

State-of-the-art of alkaline rechargeable batteries

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Abstract

Alkaline rechargeable batteries represented by Ni–Cd and Ni–MH batteries are expanding their market, continuously meeting an increasing demand. Approximately 30 years have elapsed since the first sealed Ni–Cd battery was commercialized for consumer use, and the production of these alkaline batteries is still expanding. The high power performance and good cost performance of these batteries are the outstanding features, which are leading to new battery applications. Continuous R&D of many researchers and engineers has improved these features. Since first coming to the market in 1990, Ni–MH batteries have been extending their application as power sources for portable advanced information and communication equipment. Improvements in electrode materials and other components have increased the energy density of current Ni–MH batteries to values of 91 Wh/kg and 340 Wh/l. Recently, novel metallic alloys for hydrogen storage have been proposed to increase their capacity further, and further improvement in the performance of these batteries is expected. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkaline storage battery; Ni–Cd battery; Ni–MH battery

1. Introduction

Recently, boosted by advances in electronic devices, significant technological progress has been occurring in the technical field of small rechargeable batteries for consumer use. Up to the 1980s, rechargeable batteries used for cordless electronic and electric equipments were exclusively Ni–Cd batteries. Currently, however, Ni–MH batteries (a new family of alkaline rechargeable battery) and Li-ion batteries are available and are widely used for information and communication equipment such as mobile phones and notebook computers. Among these, an increase in the energy density of Li-ion batteries has been outstanding. The performance, production quantities and application areas of Ni–Cd and Ni–MH batteries, especially in small size are also increasing. Alkaline rechargeable batteries will continue to play an important role in future society using mobile devices for advanced network and emission-free portable energy sources.

In this paper, we focus on the current technological achievements and projected future trends with Ni–Cd and Ni–MH batteries, which are currently boasting the largest production and outstanding marketability among small rechargeable batteries for consumer use.

2. Alkaline rechargeable batteries

The Ni–Cd battery is well-established in the market place. After the invention of sealing technology by Neumann et al. in the late 1940s, the manufacture of this battery began in the late 1950s in Europe and USA. In Japan, Sanyo started the production and marketing of the similar battery design based on an indigenous sealed construction using sintered electrodes in 1963. Until the Ni–MH battery was commercialized in 1991, Ni–Cd batteries were used as the power supply on virtually all portable electronic equipment. During the course of its development, the Ni–Cd battery has made a remarkable advance and much experience about the application of this technology has been accumulated. In short, the Ni–Cd battery has led and expanded the market for cordless electronic and electric equipment.

The Ni–MH battery is a unique rechargeable battery type employing a negative electrode consisting of a metal alloy that stores hydrogen at high density, and this battery was successfully commercialized by Sanyo and Matsushita in Japan in 1990. A Ni–H battery had already been developed before the Ni–MH battery, and was used in a limited quantity for special purposes. This type one does not fit with the requirement of commercial applications. A Phillips Laboratory discovery [1] of $\text{LaNi}_{2.5}\text{Co}_{2.5}$ in 1984 suggesting a new type of negative electrode material for rechargeable batteries triggered the development of nickel metal hydride batteries.

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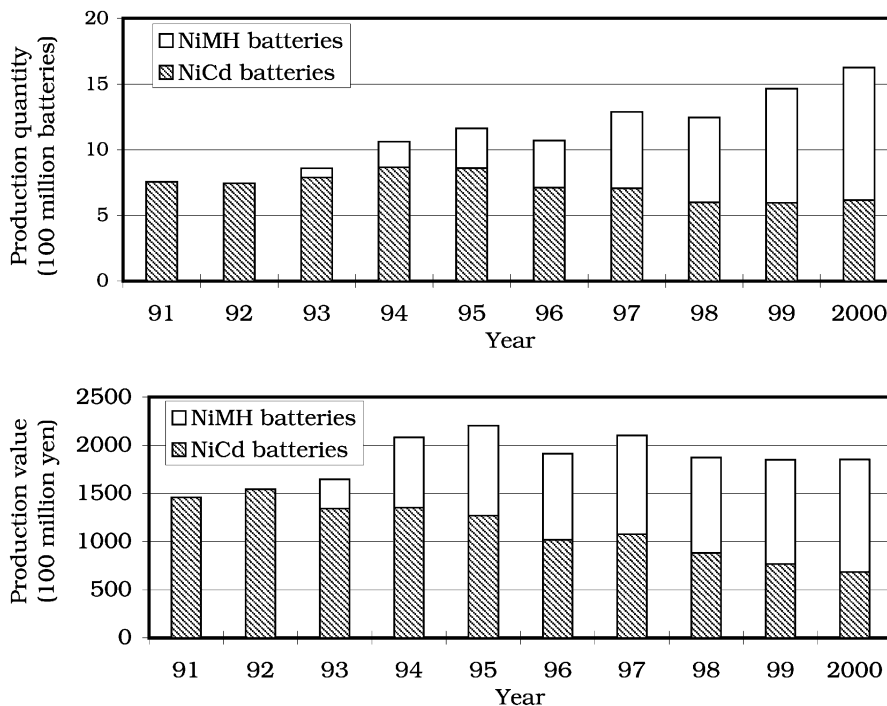


Fig. 1. Trends in production of small alkaline rechargeable batteries in Japan.

