0	65	1.224
example E4	Co+Sr	2.9	3.0	67	1.221
example E5	Co+Sc	2.9	3.0	70	1.224
example E6	Co+Y	2.9	3.0	73	1.230
example E7	Co+La	2.9	3.0	66	1.225
example E8	Co+Ce	2.9	3.0	69	1.226
example E9	Co+Pr	2.9	3.0	66	1.224
example E10	Co+Nd	2.9	3.0	65	1.223
example E11	Co+Eu	2.9	3.0	67	1.221
example E12	Co+Yb	2.9	3.0	73	1.227
example E13	Co+Bi	2.9	3.0	72	1.226

As apparent from this table, the alkaline secondary batteries of Examples E1 to E13 employing the nickel electrodes, wherein the first coating layer of complex hydroxide of Co and an element selected from the group of

Mg, Ca, Ba, Sr, Sc, Y, La, Ce, Pr, Nd, Eu, Yb and Bi is formed on the nickel hydroxide-based active material loaded into the sintered nickel substrate and the second coating layer of cobalt hydroxide is laid on the first coating layer, attain even greater improvement in the high temperature storability and greater working voltages as compared with those of Examples D1 to D13 including the first coating layer of hydroxide of an element selected from the group of Mg, Ca, Ba, Sr, Sc, Y, La, Ce, Pr, Nd, Eu, Yb and Bi and the second coating layer of cobalt hydroxide.

(Examples E6.1 to E6.9)

Similarly to Example E6, Examples E6.1 to E6.9 used the aqueous nitrate solution containing cobalt (Co) nitrate and yttrium (Y) nitrate in the weight ratio of 1:1 for forming first coating layers on the nickel hydroxide-based active material loaded into the sintered nickel substrate.

In Examples E6.1 to E6.9, the aqueous nitrate solution was varied in the combined weight percentage of cobalt nitrate and yttrium nitrate within the range of 0.1 to 7.2 wt%, so as to form, on the active material, the first coating layers varied in the concentration of complex hydroxide of cobalt and yttrium. Subsequently, the same procedure as in Example E6 was taken to form the second coating layer of cobalt hydroxide over the above first

coating layer. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

The weight percentages of the complex hydroxide of cobalt (Co) and yttrium (Y) in the first coating layer and of cobalt hydroxide in the second coating layer were respectively determined based on the total weight of all the loaded materials of the first and second coating layers and active material. The results are listed in Table 19 as below.

Alkaline secondary batteries of Examples E6.1 to E6.9 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples D1 to D13 and Comparative examples d1 to d15, the high temperature storability and the working voltage were determined for the respective alkaline secondary batteries of Examples E6.1 to E6.9. The results along with that of Example E6 are listed in Table 19 as below.

Table 19

	hydroxide in first coating layer		weight percentage of cobalt hydroxide in second coating layer (wt%)	high-temperature storability (%)	working voltage (V)
	element	weight percentage (wt%)			
example E6.1	Co+Y	0.1	3.1	61	1.230
example E6.2	Co+Y	0.3	3.1	66	1.230
example E6.3	Co+Y	0.5	3.1	70	1.231
example E6.4	Co+Y	1.0	3.1	71	1.231
example E6.5	Co+Y	2.0	3.0	72	1.231
example E6	Co+Y	2.9	3.0	73	1.230
example E6.6	Co+Y	4.0	3.0	74	1.229
example E6.7	Co+Y	5.0	2.9	74	1.228
example E6.8	Co+Y	6.0	2.9	74	1.224
example E6.9	Co+Y	7.0	2.9	74	1.219

As apparent from this table, the improvement in the high temperature storability and the great working voltage are attained with the combination of the first coating layer which is formed on the active material loaded into the sintered nickel substrate and contains the complex hydroxide of cobalt and yttrium in the weight percentage of 0.5 to 5 wt% based on the total weight of all the loaded

materials loaded into the sintered nickel substrate and the second coating layer cobalt hydroxide on the first coating layer. Although Examples E6, E6.1 to E6.9 cite the first coating layers of complex hydroxide of cobalt and yttrium formed on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the first coating layer based on the complex hydroxide of cobalt (Co) and an element selected from the group consisting of Mg, Ca, Ba, Sr, Sc, La, Ce, Pr, Nd, Eu, Yb and Bi.

(Examples E6.10 to E6.18)

In Examples E6.10 to E6.18, the same procedure as in Example E6 was taken to load the nickel hydroxide-based active material into the sintered nickel substrate and then to form, on the active material, the first coating layer of complex hydroxide of cobalt and yttrium.

In Examples E6.10 to E6.18, the aqueous solution of cobalt nitrate was varied the concentration of cobalt nitrate within the range of 0.1 to 7 wt%, so as to form, over the first coating layer, second coating layers varied in the concentration of cobalt hydroxide. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

The weight percentages of the complex hydroxide of cobalt (Co) and yttrium (Y) in the first coating layer and

of cobalt hydroxide in the second coating layer were respectively determined based on the total weight of all the loaded materials of the first and second coating layers, and active material. The results are listed in Table 20 as below.

Alkaline secondary batteries of Examples E6.10 to E6.18 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples D1 to D13 and Comparative examples d1 to d15, the high temperature storability and the working voltage were determined for the respective alkaline secondary batteries of Examples E6.10 to E6.18. The results along with that of Example E6 are listed in Table 20 as below.

Table 20

	hydroxide in first coating layer		weight percentage of cobalt hydroxide in second coating layer (wt%)	high-temperature storability (%)	working voltage (V)
	element	weight percentage (wt%)			
example E6.10	Co+Y	3.0	0.1	74	1.212
example E6.11	Co+Y	3.0	0.3	74	1.214
example E6.12	Co+Y	3.0	0.5	74	1.219
example E6.13	Co+Y	3.0	1.0	73	1.221
example E6.14	Co+Y	2.9	2.0	73	1.229
example E6	Co+Y	2.9	3.0	73	1.230
example E6.15	Co+Y	2.9	4.0	72	1.230
example E6.16	Co+Y	2.8	5.0	71	1.231
example E6.17	Co+Y	2.8	6.0	67	1.231
example E6.18	Co+Y	2.8	7.0	62	1.231

As apparent from this table, the improvement in the high temperature storability and the great working voltage are attained with the combination of the first coating layer of complex hydroxide of cobalt and yttrium laid on the active material loaded into the sintered nickel substrate, and the second coating layer which is formed over the first coating layer and contains cobalt hydroxide

in the weight percentage of 0.5 to 5 wt% based on the total weight of all the loaded materials loaded into the sintered nickel substrate. Although Examples E6, E6.10 to E6.18 cite the first coating layers of complex hydroxide of cobalt and yttrium laid on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the first coating layer based on the complex hydroxide of cobalt (Co) and an element selected from the group consisting of Mg, Ca, Ba, Sr, Sc, La, Ce, Pr, Nd, Eu, Yb and Bi.
(Examples F1 to F10)

In Examples F1 to F10, the same procedure as in Examples A1 to A15 was taken to load the nickel hydroxide-based active material into the sintered nickel substrate.

As shown in Fig.2, the coating layer 3 based on the complex hydroxide of an element selected from the group of cobalt and nickel and an element selected from the group of manganese, aluminum, iron, copper and silver was formed on the nickel hydroxide-based active material 2 loaded into the sintered nickel substrate 1.

Preparatory to the formation of the coating layers of the above complex hydroxides on the active material loaded into the sintered nickel substrate, aqueous nitrate solutions were prepared which each contained nitrates of two of the above elements in the weight ratio of 1:1 and in

the combined weight percentage of 3 wt%. Specifically, nitrates of cobalt and manganese were used in Example F1; nitrates of cobalt and aluminum in Example F2; nitrates of cobalt and iron in Example F3; nitrates of cobalt and copper in Example F4; nitrates of cobalt and silver in Example F5; nitrates of nickel and manganese in Example F6; nitrates of nickel and aluminum in Example F7; nitrates of nickel and iron in Example F8; nitrates of nickel and copper in Example F9; and nitrates of nickel and silver in Example F10.

