

COMPARISON OF "AA" NICKEL METAL HYDRIDE CELLS WITH "AA" NI-CD CELLS

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Abstract

This paper compares "AA" size nickel metal hydride (Ni-MH) cells with comparable "AA" nickel cadmium (Ni-Cd) cells both of which were obtained in 1993. The Ni-MH cells were found to be a suitable substitute for conventional Ni-Cd cells. Both these cell types have similar voltages and discharge characteristics. The Ni-MH cells, though had nearly twice the capacity as comparable Ni-Cd cells. There was no significant difference in self discharge between the two types of cells. The Ni-MH cells also performed as well as Ni-Cd cells at rates lower than 5 amperes and at temperatures higher than 0°C (32°F). The most interesting finding is that the Ni-MH cells showed an irreversible decay of the discharge voltage with each cycle which was more noticeable during pulses. Eventually the Ni-MH packs fail, not because of loss of capacity, but because of low voltage during the pulse.

Introduction

This paper compares the performance characteristics of "AA" size general purpose nickel metal hydride (Ni-MH) cells with comparably tested "AA" nickel cadmium (Ni-Cd) cells both of which were obtained in 1993. Among the characteristics this paper will examine are charging, high rate discharge, pulse discharges, and self discharge.

Ni-MH system appears to be an ideal direct replacement for existing Ni-Cd cells and batteries. This system has

essentially the same operating voltage and may even be able to operate using existing Ni-Cd support equipment.

A test program was developed that was to characterize the performance of "AA" Ni-MH cells and to compare them with standard "AA" Ni-Cd cells to determine the feasibility of a one to one replacement for certain applications. The "AA" size cell was chosen because NAVSURFWARCENDIV Crane has extensive cycling data for this size cell. There was a concurrent evaluation being performed where 3 packs of Ni-Cd "AA" cells (0.6 Ah nominal rating) were on a long term cycling test, the results of which will be compared with Ni-MH test results. The Ni-MH cells are being tested using present Ni-Cd cell testing procedures (summarized in Methods) with as little modification as possible. The only significant variation was that the current levels during charge were adjusted upward to compensate for the increase in capacity of the Ni-MH cells. The three charge methods used in this test best replicate the chargers that are currently fielded.

Background

The U. S. Navy and the rest of the Department of Defense (DoD) have for over 20 years been using small sealed rechargeable Nickel Cadmium (Ni-Cd or Nicad) cells for power sources in various electronic devices. Throughout the DoD there have been many efforts to find replacements for Ni-Cd cells and batteries that will provide improved performance and lower environmental risks.

Work is underway in both the DoD and private industry to develop an improved replacement for the Ni-Cd cylindrical cell. The Ni-Cd battery has some major concerns that affect both developers and users of these batteries. The current generation of Ni-Cd cells has significantly lower (less than 40%) capacity than comparable non-rechargeable batteries. These cells also require special charging equipment and procedures for normal operation. In addition production of these cells in the future may be severely curtailed because cadmium, a toxic and hazardous metal, is being increasingly regulated.

The small sealed Ni-Cd cells are rugged cells with operating characteristics similar to those of common commercial dry cells. The discharge voltage ranges from approximately 1.3 volts (V) to just below 1.0 V (which is comparable in most applications to the working voltage of dry cells), the cells have a very flat discharge voltage at rates where most alkaline voltages drop sharply, and these cells have superior low temperature performance. The cells also have some problems inherent in many sealed rechargeable designs such as requiring special charging equipment, charging procedures, and susceptibility to charge abuse. Ni-Cd cells are initially more costly than most non-rechargeable cells, and there is also some additional cost for maintenance. A list of characteristics for a "AA" Ni-Cd cell is provided in Table 1.