R&D on alloy compositions has been pursued extensively and has resulted in $Mm(Ni-Co-Mn-Al)_x$ as a current AB_5 metal alloy of choice. The energy density of a battery adopting this composition, as a result of the high negative electrode capability, is enhanced by 30–50% over that of Ni–Cd batteries. The composition of much of the Ni–MH battery is identical to that of Ni–Cd batteries, i.e. a nickel oxide as a material for positive electrode, electrolyte, configuration and sealing principle are identical to Ni–Cd.

Changes in the production of these alkaline rechargeable batteries in Japan in the past 10 years are listed in Fig. 1. As is shown, both the quantity and value of Ni–Cd battery sales are decreasing. This is due to the shift of production in Japan to Ni–MH batteries as well as due to a transfer of production sites outside Japan. The quantity and value of Ni–Cd battery production are, however, still increasing world-wide. At the same time, a rapid expansion in the use of mobile electronic devices such as personal computers and mobile phones, is encouraging both the quantity and the value of Ni–MH battery production to increase also. Thus, the market of alkaline rechargeable batteries appears to be set to expand further.

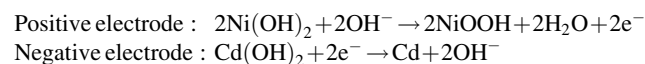
3. Ni–Cd batteries

3.1. Composition and features

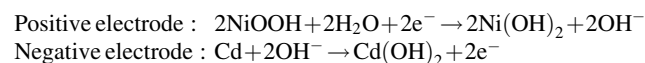
Three fundamental components of Ni–Cd battery are the nickel species as the positive electrode active material, the

cadmium species as the negative electrode active material, and the aqueous alkali solution as electrolyte. The battery shows a nominal voltage rated at 1.2 V. The charge–discharge reactions of this battery are described by the following equations.

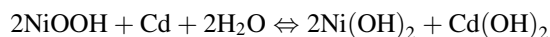
- Charge:



- Discharge:



- Total:



The forms of the active materials during the charge operation are NiOOH for the positive electrode and metallic cadmium as the negative electrode; during the discharge operation, these are Ni(OH)₂ and Cd(OH)₂, respectively. The sealed technology is one of the most important features of Ni–Cd battery. Sealed operation was accomplished by transferring oxygen evolved on the positive electrode in overcharging through the separator to the metallic cadmium negative electrode which reacts with the oxygen to form Cd(OH)₂. In order to ensure the sealing by means of the oxygen absorption by the negative electrode, the capacity of

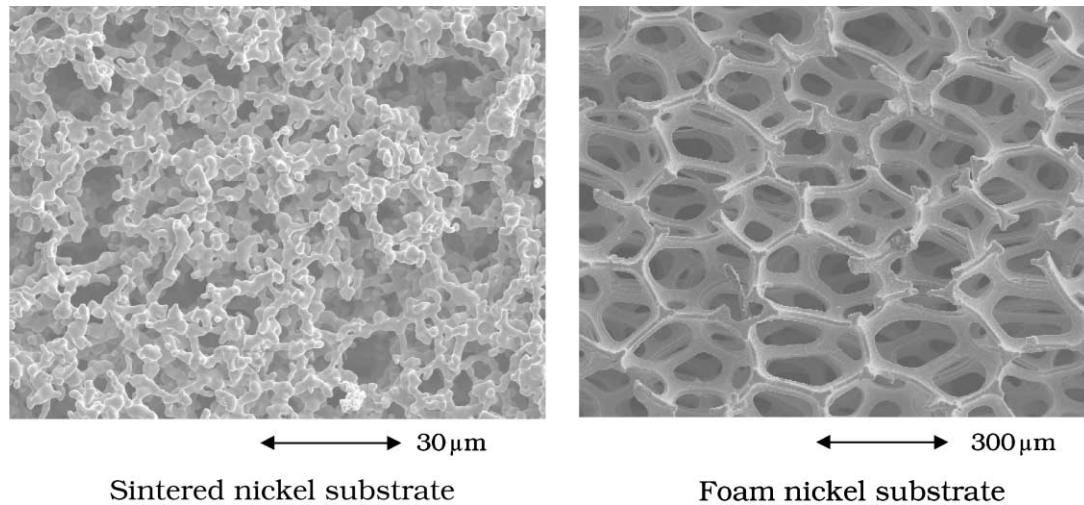


Fig. 2. Enlarged view of sintered nickel and foam nickel substrates.

the negative electrode is designed to be larger than that of the positive electrode so that the negative electrode does not reach a state of full charge. When the design capacity of the negative electrode is low so that the electrode reaches the fully charged state, a sharp pressure rise occurs in the battery. Since the reaction of oxygen with hydrogen evolved during over-charging of negative electrode is slow, hydrogen evolution itself causes a serious pressure rise inside the battery.

Two different kinds of electrode are manufactured for Ni–Cd batteries: sintered and non-sintered [2]. The sintered electrode has a nickel substrate involving innumerable fine pores (several μm diameter), which are filled with an active material composed of mostly $\text{Ni}(\text{OH})_2$ or $\text{Cd}(\text{OH})_2$ prepared by chemical or electrochemical conversion from aqueous nitrate solutions. Owing to its high electrical conductivity, the sintered electrode can display a large current discharge characteristic and quick charge characteristic. The non-sintered positive electrode is manufactured by filling directly a foam-type nickel substrate (which has three-dimensional porous texture) with an active material that is granular $\text{Ni}(\text{OH})_2$ powder. The non-sintered negative electrode is obtained by coating a Ni-plated pierced steel sheet with an active material paste composed mostly of cadmium oxide. Fig. 2 illustrates an enlarged view of both the sintered-type nickel substrate and the foam-type nickel substrate. The non-sintered electrode is advantageous in attaining a higher capacity, but is inferior to the sintered electrode in terms of electrical conductivity.