The coating layer based on the complex hydroxide of two elements listed in Table 21 as below was formed by the steps of dipping the sintered nickel substrate with the nickel hydroxide-based active material into each of the above aqueous nitrate solutions, and dipping the substrate into the 25% NaOH aqueous solution at 80°C. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples. The coating layers thus formed from the above complex hydroxides on the active material substantially had a constant weight per unit area of 5 to 6 mg/cm². The coating layers each contained the complex hydroxide in concentrations of about 3 wt% based on the total weight of all the loaded materials of the coating layer and active material.

Alkaline secondary batteries of Examples F1 to F10 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example f1)

Comparative example f1 employed the nickel electrode for alkaline secondary battery wherein only the nickel hydroxide-based active material was loaded into the porous sintered nickel substrate and the coating layer on the active material was dispensed with.

An alkaline secondary battery of Comparative Example f1 was fabricated using this nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example f2)

In Comparative Example f2, a coating layer of manganese hydroxide was formed on the active material by the steps of loading the nickel hydroxide-based active material into the sintered nickel substrate, dipping the nickel substrate into an aqueous solution of 3 wt% manganese nitrate, and dipping the substrate into the 25% NaOH aqueous solution at 80°C. Thus was fabricated a nickel electrode with the coating layer of manganese hydroxide. The resultant coating layer contained manganese hydroxide in the weight percentage of about 3 wt% based on

the total weight of all the loaded materials of the coating layer and active material. The nickel electrode thus fabricated is equivalent to the nickel electrode for alkaline secondary battery disclosed in Japanese Unexamined Patent Publication No.5(1993)-121073.

An alkaline secondary battery of Comparative Example f2 was fabricated using the resultant nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

The alkaline secondary batteries of Examples F1 to F10 and Comparative Examples f1 and f2 were cycled at room temperatures through 10 cycles with 16 hr charge using a 100 mA current and discharge to a voltage of 1.0 V using a 200 mA current.

Then, the alkaline secondary batteries cycled through 10 charge/discharge cycles at room temperatures were charged at the charge current of 100 mA for 16 hours. Subsequently, the batteries were discharged to 1.0 V at a high discharge current of 1000 mA so as to determine the battery voltage, as the working voltage, at midpoint of period during which the voltage fell to the above cutoff voltage. The results are listed in Table 21 as below.

The discharge capacity Q_{10} at cycle 10 was determined for the respective alkaline secondary batteries cycled through 10 charge/discharge cycles at room temperatures.

The same alkaline secondary batteries were subjected to the 16 hr charge on the 11th cycle using the 100 mA charge current and then, to storage at 50°C for two weeks. Subsequently, the batteries were placed under room temperatures again and discharged at 200 mA to 1.0 V so as to determine the respective discharge capacities Q_{11} at cycle 11. The high temperature storability was determined based on the following equation:

$$\text{High-temperature storability(\%)} = (Q_{11}/Q_{10}) \times 100$$

The results are listed in Table 21 as below.

The batteries cycled through 10 charge/discharge cycles at room temperatures were further cycled with 1.6 hr charge using the 1000 mA charge current and discharge to 1.0 V using the 1000 mA discharge current, so as to determine a number of cycles until the discharge capacity of each battery fell to 80 % of the discharge capacity Q_{10} at cycle 10. The number of cycles thus determined is listed in Table 21 as the cycle characteristics.

Table 21

	element of hydroxide in coating layer	working voltage (V)	high- temperature storability (%)	cycle characteristic (number of cycles)
example F1	Co+Mn	1.220	70	1000
example F2	Co+Al	1.218	68	900
example F3	Co+Fe	1.218	67	900
example F4	Co+Cu	1.217	68	950
example F5	Co+Ag	1.216	66	880
example F6	Ni+Mn	1.218	68	1050
example F7	Ni+Al	1.216	66	880
example F8	Ni+Fe	1.215	65	870
example F9	Ni+Cu	1.215	66	930
example F10	Ni+Ag	1.214	64	870
comparative example f1	-	1.200	49	500
comparative example f2	Mn	1.190	58	600

As apparent from this table, the alkaline secondary batteries of Examples F1 to F10 employing the nickel electrodes, wherein the coating layer of complex hydroxide of an element selected from the group of cobalt and nickel and an element selected from the group of manganese, aluminum, iron, copper and silver is laid on the surface

portion of the nickel hydroxide-based active material, attain such great working voltages as to permit high voltage discharge and the improvement in the high temperature storability and cycle characteristics, as compared with that of Comparative Example f1 employing the nickel electrode free from the coating layer on the active material and that of Comparative Example f2 employing the nickel electrode with the coating layer of manganese hydroxide on the active material.

(Examples F6.1 to F6.9)

In Examples F6.1 to F6.9, the nickel hydroxide-based active material was first loaded into the sintered nickel substrate. Then, similarly to Example F6, the coating layer based on the complex hydroxide of nickel and manganese was formed using the aqueous nitrate solution containing nickel nitrate and manganese nitrate in the weight ratio of 1:1.

In these examples, the aqueous nitrate solution was varied in the combined weight percentage (W1) of nitrates of nickel and manganese within the range of 0.1 to 7 wt% as listed in Table 22 as below. Using such aqueous nitrate solutions, the respective coating layers were formed which contained the complex hydroxide in weight percentages (W2) of 0.1 to 7 wt% based on the total weight of all the loaded materials of the coating layer and active material, as

listed in Table 22 as below. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

Alkaline secondary batteries of Examples F6.1 to F6.9 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples F1 to F10 and Comparative examples f1 and f2, the working voltage, the high temperature storability and the cycle characteristics were determined for the respective alkaline secondary batteries of Examples F6.1 to F6.9. The results along with that of Example F6 are listed in Table 22 as below.

Table 22

	W1 (wt%)	W2 (wt%)	working voltage (V)	high- temperature storability (%)	cycle characteristic (number of cycles)
example F6.1	0.1	0.1	1.217	61	800
example F6.2	0.3	0.3	1.217	64	900
example F6.3	0.5	0.5	1.218	67	950
example F6.4	1	1	1.218	67	1000
example F6.5	2	2	1.218	67	1050
example F6	3	3	1.218	68	1050
example F6.6	4	4	1.218	68	1050
example F6.7	5	5	1.217	68	1050
example F6.8	6	6	1.214	68	1000
example F6.9	7	7	1.210	68	1000

According to comparison among the alkaline secondary batteries of Examples F6, F6.1 to F6.9 with reference to this table, the batteries of Examples F6, and F6.3 to F6.7, which include the coating layers containing the complex hydroxide of nickel and manganese in the weight percentages (W2) of 0.5 to 5 wt% based on the total weight of all the loaded materials of the coating layer and active material, attain greater working voltages permitting the high voltage

discharge than those of Examples F6.8 and F6.9 with the above weight percentages (W2) in excess of 5 wt%. In addition, the batteries of Examples F6 and F6.3 to F6.7 attain greater improvement in the high temperature storability and cycle characteristics than those of Examples F6.1 and F6.2 with the above weight percentages (W2) less than 0.5 wt%.

Although Examples F6.1 to F6.9 cite the coating layers of complex hydroxide of nickel and manganese formed on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the coating layer based on the complex hydroxide of nickel and at least one element selected from the group consisting of aluminum, iron, copper and silver or on the complex hydroxide of cobalt and at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver.

(Examples F6.7.1 to F6.7.9)

In Examples F6.7.1 to F6.7.9, the nickel hydroxide-based active material was first loaded into the sintered nickel substrate. Then, similarly to Example F6.7, coating layers based on the complex hydroxide of nickel and manganese were formed using the aqueous nitrate solution containing nickel nitrate and manganese nitrate in the combined weight percentage (W1) of 5 wt%.