Table 1. Characteristics of Ni-Cd and Ni-MH cells tested

Characteristic	Ni-Cd	Ni-MH
Size Evaluated	ANSI "AA"	ANSI "AA"
Capacity (Ah)	0.6 Ah	1.1 Ah
Nominal cell voltage	1.2 V	1.2 V
Open circuit voltage	1.25-1.35V	1.25-1.35V
Typical end voltage	1.0 V	1.0 V
Maximum cont. amp	10 A	4.0 A
Temperature Range	-20°C/ 65°C	10°C/ 40°C
Weight	22 gms	25 gms

In many applications such as industrial transceivers, cordless telephones, and lap top computers there is no other practical alternative to rechargeable batteries. In recent years great efforts have been made to improve the performance of rechargeable batteries. The capacities of Ni-Cd cells have almost doubled in the last 15 years; for example, the "AA" size cell has increased in capacity from 0.45 ampere hours (Ah) up to about 1 Ah (high capacity design) in 1994. However, these improvements have not been able to keep up with the ever increasing demand of today's electronic market for power and operating life (capacity).

Two of the most likely candidates for Ni-Cd replacements are rechargeable lithium ion and nickel metal hydride (Ni-MH). The lithium ion system has many benefits, such as very high voltages and energy densities when compared to Ni-Cd's, but the system is still in development. Additionally the system can not be used as a direct replacement for existing Ni-Cd batteries because of size, charging techniques, and cell characteristics. The Ni-MH system appears to be an ideal direct replacement for existing Ni-Cd cells and batteries. This system has essentially the same operating voltage and may even be able to operate using existing Ni-Cd support equipment.

Methods

The Ni-MH and Ni-Cd cells were tested in nearly identical methods using NAVSURFWARCENDIV Crane test procedures developed for Ni-Cd battery testing. Once the initial capacity was verified the fully conditioned cells were stored for various lengths in the following temperatures -23°C, -4°C, 24°C, 49°C, 60°C, or 71°C. The cells were removed from temperature soak, conditioned at ambient temperature for four hours, and discharged. The cells were next tested to determine the effect of high rate discharge on performance and capacity at various temperatures. The charged cells were temperature conditioned at either -23°C, -4°C, 24°C or 49°C for four hours and then discharged at either 1,2,5, or 10 amperes.

Once the initial evaluation was complete both the Ni-MH cells and Ni-Cd cells were assembled into three packs of 10-cell each so that all the cells were exposed to the air and physically separate from each other. The only exception to this was the cell used to control the temperature cut-off charge which had an attached thermocouple and was insulated. Both types of cells were tested to the following test regimes. The packs were charged at one of the following three different rates: (1) Constant current C/10 rate for 15 hours, (2) Constant current 0.3C for 5 hours, and (3) Constant current of 0.45 amperes until the pack temperature rises 15°C. The packs were then discharge at a constant current of 0.45 amperes until the voltage drops below 10.0 volts. There was also a 36 second 4.5 ampere pulse after 50% of the estimated discharge.

Results and Discussions

The average cell initial capacity for the Ni-MH cells after five cycles was 0.986 ampere hours (Ah). The comparable "AA" Ni-Cd cells had an average capacity of 0.519 Ah. These Ni-Cd cells never reached the 0.6Ah nominal rating.

Both the Ni-MH and Ni-Cd cells appeared to have an average daily capacity loss, due to self discharge, of approximately 1% for temperatures up to 27°C (80°F). The losses due to self discharge approached 3 to 5% per day after storage at 49°C (120°F). The Ni-MH data closely tracks the self discharge data provided in both the Handbook of Batteries¹ and Maintenance-Free Batteries² for Ni-Cd cells. The self discharge of both systems appears nearly identical as should be expected as both systems have the same nickel electrode.