The shapes of Ni–Cd batteries can be roughly categorized into cylindrical, prismatic, and button types. Commercially available shapes are usually limited to the cylindrical and prismatic types.

A cylindrical Ni–Cd battery is produced by winding three-layered thin sheets of positive and negative electrodes sandwiching a separator (made from a synthetic fiber material made of polyamide or polypropylene), and then loading

the roll into a cylindrical metal casing followed by pouring in an alkaline electrolyte. The battery is next sealed by using a gasket and a seal plate which is equipped with a self-resetting gas vent.

The prismatic Ni–Cd battery has a construction of stacked sandwiching a separator. The stacked electrode composites are placed in a prismatic metal casing and then an alkaline electrolyte is poured in. The casing is sealed by welding with laser.

Ni–Cd batteries show the outstanding features of long durability and excellent high power performance, and very quick discharging and charging. Another advantage of Ni–Cd batteries is the wide variety of the product line up which permits a diversity of applications. This wide line up, includes more than 30 cell sizes with a capacity range of from 45 to 20,000 mAh. Moreover, various kinds of purpose-specific batteries have been developed, each of which features high performance optimized for a focused application. These batteries are basically identical in composition, but are designed to meet the varying requirements of various applications by selecting an optimal combination of electrode manufacturing process, component design, and parts. The development history of purpose-specific Ni–Cd batteries is summarized in Table 1, while examples of the range of Ni–Cd batteries are shown in Fig. 3.

Table 1
Development history of purpose-specific Ni–Cd batteries

Year	Purpose-specific battery type	Applications
1973	High-temperature battery	Guide lamp, emergency lighting
1975	Memory backup battery	Cash register
1978	Quick-rechargeable battery	Power tools
1979	Heat-resistant battery	Medical instrument
1986	High-capacity battery	Camcorder
1990	Extended service life battery	Cordless phone



Fig. 3. Ni–Cd battery product line.

3.2. Trends in Ni–Cd battery technology

Efforts in developing Ni–Cd batteries have been focused on the applications that utilize the advantages of Ni–Cd batteries, such as power tools, standby power supply for electrical equipment, and motor power uses. The major challenges in the future development of Ni–Cd batteries will involve larger discharge current characteristics, larger capacity and longer durability under severe operating conditions such as continuous recharging. The high drain discharge performances are required to satisfy the requirements of power tools and motor power uses. The trends for greater capacity and higher power are described below in discussing the development of technology for a high power type battery. Fig. 4 illustrates the history of the increase in the capacity of SC size batteries that are most commonly used for power tools. As can be seen, the capacity has approximately doubled in 20 years. The energy density of this type of battery is not so high as that of batteries employing the sintered-type positive and negative electrodes. For example,

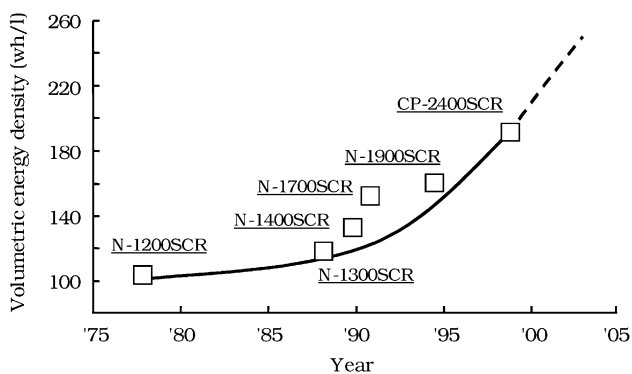


Fig. 4. Capacity increase over time.

CP2400SCR can output a current as large as approximately 30 A. Its capacity is rated at 2400 mAh, and its size is 22 mm in diameter, 42.5 mm in height. Its weight is approximately 60 g.

When designing a Ni–Cd battery of a higher capacity, it is required to pack active material as densely as possible into the electrodes. Also, it is required to increase the utilization of active material. A high volume ratio occupied by the positive and negative electrodes in the total volume of the battery gives a high capacity. Therefore, the separator, winding core space, casing and seal parts are required to occupy as small a volume as possible. Among these, it is a major challenge to reduce the space of a winding core for the positive and negative electrodes. We have focussed on the increased utilization of the $\text{Ni}(\text{OH})_2$ active material for the positive electrode, and the suppression of the volume for several parts.

First, the increased utilization of the $\text{Ni}(\text{OH})_2$ active material for the positive electrode is discussed. It is known that the utilization of active material is increased by coating the surface of the active material with $\text{Co}(\text{OH})_2$ by a chemical or electrochemical process after formation of the sintered electrode [3]. But this could not be applied to the commercial sintered electrode because of poor reproducibility of the effect. A reproducible effect was finally achieved by controlling the crystalline structure and morphology of the $\text{Co}(\text{OH})_2$. Cobalt coating technique has been utilized since the successful development of the (CP-2400SCR) battery.