In these examples, the above aqueous nitrate solution was varied in the weight ratio (Ni:Mn) between nickel nitrate and manganese nitrate within the range of 9.8-3.1:0.2-6.9 as listed in Table 23 as below, so as to form the respective coating layers containing manganese hydroxide in weight percentages (W3) of 0.1 to 3.4 wt% as listed in Table 23 as below. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

Alkaline secondary batteries of Examples F6.7.1 to F6.7.9 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples F1 to F10 and Comparative examples f1 and f2, the working voltage, the high temperature storability and the cycle characteristics were determined for the respective alkaline secondary batteries of Examples F6.7.1 to E6.7.9. The results along with that of Example F6.7 are listed in Table 23 as below.

Table 23

	Ni : Mn	W3 (wt%)	working voltage (V)	high- temperature storability (%)	cycle characteristic (number of cycles)
example F6.7.1	9.8:0.2	0.1	1.218	60	820
example F6.7.2	9.6:0.4	0.2	1.218	63	910
example F6.7.3	9.3:0.7	0.3	1.218	66	960
example F6.7.4	8:2	1.0	1.218	67	1010
example F6.7.5	7:3	1.5	1.217	67	1050
example F6.7.6	6:4	2.0	1.217	68	1050
example F6.7	1:1	2.5	1.217	68	1050
example F6.7.7	4:6	3.0	1.217	68	1050
example F6.7.8	3.5:6.5	3.2	1.214	68	1000
example F6.7.9	3.1:6.9	3.4	1.210	68	1000

According to comparison among the alkaline secondary batteries of Examples F6.7, F6.7.1 to F6.7.9 with reference to this table, the batteries of Examples F6.7, and F6.7.3 to F6.7.7, which include the coating layers containing manganese hydroxide in the weight percentages (W3) of 0.3 to 3 wt% based on the total weight of all the loaded materials of the coating layer and active material, attain greater working voltages permitting the high voltage

discharge than those of Examples F6.7.8 and F6.7.9 with the above weight percentages (W3) in excess of 3 wt%. In addition, the batteries of Examples F6.7, and F6.7.3 to F6.7.7 attain greater improvement in the high temperature storability and cycle characteristics than those of Examples F6.7.1 and F6.7.2 with the above weight percentages (W2) less than 0.3 wt%.

Although Examples F6.7.1 to F6.7.9 cite the coating layer of complex hydroxide of nickel and manganese formed on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the coating layer based on the complex hydroxide of nickel and at least one element selected from the group consisting of aluminum, iron, copper and silver or on the complex hydroxide of cobalt and at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver.

(Examples G1 to G10)

Examples G1 to G10 employed the porous sintered nickel substrate prepared the same way as in Examples A1 to A15.

In these examples, the intermediate layer 4 based on the complex hydroxide of two elements listed in Table 24 as below was formed on the sintered nickel substrate 1 and then, the nickel hydroxide-based active material 2 was

loaded into the sintered nickel substrate 1 with the intermediate layer 4, as shown in Fig.3.

Preparatory to the formation of intermediate layers of complex hydroxides of two elements listed in Table 24 on the sintered nickel substrate, aqueous nitrate solutions were prepared which each contained nitrates of two of the above elements in the weight ratio of 1:1 and in the combined weight percentage of 10 wt%. Specifically, nitrates of cobalt and manganese were used in Example G1; nitrates of cobalt and aluminum in Example G2; nitrates of cobalt and iron in Example G3; nitrates of cobalt and copper in Example G4; nitrates of cobalt and silver in Example G5; nitrates of nickel and manganese in Example G6; nitrates of nickel and aluminum in Example G7; nitrates of nickel and iron in Example G8; nitrates of nickel and copper in Example G9; and nitrates of nickel and silver in Example G10.

The intermediate layer of the complex hydroxide of two elements listed in Table 24 was formed on the sintered nickel substrate by the steps of dipping the sintered nickel substrate into each of the above aqueous nitrate solutions, and dipping the substrate into the 25% NaOH aqueous solution at 80°C.

The nickel hydroxide-based active material was loaded into the sintered nickel substrate formed with the

intermediate layer using multiple impregnation cycles where each cycle comprised the steps of dipping the above sintered nickel substrate into an aqueous solution mixture of nickel nitrate and cobalt nitrate for impregnating the aqueous solution mixture of nickel nitrate and manganese nitrate into the substrate with the intermediate layer; and dipping this substrate into the 25% NaOH aqueous solution thereby allowing hydroxides of these elements to deposit onto the sintered nickel substrate with the intermediate layer. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples. The resultant intermediate layers all contained the complex hydroxide in the weight percentage of about 5 wt% based on the total weight of all the loaded materials of the intermediate layer and active material.

Alkaline secondary batteries of Examples G1 to G10 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples F1 to F10 and Comparative examples f1 and f2, the working voltage, the high temperature storability and the cycle characteristics were determined for the respective alkaline secondary batteries of Examples G1 to G10. The results are listed in Table 24 as below.

Table 24

	element of hydroxide in intermediate layer	working voltage (V)	high- temperature storability (%)	cycle characteristic (number of cycles)
example G1	Co+Mn	1.218	68	950
example G2	Co+Al	1.215	66	850
example G3	Co+Fe	1.216	65	850
example G4	Co+Cu	1.215	66	900
example G5	Co+Ag	1.214	64	820
example G6	Ni+Mn	1.216	66	1000
example G7	Ni+Al	1.213	64	830
example G8	Ni+Fe	1.214	63	820
example G9	Ni+Cu	1.213	64	880
example G10	Ni+Ag	1.212	62	820

As apparent from this table, the alkaline secondary batteries of Examples G1 to G10 employing the nickel electrodes, which include the intermediate layer based on the complex hydroxide of nickel and an element selected from the group of manganese, aluminum, iron, copper and silver and formed between the sintered nickel substrate and the nickel hydroxide-based active material, attain greater working voltages permitting the high voltage discharge as

compared with that of Comparative Example f1. Besides, the batteries of these examples are also improved in the high temperature storability and cycle characteristics.

(Examples G6.1 to G6.9)

Similarly to Example G6, Examples G6.1 to G6.9 used the aqueous nitrate solution containing nickel nitrate and manganese nitrate in the weight ratio of 1:1 for forming intermediate layers on the porous sintered nickel substrate.

In these examples, the above aqueous nitrate solution was varied in the combined weight percentage (W4) of nitrates of nickel and manganese within the range of 0.2 to 14 wt% as listed in Table 25 as below, so as to form intermediate layers containing the complex hydroxide in weight percentages (W5) of 0.1 to 7 wt% based on the total weight of all the loaded materials of the intermediate layer and active material, as listed in the table. Subsequently, the nickel hydroxide-based active material was loaded into the sintered nickel electrodes with the intermediate layers the same way as in Examples G1 to G10, thereby fabricating nickel electrodes for alkaline secondary battery of these examples.

Alkaline secondary batteries of Examples G6.1 to G6.9 were fabricated using the respective nickel electrodes

as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples F1 to F10 and Comparative examples f1 and f2, the working voltage, the high temperature storability and the cycle characteristics were determined for the respective alkaline secondary batteries of Examples G6.1 to G6.9. The results along with that of Example G6 are listed in Table 25 as below.

Table 25

	W4 (wt%)	W5 (wt%)	working voltage (V)	high- temperature storability (%)	cycle characteristic (number of cycles)
example G6.1	0.2	0.1	1.216	59	750
example G6.2	0.6	0.3	1.216	62	850
example G6.3	1	0.5	1.217	65	900
example G6.4	2	1	1.217	65	950
example G6.5	4	2	1.217	65	1000
example G6.6	6	3	1.217	66	1000
example G6.7	8	4	1.217	66	1000
example G6	10	5	1.216	66	1000
example G6.8	12	6	1.213	66	950
example G6.9	14	7	1.209	66	950

According to comparison among the alkaline secondary batteries of Examples G6, G6.1 to G6.9 with reference to this table, the batteries of Examples G6, and G6.3 to G6.7, which include the intermediate layers containing the complex hydroxide of nickel and manganese in the weight percentages (W5) of 0.5 to 5 wt% based on the total weight of all the loaded materials of the intermediate layer and active material, attain greater working voltages permitting the high voltage discharge than those of Examples G6.8 and G6.9 with the above weight percentages (W5) in excess of 5 wt%. In addition, the batteries of Examples G6, and G6.3 to G6.7 attain greater improvement in the high temperature storability and cycle characteristics than those of Examples G6.1 and G6.2 with the above weight percentages (W5) less than 0.5 wt%.

