Development of Low Self-discharge Nickel-metal Hydride Battery

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Abstract Mechanisms of the self-discharge of a Ni-MH battery were investigated. The self-discharge is found to be caused mainly through reduction of the positive electrode , i.e.; by dissolution of Co, Mn ions from the negative electrode which deposit onto the separator and the positive electrode, and by a "shuttle effect" with nitrogenous substances. These self-discharge mechanisms can be significantly suppressed by using a superlattice alloy, which is free from Co and Mn as a negative electrode, and by improving the separator. Based on these results, we have developed a next generation Ni-MH battery named "eneloop" which has low self-discharge characteristics and is able to charge and discharge over 1,000 times.

1. Introduction

In addition to its having high output at a stable voltage, as the nickel-metal hydride (Ni-MH) can be repeatedly charged and discharged, it makes the cell particularly economical in comparison. It also has the benefit of being recyclable, as renewable resources are used in its manufacturing. The Ni-MH battery also has the appeal in the market of having a voltage at 1.2V level—near that of a dry cell. As for the Ni-MH battery market, high-drain devices such as digital cameras have been the main target, and that market continues to expand, and there has also been a general trend of increased cell capacity to meet market demands. However, Ni-MH hydride battery sales only account for 1% of sales for that of the dry-cell market. In order to expand a different market, SANYO began development of a Ni-MH rechargeable battery that has the merits of dry cells.

In a customer survey comparing rechargeable batteries and dry cells, users were mainly concerned about self-discharge for rechargeable batteries. Energy is stored in the battery which gradually depletes over time (self-discharge). For Ni-MH batteries and other alkaline rechargeable battery types, the major problem facing the industry was the fact that it could not match dry cell batteries' feature of "ready-to-use out-of-the-pack"—that is, until "eneloop", which has revolutionized the industry by providing the first low self-discharge next-generation type Ni-MH battery (Fig.1).

Fig.1 commercial nickel-metal hydride battery –"eneloop" (SANYO AA HR-3U)

In this study, we investigated the mechanism of self-discharge of Ni-MH battery and countermeasures to improve self-discharge characteristic.

2. Self-Discharge Mechanism

As shown in Fig. 2, there are 3 essential mechanisms of self-discharge of Ni-MH batteries involving the negative electrode alloy composition, positive electrode composition, and impurities in the battery:

[1] Positive Electrode Reduction Reaction due to Dissolved Negative Electrode Material:

Conventional Ni-MH batteries employ a hydrogen-absorbing alloy called AB_5 type hydrogen absorbing alloy for the negative electrode. This particular alloy usually includes Co and Mn, as well as other soluble elements in the alkaline electrolyte solution. These elements dissolve into the electrolyte solution, and due to their precipitation on the separator, the rate of reduction of the positive electrode material accelerates. 1)

[2] Decomposition of the Positive Electrode:

At battery voltages over 1.23V (electrolytic potential of H_2O), the following oxidation reaction occurs, which is responsible in part for the decomposition of oxy-hydroxide:

$$\begin{array}{rl} & NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^- \\ +) & OH^- \rightarrow 1/4O_2 + 1/2H_2O + e^- \\ \hline & NiOOH + 1/2H_2O \rightarrow Ni(OH)_2 + 1/4O_2 \end{array}$$

[3] Self-Discharge due to Shuttle Effect:

Nitrogenous compound and other impurities existing in the battery react which is called "shuttle effect", in which the nitrogenous compound goes back and forth between the positive and negative electrodes. In the following reactions, there is an electron ion exchange between the positive and negative electrodes which results in positive electrode reduction.

positive: $NH_4OH + 6NiOOH + OH^- \rightarrow 6Ni(OH)_2 + NO^{2-}$

negative: $NO^{2-} + MHx \rightarrow NH_4OH + MH_{x-6} + OH^-$

3. Technological Improvements for Self-Discharge

3-1 Improvements of Super-lattice Hydrogen-Absorbing Alloy

For conventional rare earth - Nickel hydrogen-absorbing alloys, in order to maintain cycle-life performance as well as other characteristics, Co and Mn were previously necessary for AB_5 type; however, a super-lattice alloy (rare earth-Mg-Ni type) not including these elements was adapted, which had the benefits of high capacity, high anti-corrosion properties 2). From the results of powder x-ray diffraction and TEM analysis of the super-lattice hydrogen-absorbing alloy, the structure of Ce_2Ni_7 type can be observed. (Fig.3). Whereas the cell with conventional alloy AB_5 type has a simple layer structure, with the new alloy, the sub-cell of AB_5 type and the sub-cell of AB_2 type have a well-ordered super-lattice alloy structure (A is mainly a