This improvement in the utilization of the active material is caused by the oxidation of the $\text{Co}(\text{OH})_2$ coating layer on the electrode to CoOOH during the first charging operation so that it forms a path of higher electrical conductivity. Since this oxidation takes place at a more negative potential than the potential of the nickel positive electrode and this oxidation is an irreversible reaction, so that the above-mentioned effect remains valid even after repeated charge–discharge cycles. The conductivity of the positive electrode drops during the discharging process because less conductive $\text{Ni}(\text{OH})_2$ is formed from conductive NiOOH . However, the CoOOH coating layer makes up for this loss in conductivity, and enables a thorough discharge of the positive electrode. This increase in utilization of the positive electrode is proved by measurement of the average of valence change of nickel in the positive electrode, i.e. changes of the average nickel valency from 3.05 to 2.18 with the cobalt coating during discharge, while it changes from 3.05 to 2.25 without the cobalt coating. The addition of 1.5 wt.% cobalt causes an 8% increase in the nickel utilization [4]. The data in Fig. 5 exhibit that the cobalt-coating effect remains even in high density loading electrodes.

New types of separator have been developed with materials made of non-woven polyamide or polypropylene fabrics reinforced with fibres of high mechanical strength. This development has decreased the separator thickness by 30% while maintaining its liquid-tightness and strength.

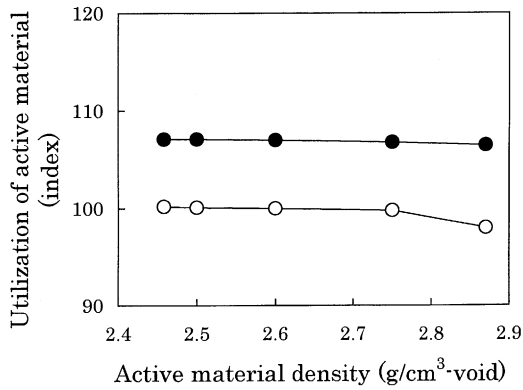


Fig. 5. Utilization of added Co and normal active materials vs. material density. After addition Co (surface addition: 1.0 wt.%): (●). Before addition Co: (○). Note: the utilization of active material density of 2.6 g/cm³-void no added Co is considered 100 (index).

The size of the winding-core has been reduced by 55% compared with the conventional winding-core. This change, on the other hand, has made the conventional arc welding to connect the casing to the negative electrode collector inappropriate because this technique requires an auxiliary electrode rod. To overcome this issue, a laser welding technique has been developed, where a laser beam is irradiated from outside the casing to weld the collector. The schematic diagram in Fig. 6 illustrates the method for laser welding on the bottom of the case. These new techniques, including thinning the other components, have increased the energy density by approximately 25% [4].

Typical characteristics of this battery are illustrated in Fig. 7. As shown in the figure, this new Ni–Cd battery can meet the requirements of power tools. Variations of this type of battery have been produced and used in many devices such as power-assisted bicycles, powered wheelchairs, scooters, carts, and small power lifts.

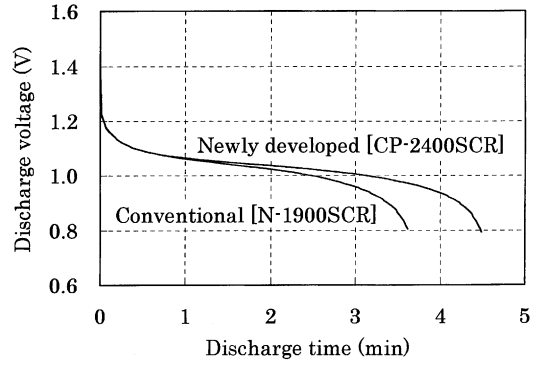


Fig. 7. Discharge characteristics at 30 A discharge.

The market for power-assisted bicycles started in 1994 in Japan and is expanding. For power-assisted bicycles, a battery pack is typically used that is composed of twenty 5.0 Ah Ni–Cd cells connected in series. When the load on riders becomes heavy at an upward slope, an assisting motor powered by the battery pack helps to decrease the load on the rider. At the end of 2000, approximately 500,000 power-assisted bicycles had been marketed in Japan.

The other promising market for Ni–Cd batteries is as a standby power source for telecommunication equipment like WLL (wireless local loop), UPS, security equipment, POS (point of sales) equipment, etc. These are sometimes employed in conjunction with solar cells as power shutters, burglary-prevention lighting, traffic signs, etc. Hitherto, standby battery packages coping with sudden power failure have been incorporated into various parts of telecommunication systems. While lead–acid batteries have been used so far for this purpose, Ni–Cd batteries have been gradually expanding in this application field because of their smaller size and higher performance. This market requires a high-temperature trickle charging performance, such as was