Although Examples G6.1 to G6.9 cite the intermediate layers of complex hydroxide of nickel and manganese formed between the sintered nickel substrate and the active material, substantially similar results may be attained by the intermediate layer based on the complex hydroxide of nickel and at least one element selected from the group consisting of aluminum, iron, copper and silver or on the complex hydroxide of cobalt and at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver.

(Examples G6.10 to G6.18)

Similarly to Example G6.7, Examples G6.10 to G6.18 used the aqueous nitrate solution containing nickel nitrate and manganese nitrate in the combined weight percentage (W4) of 10 wt% for forming intermediate layers based on the complex hydroxide of nickel and manganese.

In these examples, this aqueous nitrate solution was varied in the weight ratio (Ni:Mn) between nickel nitrate and manganese nitrate within the range of 9.8-3.1:0.2-6.9 as listed in Table 26 as below, so as to form the intermediate layers containing manganese hydroxide in weight percentages (W6) of 0.1 to 3.4 wt% based on the total weight of all the loaded materials of the intermediate layer and active material. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

Alkaline secondary batteries of Examples G6.10 to G6.18 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples F1 to F10 and Comparative examples f1 and f2, the working voltage, the high temperature storability and the cycle characteristics were determined for the respective alkaline secondary batteries

of Examples G6.10 to G6.18. The results along with that of Example G6 are listed in Table 26 as below.

Table 26

	Ni : Mn	W6 (wt%)	working voltage (V)	high- temperature storability (%)	cycle characteristic (number of cycles)
example G6.10	9.8:0.2	0.1	1.216	59	770
example G6.11	9.6:0.4	0.2	1.216	62	860
example G6.12	9.3:0.7	0.3	1.217	65	910
example G6.13	8:2	1.0	1.217	65	960
example G6.14	7:3	1.5	1.216	65	1000
example G6.15	6:4	2.0	1.216	66	1000
example G6	1:1	2.5	1.216	66	1000
example G6.16	4:6	3.0	1.216	66	1000
example G6.17	3.5:6.5	3.2	1.213	66	950
example G6.18	3.1:6.9	3.4	1.208	66	950

According to comparison among the alkaline secondary batteries of Examples G6, G6.10 to G6.18 with reference to this table, the batteries of Examples G6, and G6.12 to G6.16, which include the intermediate layers containing the manganese hydroxide in the weight percentages (W6) of 0.3 to 3 wt% based on the total weight of all the loaded

materials of the intermediate layer and active material, attain greater working voltages permitting the high voltage discharge than those of Examples G6.17 and G6.18 with the above weight percentages (W5) in excess of 3 wt%. In addition, the batteries of Examples G6, and G6.12 to G6.16 attain greater improvement in the high temperature storability and cycle characteristics than those of Examples G6.10 and G6.11 with the above weight percentages (W5) less than 0.3 wt%.

Although Examples G6.10 to G6.18 cite the intermediate layers of complex hydroxide of nickel and manganese formed between the sintered nickel substrate and the active material, substantially the same results may be attained by the intermediate layer based on the complex hydroxide of nickel and at least one element selected from the group consisting of aluminum, iron, copper and silver or on the complex hydroxide of cobalt and at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver.

(Examples H1 to H10)

In Examples H1 to H10, the nickel hydroxide-based active material was loaded into the porous sintered nickel substrate the same way as in Examples A1 to A15.

Then, as shown in Fig.2, the coating layer 3 based on the complex hydroxide of two elements was formed on the

nickel hydroxide-based active material 2 loaded into the sintered nickel substrate 1.

Preparatory to the formation of coating layers of the complex hydroxide of two elements on the active material loaded into the sintered nickel substrate, there were prepared aqueous nitrate solutions which each contained nitrates of two elements in the weight ratio of 1:1 and in the combined weight percentage of 3 wt%. Specifically, there were used nitrates of yttrium and manganese in Example H1; nitrates of yttrium and aluminum in Example H2; nitrates of yttrium and iron in Example H3; nitrates of yttrium and copper in Example H4; nitrates of yttrium and silver in Example H5, nitrates of ytterbium and manganese in Example H6; nitrates of ytterbium and aluminum in Example H7; nitrates of ytterbium and iron in Example H8; nitrates of ytterbium and copper in Example H9; and nitrates of ytterbium and silver in Example H10.

The coating layer of complex hydroxide of two elements listed in Table 27 was formed on the active material loaded into the sintered nickel substrate by the steps of dipping the nickel substrate loaded with the active material into each of the above aqueous nitrate solutions, and dipping this substrate into the 25% NaOH aqueous solution at 80°C. Thus were fabricated nickel electrodes for alkaline secondary battery of these

examples. The resultant coating layers of the above complex hydroxides on the active material substantially had a constant weight per unit area of 5 to 6 mg/cm². The coating layers each contained the complex hydroxide in concentrations of about 3 wt% based on the total weight of all the loaded materials of the coating layer and active material.

Alkaline secondary batteries of Examples H1 to H10 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example h1)

Comparative example h1 employed the nickel electrode for alkaline secondary battery wherein only the nickel hydroxide-based active material was loaded into the porous sintered nickel substrate and the coating layer on the active material was dispensed with.

An alkaline secondary battery of Comparative Example h1 was fabricated using this nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

(Comparative Example h2)

In Comparative Example h2, the coating layer of manganese hydroxide was formed on the active material by the steps of loading the nickel hydroxide-based active

material into the sintered nickel substrate, dipping the nickel substrate into an aqueous solution of 3 wt% manganese nitrate, and dipping the substrate into the 25% NaOH aqueous solution at 80°C. Thus was fabricated a nickel electrode with the coating layer of manganese hydroxide. The resultant coating layer contained manganese hydroxide in concentrations of about 3 wt% based on the total weight of all the loaded materials of the coating layer and active material. The nickel electrode thus fabricated is equivalent to the nickel electrode for alkaline secondary battery disclosed in Japanese Unexamined Patent Publication No.5(1993)-121073.

An alkaline secondary battery of Comparative Example h2 was fabricated using the resultant nickel electrode as the positive electrode therefor and the same procedure as in Examples A1 to A15.

The alkaline secondary batteries of Examples H1 to H10 and Comparative Examples h1 and h2 were cycled at 25°C through 10 cycles with 16 hr charge using a 100 mA charge current and discharge to a voltage of 1.0 V using a 200 mA discharge current.

Then, the alkaline secondary batteries cycled through 10 charge/discharge cycles at 25°C were charged at the charge current of 100 mA for 16 hours. Subsequently, the batteries were discharged to 1.0 V at the high

discharge current of 1000 mA so as to determine the battery voltage, as the working voltage, at midpoint of the period during which the voltage fell to the above cutoff voltage. The results are listed in Tables 27 as below.

The discharge capacity Q_{10} at cycle 10 was determined for the respective alkaline secondary batteries cycled through 10 charge/discharge cycles at 25°C. The same alkaline secondary batteries were subjected to the 16 hr charge on the 11th cycle using the 100 mA charge current and then, to storage at 55°C for two weeks. Subsequently, the batteries were placed under the temperature of 25°C again and discharged to 1.0 V at 200 mA so as to determine the respective discharge capacities Q_{11} at cycle 11. The high temperature storability was determined based on the following equation:

$$\text{High-temperature storability(\%)} = (Q_{11}/Q_{10}) \times 100$$

The results are listed in Table 27 as below.