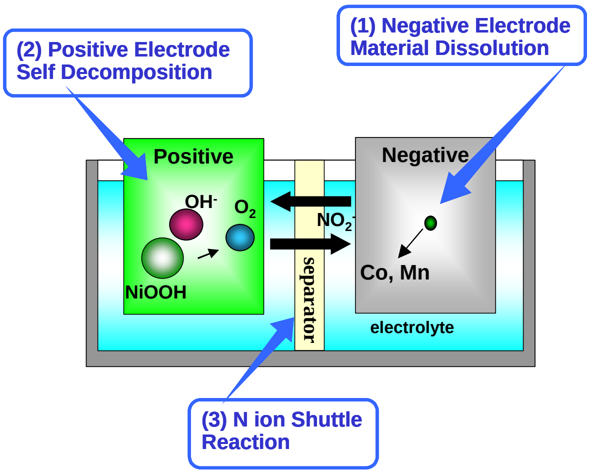

Fig. 2 mechanism of self-discharge

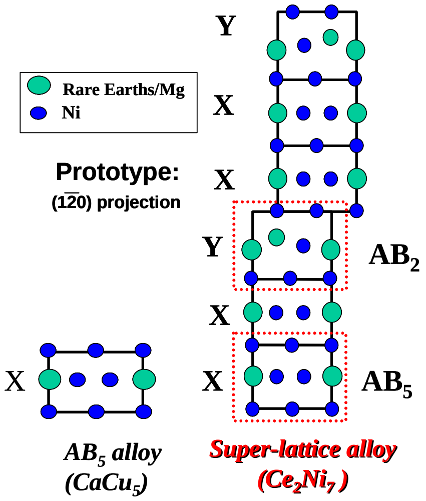

Fig. 3 crystal structure of AB_5 type alloy ($CaCu_5$ type) and super-lattice alloy Ce_2Ni_7 type.

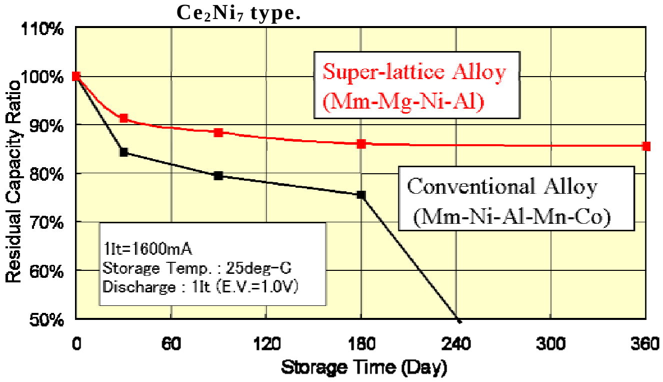

Fig. 4 comparative storage characteristics showing improved hydrogen- absorbing alloy compound of La, other rare-earth elements, and Mg, and B is mainly a compound of Ni and other transitional metal elements). Thus the crystal structure of the new alloy differs entirely from the conventional alloy's structure, and as Co and Mn are not included in the alloy, we were able to achieve significantly improved battery characteristics, especially in terms of self-discharge.

Fig. 4 shows a comparison of a cell manufactured with AB_5 type alloy and a cell manufactured with the super-lattice alloy—the figure shows the comparative capacity retention rate at storage at initial full charge at 25deg-C.

As the graph shows, the AB_5 type alloy , containing Co and Mn, suddenly decreases in capacity retention rate after 180 days of storage. However, as Co and Mn are not included in the new and improved super-lattice alloy, the cell maintains a comparatively higher residual capacity, and self-discharge is thus significantly suppressed. This is essentially due to the reason that Co and Mn are not included in the super-lattice alloy, so precipitation which may lead to conductive paths is not a concern.

Fig. 5 shows a comparison of cross-sections view of two separators (one from a cell employing the conventional alloy for the negative electrode, the other employing the super-lattice alloy structure) in EPMA analysis and quantitative analysis by ICP . The separators were taken from cells that had completed 300 cycles, thus showing the precipitation level of Co and Zn on the separator after repeated cycles. Whereas the cell incorporating the conventional AB_5 type alloy exhibits a significant amount of conductive material on the separator, the cell using the super-lattice alloy exhibits approximately only 1/10 the amount of the cell using AB_5 type alloy. In further analysis of Mn content, while levels are no-detectable for the super-lattice alloy, tests showed that for the cell using the AB_5 type alloy, Mn precipitation level was 849 $\mu g/cm^2$, significantly high in comparison. However, with the cell using the super-lattice alloy, we were able to suppress conductive material precipitation on the separator resulting in conductive paths as well as suppress self-discharge.