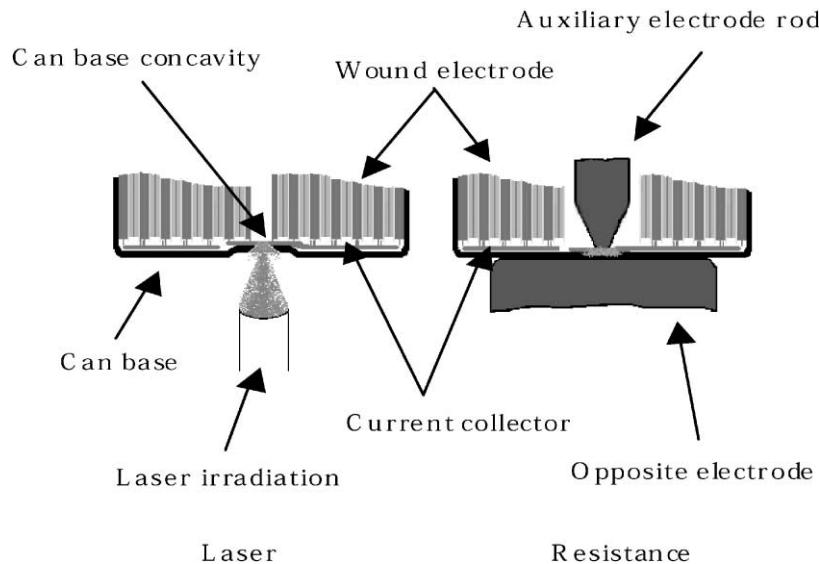


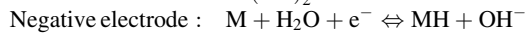
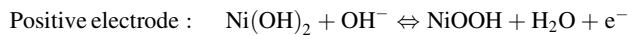
Fig. 6. Laser welding of current collector to can bottom.

required and developed for emergency lighting and guide lamps, and a wide range of temperature performance with high reliability. Examples of the developments for high-temperature trickle charged performance are: the adoption of the separator made of polypropylene, which is more stable against heat and oxidation; optimization of the electrolyte; and inhibition of Cd migration based on an improved negative electrode [5].

4. Ni–MH batteries

4.1. Composition and features

The Ni–MH battery is composed of nickel oxide as the positive electrode, metal hydride as the negative electrode and an aqueous alkali solution (such as KOH) as electrolyte. As described above, its positive electrode material and battery configuration are practically identical to those of Ni–Cd batteries. In charging, a hydrogen atom deposits on the surface of the hydrogen storage alloy by electrolysis of water. The hydrogen atom diffuses into the metal and is stored there, i.e. the metal is reduced to a metal hydride. On the positive electrode, $\text{Ni}(\text{OH})_2$ is oxidized to an NiOOH . In discharging, vice versa



In this battery, the true active material in the electrode reaction is hydrogen, and the hydrogen storage metal alloy is a medium for hydrogen storage.

The progress of improvement of the negative electrode material (hydrogen storage metal alloy), which is the most outstanding feature of this battery type, is described below. The optimization of the composition of the hydrogen storage alloy for batteries is illustrated in Fig. 8. After replacing a part of Ni in LaNi_5 with Co, prevention of fine pulverizing of the metal alloy and capacity increase were achieved by replacing a part of Ni with Mn. The oxidation resistance of the metal during the electrode manufacturing process was improved by replacing a part of Ni with Al. Furthermore, it was clarified that replacing the La with a mixture of rare earth metal elements Mm (misch metal) not only enhances the alkali resistance of the metal alloy, but also reduces the cost of metal alloy. Finally, the stoichiometry of the basic composition of the AB_5 series alloy was reviewed over the range up to $\text{A}:\text{B} = 1:5$, and it was found that $\text{A}:\text{B} = 1:4.76$ is the most favorable ratio to attain high capacity [6]. The metal alloy composition $\text{MmNi}_{3.2}\text{Co}_{1.0}\text{Al}_{0.2}\text{Mn}_{0.6}$, which is most widely used currently, shows high corrosion resistance and high capacity. The metal alloy of composition, AB_x , where $x = 4.76$, gives a discharge capacity of 330 mAh/g which is 10% higher than that obtained for the composition of $x = 5$.

A variety of Ni–MH batteries is shown in Fig. 9. Basically, as in the case of Ni–Cd batteries, their types are classified