The batteries cycled through 10 charge/discharge cycles at 25°C were further cycled with 0.8 hr charge using a 2000 mA charge current and discharge to 1.0 V using the 1000 mA discharge current, so as to determine a number of cycles until the discharge capacity of each battery fell to 80 % of the discharge capacity Q_{10} at cycle 10. The number of cycles thus determined is listed in Table 27 as the cycle characteristics.

The alkaline secondary batteries cycled through 10 charge/discharge cycles at 25°C were charged at 100 mA for 16 hours under the temperature of 60°C. Subsequently, the batteries were placed under the temperature of 25°C again and discharged to 1.0V using 200 mA discharge current, so as to determine the discharge capacity Q'_{11} at cycle 11. The high temperature chargeability was determined based on the following equation:

$$\text{High-temperature chargeability} = (Q'_{11}/Q_{10}) \times 100$$

The results are listed in Table 27 as below.

Table 27

	element of hydroxide in coating layer	working voltage (V)	high- temperature storability (%)	cycle characteristic (cycles)	high- temperature chargeability (%)
example H1	Y+Mn	1.218	75	900	90
example H2	Y+Al	1.216	73	800	88
example H3	Y+Fe	1.216	72	800	86
example H4	Y+Cu	1.215	73	850	85
example H5	Y+Ag	1.215	72	800	83
example H6	Yb+Mn	1.217	73	880	88
example H7	Yb+Al	1.215	71	780	86
example H8	Yb+Fe	1.213	70	770	84
example H9	Yb+Cu	1.213	71	840	83
example H10	Yb+Ag	1.212	69	760	81
comparative example h1	-	1.200	40	400	50
comparative example h2	Mn	1.190	52	500	55

As apparent from this table, the alkaline secondary batteries of Examples H1 to H10, which include the coating layer laid on the surface portion of the nickel hydroxide-based active material and based on the complex hydroxide of one element selected from the group of yttrium and ytterbium and one element selected from the group of

manganese, aluminum, iron, copper and silver, attain such great working voltages as to permit the high voltage discharge and notable improvement in the high temperature storability, cycle characteristics and high temperature chargeability as compared with that of Comparative Example h1 without the coating layer on the active material, and that of Comparative Example h2 with the coating layer of manganese hydroxide on the surface portion of the active material.

(Examples H1.1 to H1.9)

Similarly to Example H1, Examples H1.1 to H1.9 used the aqueous nitrate solution mixture containing yttrium nitrate and manganese nitrate in the weight ratio of 1:1 for forming coating layers of complex hydroxide of yttrium and manganese on the nickel hydroxide-based active material loaded into the sintered nickel substrate.

In these examples, the above aqueous nitrate solution was varied in the combined weight percentage (W7) of yttrium nitrate and manganese nitrate within the range of 0.1 to 7 wt% as listed in Table 28 as below, so as to form coating layers containing the complex hydroxide in weight percentages (W8) of 0.1 to 7 wt% based on the total weight of all the loaded materials of the coating layer and active material. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

Alkaline secondary batteries of Examples H1.1 to H1.9 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples H1 to H10 and Comparative examples h1 and h2, the working voltage, the high temperature storability, the cycle characteristics and the high temperature chargeability were determined for the respective alkaline secondary batteries of Examples H1.1 to H1.9. The results along with that of Example H1 are listed in Table 28 as below.

Table 28

	W7 (wt%)	W8 (wt%)	working voltage (V)	high- temperature storability (%)	cycle characteris- tic (cycles)	high- temperature chargeabili- ty (%)
example H1.1	0.1	0.1	1.217	67	700	72
example H1.2	0.3	0.3	1.217	70	800	80
example H1.3	0.5	0.5	1.218	74	850	87
example H1.4	1	1	1.218	74	900	88
example H1.5	2	2	1.218	74	900	89
example H1	3	3	1.218	75	900	90
example H1.6	4	4	1.217	75	900	91
example H1.7	5	5	1.216	75	900	92
example H1.8	6	6	1.213	75	850	92
example H1.9	7	7	1.208	75	850	92

According to comparison among the alkaline secondary batteries of Examples H1, H1.1 to H1.9 with reference to this table, the batteries of Examples H1, and H1.3 to H1.7, which include the coating layers containing the complex hydroxide of yttrium and manganese in the weight percentages (W8) of 0.5 to 5 wt% based on the total weight of all the loaded materials of the coating layer and active material, attain greater working voltages permitting the

high voltage discharge than those of Examples H1.8 and H1.9 with the above weight percentages (W8) in excess of 5 wt%. In addition, the batteries of Examples H1, and H1.3 to H1.7 attain greater improvement in the high temperature storability, cycle characteristics and high temperature chargeability than those of Examples H1.1 and H1.2 with the above weight percentages (W8) less than 0.5 wt%.

Although Examples H1.1 to H1.9 cite the coating layers of complex hydroxide of yttrium and manganese formed on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the coating layer based on the complex hydroxide of yttrium and at least one element selected from the group consisting of aluminum, iron, copper and silver or on the complex hydroxide of ytterbium and at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver.

(Examples H1.7.1 to H1.7.13)

Similarly to Example H1.7, Examples H1.7.1 to H1.7.13 used the aqueous nitrate solution mixture containing yttrium nitrate and manganese nitrate in the combined weight percentage (W7) of 5 wt% for forming coating layers of complex hydroxide of yttrium and manganese on the nickel hydroxide-based active material loaded into the sintered nickel substrate.

In these examples, the above aqueous nitrate solution was varied in the weight ratio (Y:Mn) between yttrium nitrate and manganese nitrate as shown in Table 29 as below, so as to form the coating layers on the active material. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples. The weight percentage (W9) of manganese hydroxide in the coating layer and the weight percentage (W10) of yttrium hydroxide therein were determined for the respective nickel electrodes thus formed with the coating layers. The results along with that of Example H1.7 are listed in Table 29 as below.

Table 29

	weight percentage in aqueous nitrate solution Y : Mn	W9 (wt%)	W10 (wt%)
example H1.7.1	9.8:0.2	0.1	4.9
example H1.7.2	9.6:0.4	0.2	4.8
example H1.7.3	9.4:0.6	0.3	4.7
example H1.7.4	8:2	1.0	4.0
example H1.7.5	7:3	1.5	3.5
example H1.7.6	6:4	2.0	3.0
example H1.7	1:1	2.5	2.5
example H1.7.7	4:6	3.0	2.0
example H1.7.8	3.6:6.4	3.2	1.8
example H1.7.9	3.2:6.8	3.4	1.6
example H1.7.10	2:8	4.0	1.0
example H1.7.11	0.6:9.4	4.7	0.3
example H1.7.12	0.4:9.6	4.8	0.2
example H1.7.13	0.2:9.8	4.9	0.1

Alkaline secondary batteries of Examples H1.7.1 to H7.1.13 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to a15.

Similarly to Examples H1 to H10 and Comparative examples h1 and h2, the working voltage, the high temperature storability, the cycle characteristics and the high temperature chargeability were determined for the respective alkaline secondary batteries of Examples H1.7.1 to H1.7.13. The results along with that of Example H1.7 are listed in Table 30 as below.