3-2 Improvements due to Suppression of Decomposition of the Positive Electrode

As explained in 2., for oxy-nickel hydroxide, which is the charged active material for Ni-MH batteries, due to a reaction that occurs in the electrolyte when the battery is in storage, decomposition with oxygen generation occurs and it becomes nickel hydroxide in a discharged state. In order to suppress this reaction, we considered adding additives for the positive electrode in order to increase oxygen over-voltage, as well as optimization of the electrolyte composition. Specifically, as shown in Fig. 6, residual capacities were measured for a cell containing mainly KOH and a cell containing mainly NaOH. The cells were stored at 25deg-C. The data shows that the electrolyte containing mostly NaOH was able to retain a higher capacity, and in comparison to the electrolyte containing mostly KOH, even after 1 year, it was able to retain 10% higher capacity.

3-3 Improvements due to Suppression of Shuttle Effect

As explained in 2., when nitrogenous compounds are incorporated in the manufacturing process of nickel hydroxide, used in Ni-MH batteries—due to a shuttle effect of the nitrogen ions, there is significant self-discharge. As a countermeasure, we considered adapting a more suitable hydrophilic treatment method of the separator, and in so doing, were successfully able to "capture" these shuttling nitrogen ions on the surface of the separator, which go back and forth between the electrodes. As Fig. 7 shows, there was significant improvement in the residual capacity when comparing the improved separator with the conventional separator (cells stored at 25deg-C). As the improved hydrophilic treatment was able to "capture" nitrogen ions, as the data shows, the cell was able to retain 25% higher capacity after one year in comparison.

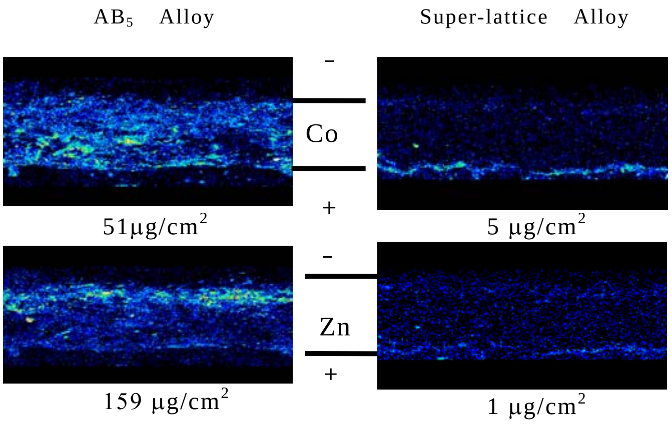

Fig. 5 comparison of AB$_5$ alloy separator and super-lattice alloy separator

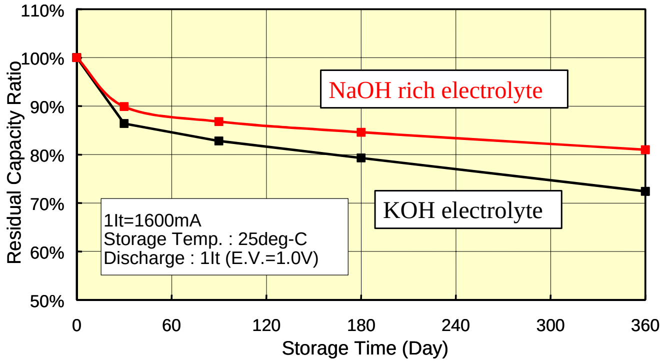

Fig. 6 comparative storage characteristics with different electrolytes

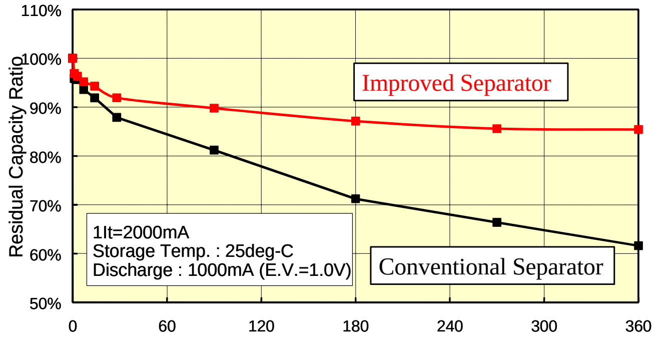

Fig. 7 comparative storage characteristics with different separators

4. Battery Performance of “eneloop”

Through various technological innovations as we have explained thus far, we were successfully able to control self-discharge. In trying to improve upon the conventional positive electrode, electrolyte and separator in order to control self-discharge in the past, there was the issue of performance loss for other areas due to decreased conductivity; however, in adapting the reactive super-lattice alloy for the negative electrode, we were successful in achieving a high capacity cell, as well as improve self-discharge, without affecting other characteristics.

As a result of adapting the super-lattice alloy component , battery voltage increased, as well. For high current devices such as digital cameras, high end-voltage settings cause the device’s cell capacity indicator to display low cell early; in the past, this has posed a concern for Ni-MH batteries, as some devices would even shutdown immediately after a fully charged battery was stored for some time and the device was turned on. However, with the advantage of increased voltage, this problem has been solved, which is particularly advantageous to the general user.