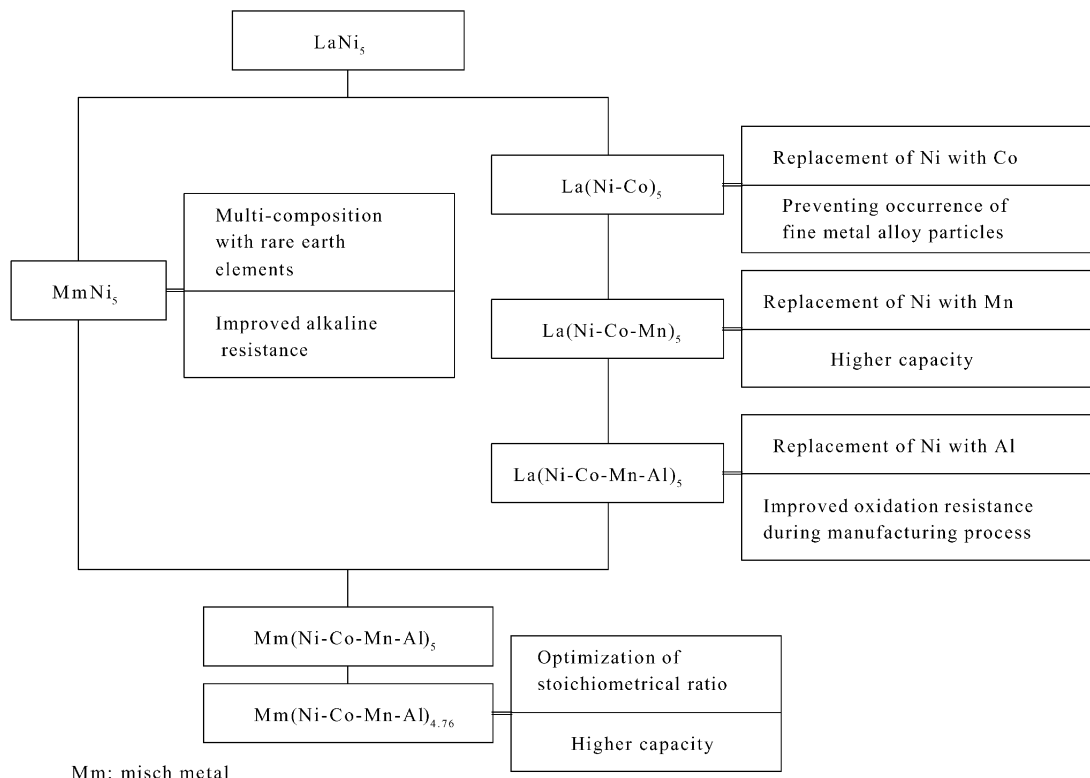


Fig. 8. Process optimizing the composition of hydrogen storage alloys for batteries.

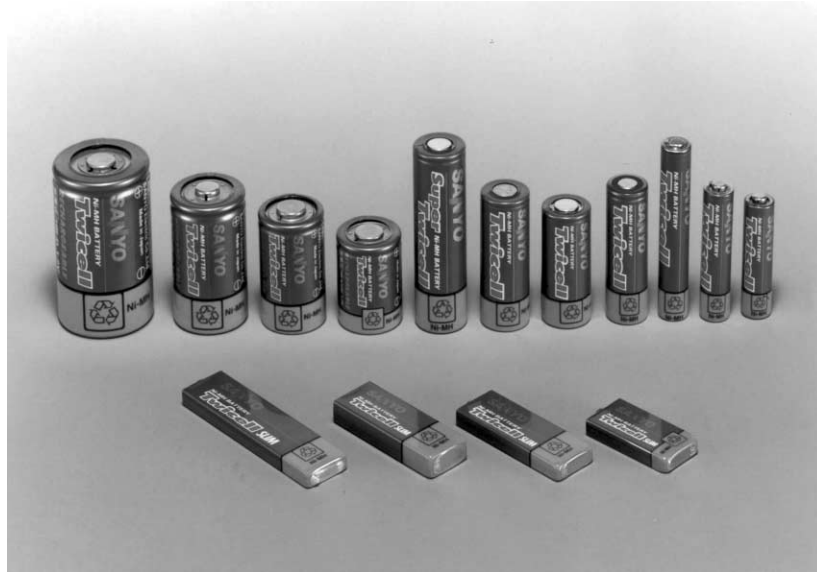


Fig. 9. A section of Ni-MH batteries.

into two types: cylindrical and prismatic. Their internal construction is very similar to that of Ni-Cd batteries.

The charge characteristics of Ni-MH batteries are summarized in Fig. 10. As is shown, a quick charge operation can be completed in approximately 1.3 h after a full discharge. The charge control methods are generally based on the peak voltage control (detecting the maximum value of the battery voltage) and dT/dt control (detecting battery temperature increase appearing at full charge).

The most outstanding advantage of Ni-MH batteries is the high volume capacity, reaching a value of 1.3–1.5 times that for comparable Ni-Cd batteries. Their other features are roughly identical to those of Ni-Cd batteries; their discharge voltage is the same as that of Ni-Cd batteries. Thus, Ni-MH batteries can easily replace the Ni-Cd battery.

4.2. Trends in Ni-MH battery technology

The progress of increase in energy density for Ni-MH batteries, cylindrical 4/3 A size batteries (diameter: 17 mm and height: 67 mm) and prismatic C1 size batteries (width: 17 mm, height: 35.5 mm and thickness; 6.1 mm) is summarized in Fig. 11.

Since coming on to the market in 1990, our Ni-MH batteries have met market needs for higher energy density (an increase of approximately 1.7 times during these 10 years based on 3/4 A size battery, and approximately 1.8 times based on C1 size). Requirements for small and lighter weight batteries with high capacity have been increasing recently, especially for application to notebook computers and mobile phones. To satisfy this requirement, development

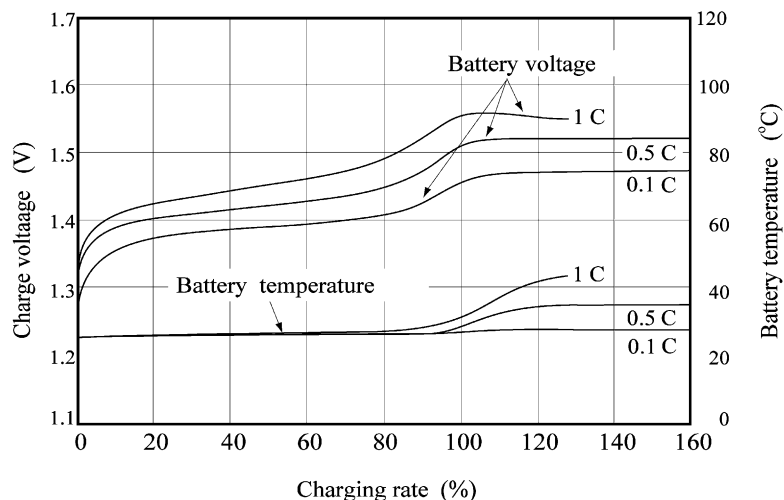


Fig. 10. Charging characteristics of Ni-MH batteries. Model: HR-4/5AU; charge: 1 C for 1.3 h; 0.5 C for 3.2 h; 0.1 C for 16 h.