Table 30

	working voltage (V)	high- temperature storability (%)	cycle characteristic (cycles)	high- temperature chargeability (%)
example H1.7.1	1.218	65	730	92
example H1.7.2	1.218	67	780	92
example H1.7.3	1.218	69	820	92
example H1.7.4	1.218	71	850	92
example H1.7.5	1.217	73	880	92
example H1.7.6	1.217	74	900	92
example H1.7	1.216	75	900	92
example H1.7.7	1.215	76	900	91
example H1.7.8	1.210	76	900	90
example H1.7.9	1.209	76	900	88
example H1.7.10	1.207	76	900	87
example H1.7.11	1.206	76	900	85
example H1.7.12	1.205	76	900	80
example H1.7.13	1.204	76	900	74

According to comparison among the alkaline secondary batteries of Examples H1.7, H1.7.1 to H1.7.13 with reference to this table, the batteries of Examples H1.7, and H1.7.3 to H1.7.7, which include the coating layers

containing manganese hydroxide in the weight percentages (W9) of 0.3 to 3 wt% based on the total weight of all the loaded materials of the coating layer and active material, attain greater working voltages permitting the high voltage discharge and greater high temperature chargeability than those of Examples H1.7.8 to H1.7.13 with the above weight percentages (W9) in excess of 3 wt%. In addition, the batteries of Examples H1.7, and H1.7.3 to H1.7.7 attain greater improvement in the high temperature storability and cycle characteristics than those of Examples H1.7.1 and H1.7.2 with the above weight percentages (W9) less than 0.3 wt%.

The batteries of Examples H1.7, and H1.7.6 to H1.7.11, which include the coating layers containing yttrium hydroxide in the weight percentages (W10) of 0.3 to 3 wt% based on the total weight of all the loaded materials of the coating layer and active material, attain greater high temperature storability and cycle characteristics than those of Examples H1.7.1 to H1.7.5 with the above weight percentages (W10) in excess of 3 wt%. Further, the batteries of Examples H1.7, and H1.7.6 to H1.7.11 attain greater working voltages permitting the high voltage discharge and greater high temperature chargeability than those of Examples H1.7.12 and H1.7.13 with the above weight percentages (W10) less than 0.3 wt%.

Particularly favorable results with great working voltage as well as excellent high temperature storability, cycle characteristics and high temperature chargeability are achieved by the batteries of Examples H1.7, H1.7.6 and H1.7.7 which have the respective weight percentages of manganese hydroxide and yttrium hydroxide in the range of 2 to 3 wt% based on the total weight of all the loaded materials of the active material and coating layer.

Although Examples H1.7.1 to H1.7.13 cite the coating layers of complex hydroxide of yttrium and manganese formed on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the coating layer based on the complex hydroxide of yttrium and at least one element selected from the group consisting of aluminum, iron, copper and silver or on the complex hydroxide of ytterbium and at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver.

(Examples I1 to I20)

In Examples I1 to I20, the nickel hydroxide-based active material was loaded into the porous sintered nickel substrate the same way as in Examples A1 to A15.

Then, as shown in Fig.2, the coating layer 3 based on the complex hydroxide of three elements was formed on

the nickel hydroxide-based active material 2 loaded into the sintered nickel substrate 1.

Preparatory to the formation of the coating layer of the complex hydroxide of three elements on the active material loaded into the sintered nickel substrate, there were prepared aqueous nitrate solutions which each contained nitrates of three elements in the weight ratio of 1:1:1 and in the combined weight percentage of 3 wt%. Specifically, there were used nitrates of cobalt, yttrium and manganese in Example I1; nitrates of cobalt, yttrium and aluminum in Example I2; nitrates of cobalt, yttrium and iron in Example I3; nitrates of cobalt, yttrium and copper in Example I4; nitrates of cobalt, yttrium and silver in Example I5; nitrates of cobalt, ytterbium and manganese in Example I6; nitrates of cobalt, ytterbium and aluminum in Example I7; nitrates of cobalt, ytterbium and iron in Example I8; nitrates of cobalt, ytterbium and copper in Example I9; nitrates of cobalt, ytterbium and silver in Example I10; nitrates of nickel, yttrium and manganese in Example I11; nitrates of nickel, yttrium and aluminum in Example I12; nitrates of nickel, yttrium and iron in Example I13; nitrates of nickel, yttrium and copper in Example I14; nitrates of nickel, yttrium and silver in Example I15; nitrates of nickel, ytterbium and manganese in Example I16; nitrates of nickel, ytterbium and aluminum in

Example I17; nitrates of nickel, ytterbium and iron in Example I18; nitrates of nickel, ytterbium and copper in Example I19; and nitrates of nickel, ytterbium and silver in Example I20.

The coating layer of complex hydroxide of three elements listed in Table 31 was formed on the active material loaded into the sintered nickel substrate by the steps of dipping the nickel substrate loaded with the active material into each of the above aqueous nitrate solutions, and dipping this substrate into the 25% NaOH aqueous solution at 80°C. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples. The resultant coating layers of the above complex hydroxides on the active material substantially had a constant weight per unit area of 5 to 6 mg/cm². The coating layers each contained the complex hydroxide in concentrations of about 3 wt% based on the total weight of all the loaded materials of the coating layer and active material.

Alkaline secondary batteries of Examples I1 to I20 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples H1 to H10 and Comparative examples h1 and h2, the working voltage, the high

temperature storability, the cycle characteristics and the high temperature chargeability were determined for the respective alkaline secondary batteries of Examples I1 to I120. The results are listed in Table 31 as below.

Table 31

	element of hydroxide in coating layer	working voltage (V)	high- temperature storability (%)	cycle characteris- tic (cycles)	high- temperature chargeability (%)
example I1	Co+Y+Mn	1.219	72	940	87
example I2	Co+Y+Al	1.217	69	840	86
example I3	Co+Y+Fe	1.217	69	840	83
example I4	Co+Y+Cu	1.216	68	880	81
example I5	Co+Y+Ag	1.216	69	830	78
example I6	Co+Yb+Mn	1.218	70	920	85
example I7	Co+Yb+Al	1.215	68	820	83
example I8	Co+Yb+Fe	1.213	67	810	80
example I9	Co+Yb+Cu	1.214	68	870	78
example I10	Co+Yb+Ag	1.213	66	790	77
example I11	Ni+Y+Mn	1.220	73	950	88
example I12	Ni+Y+Al	1.218	71	850	86
example I13	Ni+Y+Fe	1.218	70	850	84
example I14	Ni+Y+Cu	1.217	70	850	83
example I15	Ni+Y+Ag	1.217	70	900	80
example I16	Ni+Yb+Mn	1.219	71	850	86
example I17	Ni+Yb+Al	1.217	69	930	84
example I18	Ni+Yb+Fe	1.215	68	830	82
example I19	Ni+Yb+Cu	1.215	69	890	80
example I20	Ni+Yb+Ag	1.214	67	810	79

As apparent from this table, the alkaline secondary batteries of Examples I1 to I20, wherein the coating layer of complex hydroxide of one element selected from the group of cobalt and nickel, one element selected from the group of yttrium and ytterbium, and one element selected from the group of manganese, aluminum, iron, copper and silver, is formed on the active material loaded into the sintered nickel substrate, attain greater working voltages permitting the high voltage discharge and much greater improvement in the high temperature storability, cycle characteristics and high temperature chargeability than those of Comparative Examples h1 and h2.

(Examples I11.1 to I11.9)

Similarly to Example I11, Examples I11.1 to I11.9 used the aqueous nitrate solution mixture containing nickel nitrate, yttrium nitrate and manganese nitrate in the weight ratio of 1:1:1 for forming coating layers of complex hydroxide of nickel, yttrium and manganese on the nickel hydroxide-based active material loaded into the sintered nickel substrate.

In these examples, the above aqueous nitrate solution was varied in the combined weight percentage (W11) of nitrates of nickel, yttrium and manganese within the range of 0.1 to 7 wt% as listed in Table 32 as below, so as to form the coating layers containing the complex hydroxide

in weight percentages (W12) of 0.1 to 7 wt% based on the total weight of all the loaded materials of the coating layer and active material, as listed in the table. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples.

Alkaline secondary batteries of Examples I11.1 to I11.9 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples H1 to H10 and Comparative examples h1 and h2, the working voltage, the high temperature storability, the cycle characteristics and the high temperature chargeability were determined for the respective alkaline secondary batteries of Examples I11.1 to I11.9. The results along with that of Example I11 are listed in Table 32 as below.