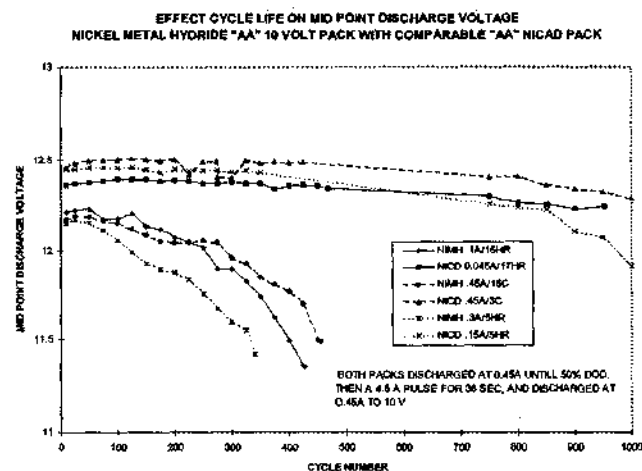
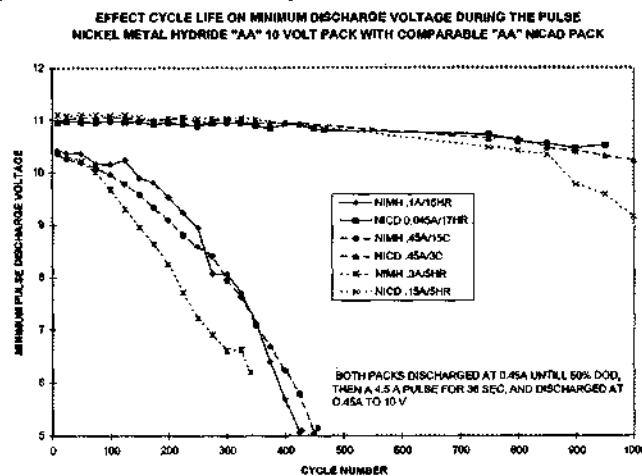
The rate carrying capability of Ni-MH cells is similar to Ni-Cd cells at currents below 5 amperes and at temperatures between 0°C and 49°C. At the 1 and 2 ampere rates and at temperatures above 0°C (32°F) there was little difference between both types of cells. At the 5 ampere rate the Ni-MH cells were only able to perform as well as the Ni-Cd cells at 49°C. For rates higher than 5 amperes the Ni-MH cells provided almost no capacity.

The Ni-MH cell packs charged using the temperature cut off method and the C/10 rate for 15 hours provided the best over all performance in the pack cycle life evaluation. The cells were assembled into packs and cycled using the same discharge method but with three different charge methods. All the Ni-MH packs failed in the end not because of loss of capacity but because of voltage decay during the mid discharge 36 second 4.5 ampere pulse.

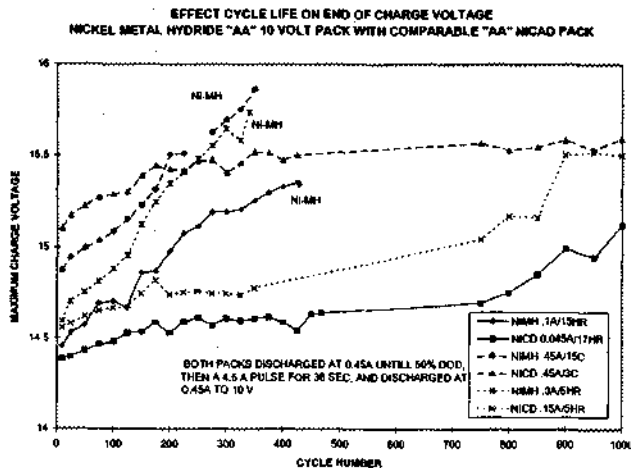
The most surprising result of the cycling study was that the Ni-MH minimum voltage during the 4.5 ampere pulse constantly decayed at a significant rate. This eventually caused the packs to fall below the minimum pulse voltage and fail long before the capacity began to drop noticeably. This characteristic was not evident in comparably tested Ni-Cd packs. For example the minimum voltage during pulse of the pack charged at 0.3 amperes for 5 hours fell below the 5 volt limit at approximately 340 cycles while the comparable Ni-Cd packs show no noticeable decay (Figure 1). This decay was evident in the other Ni-MH packs but to a lesser degree. The remaining two packs, 15 hr C/10 and delta charging, failed after 428 and 456 cycles respectively. Again none of the comparably tested Ni-Cd packs showed any decay of the minimum pulse voltage.

The drop in the minimum voltage appears to be natural characteristic of the Ni-MH system that has been exacerbated by the exceedingly high discharge pulse. Reference (1) shows the cell internal resistance increases with cycle life resulting in a continuous drop in the mid-point voltage and an increase in the end of charge

voltage. These Ni-MH packs showed a similar decay in the mid-point voltage (this is the voltage just prior to the pulse and can be seen in Figure 2).