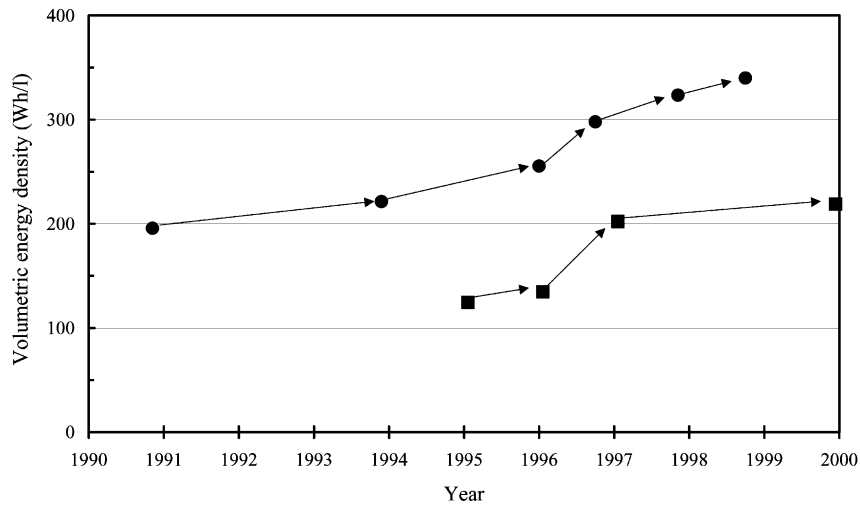


Fig. 11. Capacity increase of the Ni–MH battery (HR-4/3AU, HFC1U). HR-4/3AU (cylindrical): (●); HFC1U (prismatic): (◆).

and improvement of battery materials are necessary. In particular, enhancement of the hydrogen storage capacity of alloys has been of vital importance.

The target for advanced hydrogen storage alloy is to enhance the hydrogen storage capacity and to protect against fine pulverization as well as oxidation-induced deterioration that occurs as a result of repeated expansion/shrinking during charge–discharge cycles. To achieve this, the composition of this alloy has been extensively examined as discussed above. One of the current interests for the improvement of the performance is to prepare a homogeneous alloy that suppresses segregation of manganese and eliminates the lattice distortion occurring during quenching of the alloy [7]. The reactivity of the alloy surface is moderated by a treatment with acid or alkaline aqueous solution [8]. The influence of acid treatment is described in Fig. 12. The treatment enhances the limiting current density (per weight), which leads to an increased power capability of the electrode [9]. The influence of acid treatment on capacity is shown in Fig. 13, which shows that

the increase in capacity is limited to about the fifth cycle [10].

One of the key technologies to enhance Ni–MH battery capacity is to develop a Ni-based positive electrode with a higher capacity. Adding to the technologies described in Section 3, further improvement has been accomplished by the air-oxidation of $\text{Co}(\text{OH})_2$ in the alkaline electrolyte containing NaOH, which leads to the formation of a cobalt oxide more conductive than CoOOH . The cobalt oxide formed containing Na shows electric conductivity 4 orders of magnitude higher than the conductivity of CoOOH . Recently, the addition of rare earth oxides to the nickel positive electrode has been shown to increase the utilization of the positive electrode. The addition of Y_2O_3 increases $\text{Ni}(\text{OH})_2$ utilization as shown in Fig. 14 [11].

Some of the oxygen evolved during overcharging oxidizes the separator. Then the charge reserve of the negative electrode decreases and the cycle durability of the battery is decreased. Oxidation of the separator must be strictly avoided. The use of an oxidation-proof PP separator enhances the durability of the battery. Typical durability during over-charge cycles at high temperature as shown in Fig. 15.

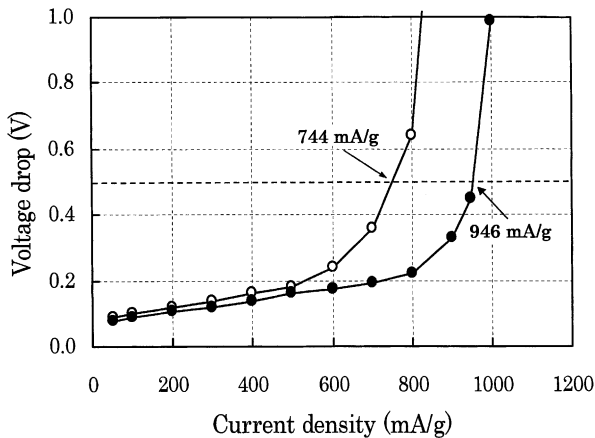


Fig. 12. Limiting current density before and after surface treatment. After surface treatment: (●); before surface treatment: (○).

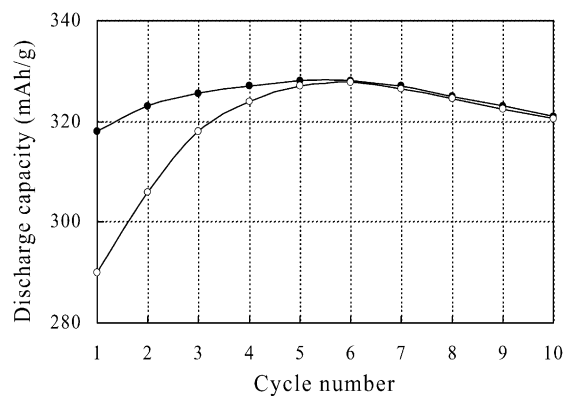


Fig. 13. Charge–discharge cycle characteristic before and after surface treatment. After surface treatment: (●); before surface treatment: (○).