Table 32

	W11 (wt%)	W12 (wt%)	working voltage (V)	high- temperature storability (%)	cycle characteris- tic (cycles)	high- temperature chargeabili- ty (%)
example I11.1	0.1	0.1	1.219	65	750	69
example I11.2	0.3	0.3	1.219	68	850	78
example I11.3	0.5	0.5	1.220	72	900	85
example I11.4	1	1	1.220	72	950	86
example I11.5	2	2	1.220	72	950	87
example I11	3	3	1.220	73	950	88
example I11.6	4	4	1.219	73	950	89
example I11.7	5	5	1.218	73	950	90
example I11.8	6	6	1.215	73	900	90
example I11.9	7	7	1.210	73	900	90

According to comparison among the alkaline secondary batteries of Examples I11, I11.1 to I11.9 with reference to this table, the batteries of Examples I11, and I11.3 to I11.7, which include the coating layers containing the complex hydroxide of nickel, yttrium and manganese in the weight percentages (W12) of 0.5 to 5 wt% based on the total weight of all the loaded materials of the coating layer and active material, attain greater working voltages permitting

the high voltage discharge than those of Examples I11.8 and I11.9 with the above weight percentages (W12) in excess of 5 wt%. In addition, the batteries of Examples I11, and I11.3 to I11.7 attain greater improvement in the high temperature storability, cycle characteristics and high temperature chargeability than those of Examples I11.1 and I11.2 with the above weight percentages (W12) less than 0.5 wt%.

Although Examples I11.1 to I11.9 cite the coating layers of complex hydroxide of nickel, yttrium and manganese formed on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the coating layer based on the complex hydroxide of yttrium, cobalt and at least one element selected from the group consisting of aluminum, iron, copper and silver or on the complex hydroxide of ytterbium, at least one element selected from the group of cobalt and nickel, and at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver. (Examples I11.7.1. to I11.7.13)

Similarly to Example I11.7, Examples I11.7.1 to I11.7.13 used the aqueous nitrate solution mixture containing nickel nitrate, yttrium nitrate and manganese nitrate in the combined weight percentage (W11) of 5 wt% for forming coating layers of complex hydroxide of nickel,

yttrium and manganese on the nickel hydroxide-based active material loaded into the sintered nickel substrate.

In these examples, the above aqueous nitrate solution was varied in the weight ratio (Ni:Y:Mn) among nickel nitrate, yttrium nitrate and manganese nitrate as listed in Table 33 as below, so as to form the coating layers. Thus were fabricated nickel electrodes for alkaline secondary battery of these examples. The weight percentage (W13) of manganese hydroxide in the coating layer and the weight percentage (W14) of yttrium hydroxide therein were determined for the respective nickel electrodes thus formed with the coating layers. The results are also listed in Table 33 as below.

Table 33

	weight percentage in aqueous nitrate solution Ni : Y : Mn	W13 (wt%)	W14 (wt%)
example I11.7.1	2.0:7.8:0.2	0.1	3.9
example I11.7.2	2.0:7.6:0.4	0.2	3.8
example I11.7.3	2.0:7.4:0.6	0.3	3.7
example I11.7.4	2.0:6.0:2.0	1.0	3.0
example I11.7.5	2.0:5.0:3.0	1.5	2.5
example I11.7.6	2.0:4.0:4.0	2.0	2.0
example I11.7.7	2.0:3.0:5.0	2.5	1.5
example I11.7.8	2.0:2.0:6.0	3.0	1.0
example I11.7.9	2.0:1.6:6.4	3.2	0.8
example I11.7.10	2.0:1.2:6.8	3.4	0.6
example I11.7.11	2.0:0.6:7.4	3.7	0.3
example I11.7.12	2.0:0.4:7.6	3.8	0.2
example I11.7.13	2.0:0.2:7.8	3.9	0.1

Alkaline secondary batteries of Examples I11.7.1 to I11.7.13 were fabricated using the respective nickel electrodes as the positive electrode therefor and the same procedure as in Examples A1 to A15.

Similarly to Examples H1 to H10 and Comparative examples h1 and h2, the working voltage, the high temperature storability, the cycle characteristics and the high temperature chargeability were determined for the respective alkaline secondary batteries of Examples I11.7.1 to I11.7.13. The results are listed in Table 34 as below.

Table 34

	working voltage (V)	high- temperature storability (%)	cycle characteristic (cycles)	high- temperature chargeability (%)
example I11.7.1	1.220	68	770	86
example I11.7.2	1.220	71	840	86
example I11.7.3	1.220	73	900	86
example I11.7.4	1.219	74	940	86
example I11.7.5	1.219	74	950	86
example I11.7.6	1.218	75	950	86
example I11.7.7	1.217	76	950	85
example I11.7.8	1.215	76	950	84
example I11.7.9	1.210	76	950	83
example I11.7.10	1.208	76	950	82
example I11.7.11	1.206	76	950	81
example I11.7.12	1.205	76	950	75
example I11.7.13	1.204	76	950	68

According to comparison among the alkaline secondary batteries of Examples I11.7.1 to I11.7.13 with reference to this table, the batteries of Examples I11.7.3 to I11.7.8, which include the coating layers containing manganese hydroxide in the weight percentages (W13) of 0.3 to 3 wt% based on the total weight of all the loaded materials of the coating layer and active material, attain greater working voltages permitting the high voltage discharge and greater high temperature chargeability than those of Examples I11.7.9 to I11.7.13 with the above weight percentages (W13) in excess of 3 wt%. In addition, the batteries of Examples I11.7.3 to I11.7.8 attain greater improvement in the high temperature storability and cycle characteristics than those of Examples I11.7.1 and I11.7.2 with the above weight percentages (W13) less than 0.3 wt%.

The batteries of Examples I11.7.4 to I11.7.11 with the coating layers containing yttrium hydroxide in the weight percentages (W14) of 0.3 to 3 wt% based on the total weight of all the loaded materials of the coating layer and active material, attain greater improvement in the high temperature storability and cycle characteristics than those of Examples I11.7.1 to I11.7.3 with the above weight percentages (W14) in excess of 3 wt%. Further, the batteries of Examples I11.7.4 to I11.7.11 attain greater working voltages permitting the high voltage discharge and

greater high temperature chargeability than those of Examples I11.7.12 and I11.7.13 with the above weight percentages (W14) less than 0.3 wt%.

Although Examples I11.7.1 to I11.7.13 cite the coating layers of complex hydroxide of nickel, yttrium and manganese formed on the active material loaded into the sintered nickel substrate, substantially the same results may be attained by the coating layer based on the complex hydroxide of yttrium, cobalt and at least one element selected from the group consisting of aluminum, iron, copper and silver or on the complex hydroxide of ytterbium, at least one element selected from the group of cobalt and nickel, and at least one element selected from the group consisting of manganese, aluminum, iron, copper and silver.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A sintered nickel electrode, which employs a porous sintered nickel substrate obtained by sintering and is fabricated by chemically impregnating the porous sintered nickel substrate with an active material, for alkaline secondary battery, comprising:

a porous sintered nickel substrate;

a nickel hydroxide-based active material layer provided on the porous sintered nickel substrate; and

a coating layer which is provided on the active material layer and is based on a complex compound of nickel and cobalt, calcium, strontium, scandium, yttrium, lanthanide, bismuth, magnesium or barium.

2. A nickel electrode for alkaline secondary battery according to claim 1, wherein the lanthanide in said layer is comprised of lanthanum, cerium, praseodymium, neodymium, europium or ytterbium.