The maximum charge voltage also increased with cycle life. This same characteristic was noted in Reference (1). This increase in charge voltage was more pronounced in cells that received the higher charge rates in excess of 0.10 amperes (Figure 3). During the same period only one of the Ni-Cd packs, which was charged at a high rate (0.45A to a rise of 3°C) also exhibited this high voltage but at level lower than the comparable Ni-MH pack. The final end of charge voltage for the packs was above 1.53 volts for all the Ni-MH packs.



Conclusions

Ni-MH cells can provide an effective alternative to conventional Ni-Cd cells in most applications that do not demand very high rates (for example lower than 4 amperes for these "AA" cells) and operate in temperatures near or slightly below 0°C (32°F). The operating life and self discharge of both Ni-MH and Ni-Cd cells suffer if

operated extensively at temperatures above 40°C. Applications that require performance significantly lower than 0°C should most likely remain with Ni-Cd's. The Ni-MH cells can be discharged at rates higher than 4 amperes but this will significantly shorten the service life by permanently depressing the operating voltage. Eventually the operating voltage will drop below the minimal threshold resulting in a premature failure.

The Ni-MH cells may not be able to handle long duration pulses in excess of 4 amperes without adversely affecting cycle life. The manufacturer's data showed that the maximum rated continuous current for the cell was 4 amperes which is slightly lower than the pulse value of 4.5 amperes. The length of the pulse may have been too long for the cell and may have caused irreversible damage, evidenced by the depressed pulse voltage which worsened with cycle life. The depressed operating voltage and increased charge voltage seem to be evidence of increased cell internal resistance.

The Ni-MH cells tested exhibited an ever decreasing discharge voltage which eventually caused pack failure. The mid point discharge voltage and the minimum pulse voltage appear to constantly decrease as the cell is cycled. This depressed voltage appears irreversible and is thought to be the result of an increase in the internal resistance of the cell. The most likely cause of this increase may be either the loss of electrolyte or permanent change in the

metal hydride electrode. Under the profile tested, which included a 4.5 ampere pulse for 36 seconds, the Ni-MH packs fell below the pulse minimum voltage of 5 V after between 340 to 456 cycles. The pack charged at 0.3 amperes for 5 hours appears to be the most severely abused pack and failed after 340 cycles and the rest failed after approximately 430 cycles.

The benefits of Ni-MH cells far outweigh the limitations when compared with Ni-Cd cells. Even though the Ni-MH cells have a shorter cycle life and require more stringent operating controls they provide significantly higher capacities than Ni-Cd cells. The cells tested in this study had an average capacity of 1 Ah as compared to the comparable capacity for Ni-Cd cells of between 0.5 and 0.6 Ah. The newest Ni-MH "AA" size cells claim an even higher capacity of approximately 1.8 Ah. The cycle life issue may be a moot point because if the Ni-MH cell lasts only half as long as a Ni-Cd but provides nearly twice the operating life then the Ni-MH is far the better choice. The only two major liabilities, barring cost would be that these cells do not operate as well at low temperatures or provide the same power as Ni-Cd cells.

The best overall charging scheme, where practicable, is a 0.10 ampere (C/10) constant current charge of 15 hours. This rate had the least effect on both the increase in end of charge voltage and decreases in pulses and midpoint voltages. The cells, when charged at this lower rate, may be less susceptible to degradation caused by electrolyte loss due to heating and over charge. The charge method that showed the next best performance was the 0.45 ampere charge to a 15°C temperature change cut-off. This charge showed only moderately higher rates of decrease in both pulse and mid point voltages while it had the highest end of charge voltages. Unfortunately the failure mode of all these packs is not capacity loss but failure to meet the minimum voltage requirement during the pulse.

References

1. David Linden, Ed, Handbook of Batteries, 2nd ed, McGraw Hill, New York, 1995
2. D. Berndt, Maintenance-Free Batteries Lead-Acid, Nickel/Cadmium, Nickel/Hydride A Handbook of Battery Technology, John Wiley & Sons Inc NY 1993