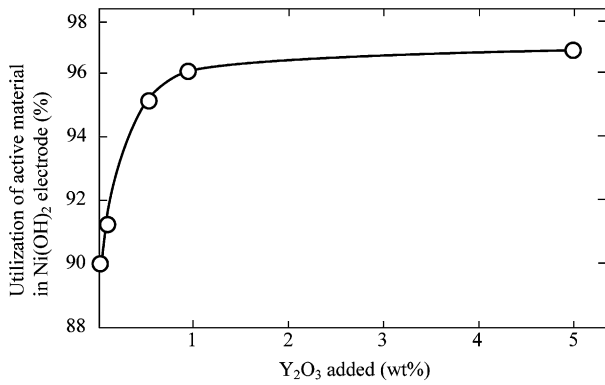


Fig. 14. Influence of the amount of Y₂O₃ on active material utilization. Charge: 0.1 C, 16 h; discharge: 1/3 C (cut-off voltage 1.0 V).

Some new kinds of hydrogen storage alloys such as the AB₂ type, Mg–Ni type and bcc type represented by V₃Ti are being investigated, which are expected to offer a larger

capacity (in particular, the capacity of the bcc type is two times larger than that of AB₅). However, some problems to be solved for these new alloys remain; these new alloys are easily corroded in an electrolyte and this causes serious deterioration during cycling. Nevertheless, research and development on these alloys is in progress although they have not yet been brought into practical application. The problems to be solved for the new high-capacity alloys are summarized in Fig. 16 [12–14].

The world production of Ni–MH batteries has continuously increased and reached approximately 1.2 billion in 2000. The increase in the market for electronic equipment such as notebook computers and mobile phones, and the continued endeavor to meet the demands from such equipment have kept production increasing. The merit of high performance and excellent environmental compatibility will accelerate the further expansion of Ni–MH batteries in new and current application areas including HEVs, UPS, power-assisted bicycle, and others in the future.

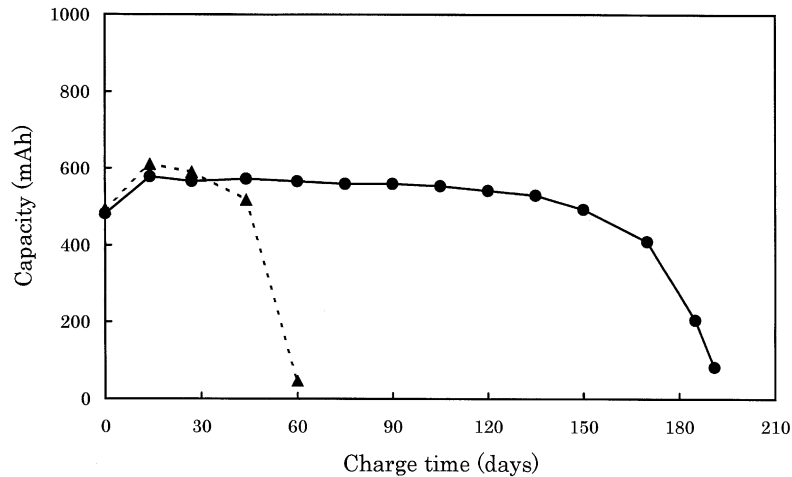


Fig. 15. Endurance in overcharge cycles at high temperature. PP separator: (●); nylon separator: (▲); charge at 0.2 C at 60°C; discharge at 1 C (cut-off voltage 1.0 V) at 25°C.

AB ₂ type	bcc type	Mg-Ni type
Ex.: Zr(MnVCrNi) ₂	Ex.: V ₃ Ti	Ex.: Mg ₂ Ni+2Ni
-Capacity is 30% greater than that of AB ₅ -Poor high-rate discharge characteristics	-Capacity is twice that of AB ₅ -Surface deposition of collector function phase (TiNi)	-Capacity is 1.5 times that of AB ₅ -Mechanical alloying procedure
Shared drawbacks		
-Poor corrosion resistance as compared with AB ₅ -Shorter charge-discharge endurance -Problems with initial activation and low operating voltage		

Fig. 16. New high-capacity MH alloys.

5. Conclusion

Ni–Cd batteries, which do have environmental issues, also have many advantages, e.g. high-power output, super-rapid charging, low cost, and high durability. Although new rechargeable batteries such as Ni–MH batteries and Li-ion batteries have been commercialized, Ni–Cd batteries still boast the largest production throughout the world even 30 years after their first commercial marketing. It is expected that Ni–Cd batteries will keep their share of this market. Ni–MH batteries has reached an energy density of 91 Wh/kg and 340 Wh/l. As compared with lithium ion batteries, the former parameters is less but the latter (volumetric energy density) is equal. The Ni–MH battery shows much higher safety than Li-ion. The merits of volumetric energy density and safety will sustain a help to expand the application of Ni–MH batteries further, for example, is HEVs, dispersed electricity storage, a UPS. Furthermore, new hydrogen storage alloys are expected to bring a new break-through in their performance.

R&D of these alkaline rechargeable batteries is directed both to common applications and to specific uses and remarkable progress is expected in both directions.

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