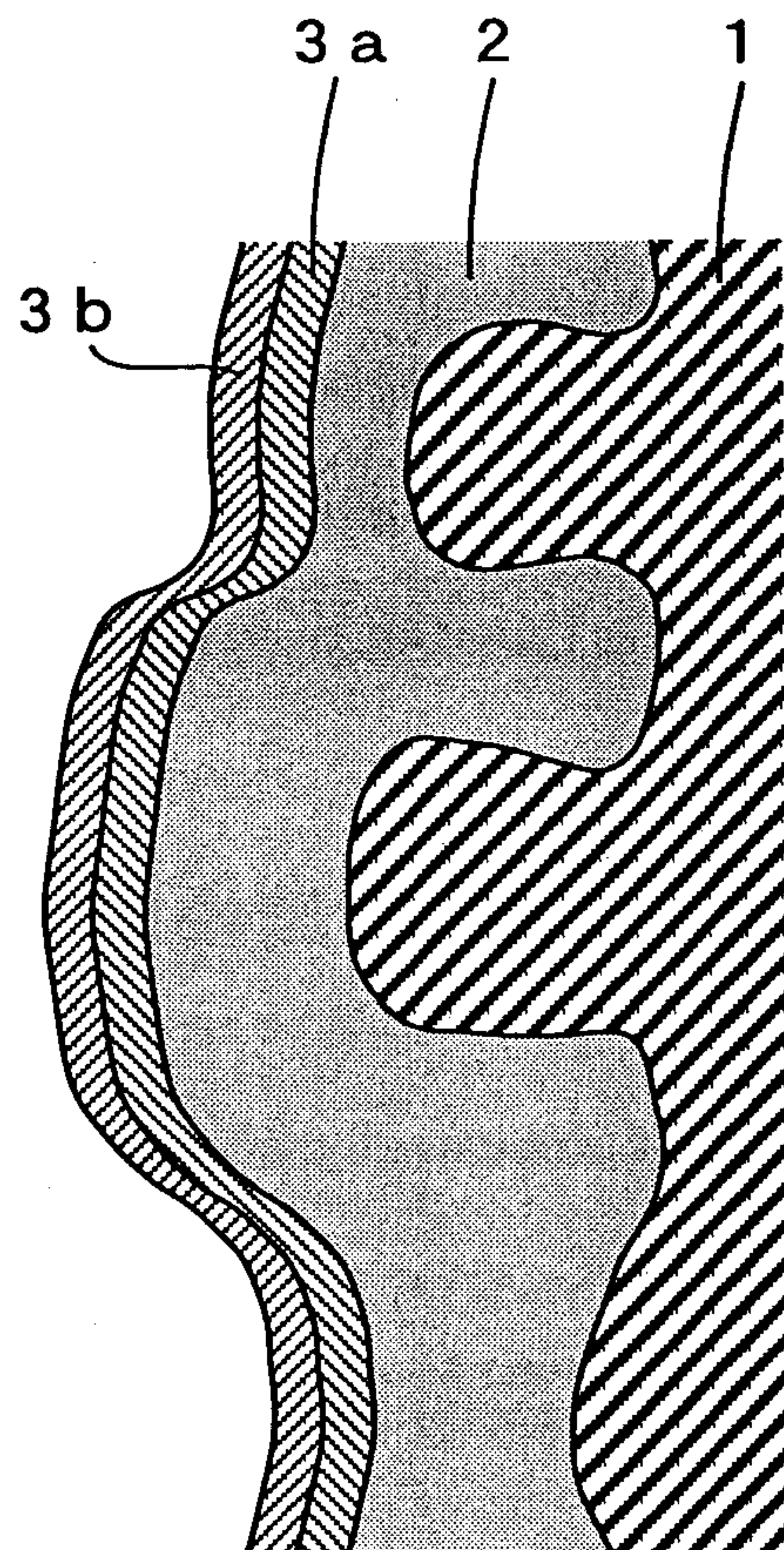
3. A nickel electrode for alkaline secondary battery according to claim 1 or 2, wherein the complex compound in said layer is comprised of a hydroxide, an oxide, or a mixture thereof.

4. A nickel electrode for alkaline secondary battery according to any one of claims 1, 2 or 3, wherein said coating layer contains the complex compound in weight percentage of 0.5 to 5 wt % based on the total weight of said active material layer and the coating layer.

5. A nickel electrode for alkaline secondary battery according to any one of claims 1 to 4, wherein said coating layer contains cobalt, calcium, strontium, scandium, yttrium, lanthanide, bismuth, magnesium or barium, in a total weight percentage of 0.3 to 3 wt % based on the total weight of said active material layer and said coating layer.

6. An alkaline secondary battery employing the nickel electrode for alkaline secondary battery as defined in any one of claims 1 to 5, as a positive electrode.

Fig 1



F i g 2

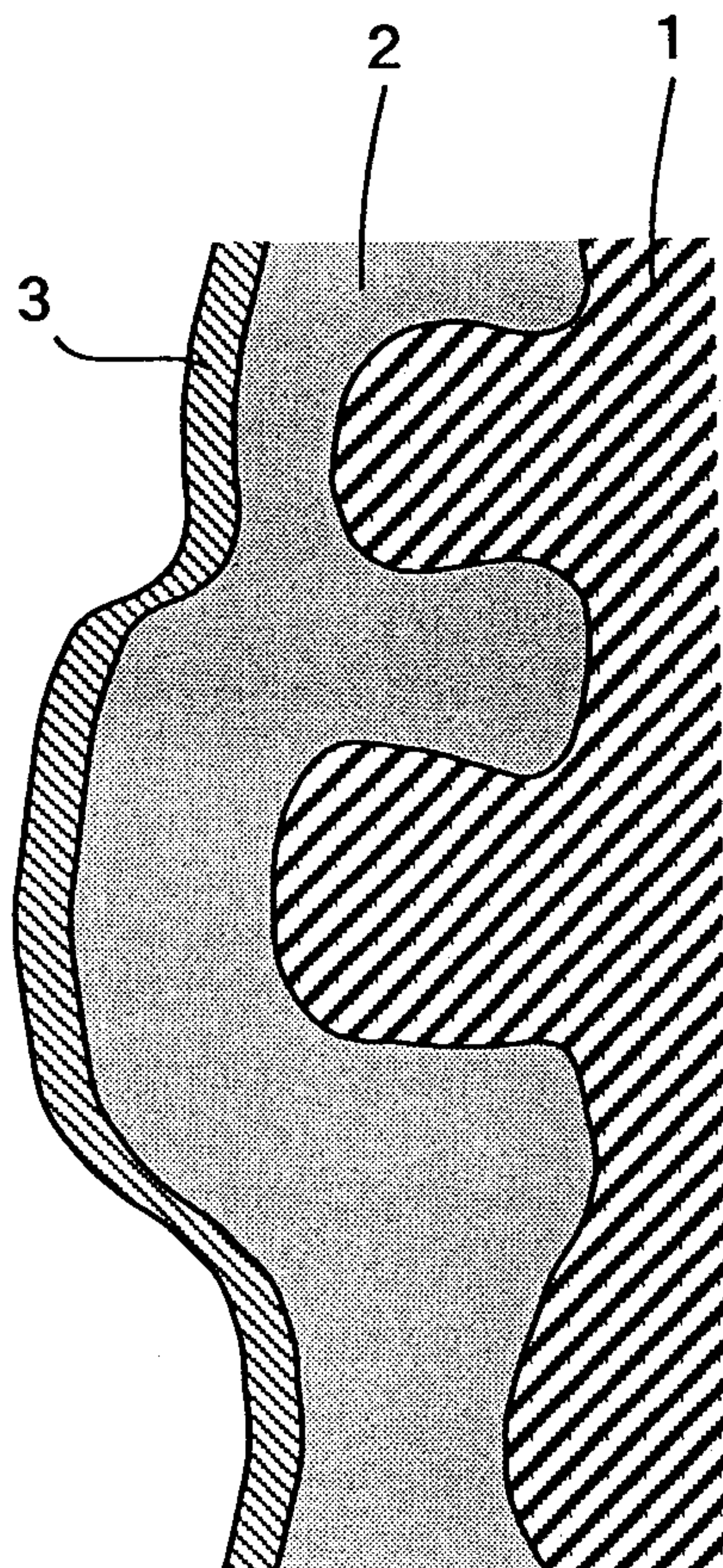


Fig 3