Fig. 8 shows a comparison of a conventional high-capacity cell with “eneloop”, stored at 20deg-C, showing residual capacity and mid-voltage during discharge over time. As the graphs show, “eneloop” retains a higher capacity and operating voltage in comparison to the conventional high-capacity cell. Stored at 20deg-C for one year, the “eneloop” retains 85% capacity, which is 20% higher than the conventional cell, and the mid-point voltage is 35mV higher.

Fig. 9 shows a comparison of cycle life performance according to IEC standards. Whereas the conventional high-capacity cell has a cycle life of about 550 cycles, “eneloop” is about 1000 cycles, about 2 times more. It is due to its 1000-times cycle lifeand that “eneloop” is not only an environmentally-friendly cell, but it is also economically advantageous.

Fig. 10 shows a comparison of overall performance characteristics. In comparison with the conventional high-capacity Ni-MH2500—apart from capacity—“eneloop” surpasses the conventional Ni-MH battery in terms of high-rate discharge characteristics, low-temperature discharge characteristics, recovery characteristic after storage with resistance, and especially cycle life and residual capacity.

5. Conclusion

The new “eneloop” is, in short, “a rechargeable battery with the merits of a dry cell”. That is to say, it is not only completely recyclable, but it has a high capacity so can be used for a long time as a rechargeable battery, but it is also a Ni-MH battery that is ready-to-use out-of-the-pack, is storable, and can be used in any application.

Reference

1) K. Shinyama Y. Magari, H. Akita, K. Kumagae, H. Nakamura, S. Matsuta, T. Nohma M. Takee, K.Isiwa Investigation into the decomposition in storage characteristics of nickel-metal hydride batteries during cycling, J. Power Sources Vol.143 (2005) P.265.

2) S. Yasuoka, Y. Magari, T. Murata, T. Tanaka, J. Ishida, H. Nakamura, T. Nohma, M. Kihara, Y. Baba, H. Teraoka, Development of high capacity nickel-metal hydride batteries using superlattice hydrogen–absorbing alloys,J Power Sources, Vol.156, (2006)P.665.

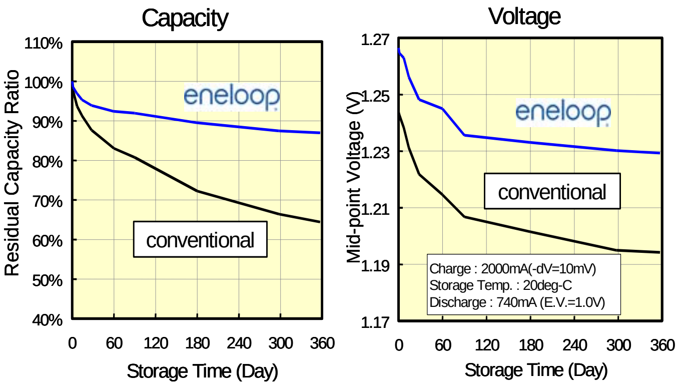

Fig. 8 comparative storage characteristics of conventional vs. “eneloop”

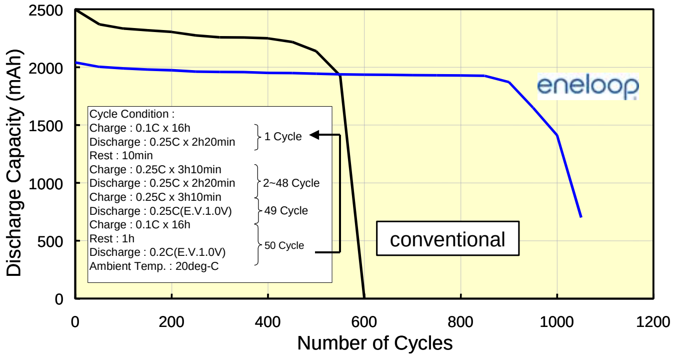

Fig. 9 comparative cycle life data for conventional vs. “eneloop”

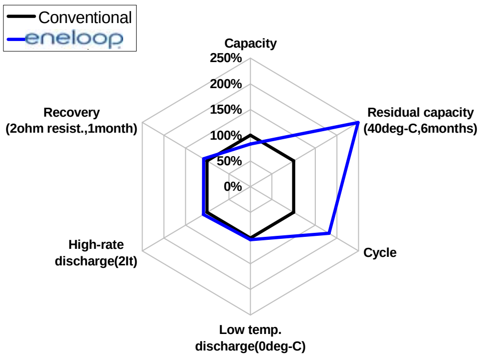

Fig. 10 comparative cycle life data for conventional vs. “eneloop”