
LINDEN'S HANDBOOK OF BATTERIES

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Fourth Edition



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Exhibit 2008

Ningde Amperex Technology Ltd.

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Linden's Handbook of Batteries, Fourth Edition

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CHAPTER 22

NICKEL-METAL HYDRIDE BATTERIES

Michael Fetcenko and John Koch

22.1 INTRODUCTION

Nickel-metal hydride (NiMH) batteries have become a commercially important rechargeable battery system in high volume production for multiple consumer and vehicle propulsion applications. From commercial introduction in 1989 for portable PCs, today NiMH has enabled widespread commercialization of hybrid vehicles and is increasingly important in many consumer applications. In 2008, the NiMH market became a \$1.2B business, gaining a 10% share of the total rechargeable battery industry. The key driving forces for the rapid growth of NiMH have been the growth of HEVs and the development of NiMH batteries as direct replacements for alkaline primary batteries.

NiMH was first studied in the 1960s as a derivative of both The NiCd and The NiH_2 batteries used in satellites. The key motivations for the NiMH studies were the environmental advantages associated with higher energy, lower pressure, and cost of NiMH compared to NiCd. Implementation issues included corrosion and catalytic stability of the hydrogen storage alloy in a hostile alkaline environment. Key research organizations during the 1970s included Battelle (Beccu et al.) and Anwar (Percheron et al.), where progress was reported. Accelerated R&D efforts in the 1980s by Philips (Willems et al.) and Ovonic (Ovshinsky et al.) targeted advanced materials to overcome technical limitations that hindered commercial introduction.

In the mid-1970s, electric vehicles emerged due to what turned out to be temporary gasoline shortages. In the early 1990s, vehicle electrification reemerged due to environmental air quality concerns in urban areas. Today, NiMH is the rechargeable battery chemistry of choice for commercial HEVs, providing overall excellent performance, reliability, and cost. NiMH dominates HEV applications through a combination of desirable performance attributes such as high energy and power, an excellent range of operating temperatures, and low cost. Further, NiMH has demonstrated excellent safety, abuse resistance, and cycle life, which have translated into superior field reliability for advanced vehicular applications and overall performance in consumer applications since 1991.

The early 1990s also saw the parallel introduction of rechargeable lithium technologies, which featured still higher gravimetric energy density. Markets that were once dominated by NiCd and NiMH, laptop computers and cell phones, have been replaced by Li-ion. Yet, NiMH technology has expanded into new markets that were until recently the exclusive domain of alkaline primary cells. The recent introduction of NiMH rechargeable batteries, with their "ready to use" capability and equal or better performance than alkaline, has achieved wide market acceptance. The key to this NiMH technology advancement is charge retention, which has significantly improved to a remarkable 85% for 1 year. Further NiMH market growth based on its other performance attributes, such as cost, safety, life, and versatility of cell sizes and geometry, is expected to continue.

22.1

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22.2 GENERAL CHARACTERISTICS

Table 22.1 summarizes the key advantages and disadvantages of the sealed NiMH battery. In addition to the essential characteristics of low cost, reliability, cycle life, and operating temperature, the following features of NiMH^{1,2} have helped establish the technology's preeminence:

- Flexible cell sizes from 0.06 to 250 Ah
- Safe operation at high voltage (320+ V)
- Excellent volumetric energy and power, flexible vehicle packaging
- Easy application to series and series/parallel strings
- Choice of cylindrical or prismatic cells
- Safety in charge and discharge, including tolerance to abusive overcharge and overdischarge
- Maintenance free
- Excellent thermal properties (-30 to 70° C)
- Capability to utilize regenerative braking energy
- Simple and inexpensive charging and electronic control circuits
- Environmentally acceptable and recyclable materials

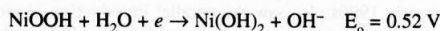
TABLE 22.1 Major Advantages and Disadvantages of Sealed Nickel-Metal Hydride Batteries

Advantages	Disadvantages
Higher energy density and specific energy compared to lead-acid and nickel-cadmium	Higher cost than lead-acid
Good high-temperature and high-rate capability	Lower specific energy and specific power compared to Li-ion
Good charge retention	Decreased performance at low temperature
Long cycle life	
Rapid recharge capability	
Long shelf life	
Sealed maintenance-free design	
Safe	

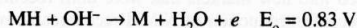
22.3 NiMH BATTERY CHEMISTRY

22.3.1 Chemical Reactions

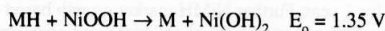
During discharge, nickel oxyhydroxide is reduced to nickel hydroxide



and the metal hydride (MH) is oxidized to the metal alloy (M).



The overall reaction on discharge is



The process is reversed during charge.

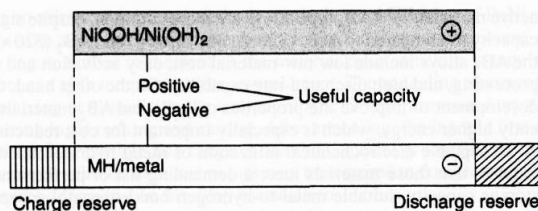
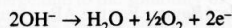


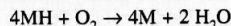
FIGURE 22.1 Schematic representation of electrodes of sealed nickel-metal hydride cell, divided into useful capacity, charge reserve, and discharge reserve.

The sealed nickel-metal hydride cell uses an oxygen-recombination mechanism to prevent the buildup of pressure that may result from the generation of gases toward the end of the charge and in overcharge. This is shown schematically in Fig. 22.1. During charge the positive electrode reaches full charge before the negative and begins to evolve oxygen.



The oxygen gas diffuses through the separator to the negative electrode facilitated by the starved-electrolyte design and the use of an appropriate separator.

At the negative electrode, the oxygen reacts with the hydrogen electrode to produce water. This results in stabilizing the internal pressure of the battery.



Furthermore, the negative electrode does not become fully charged, which prevents the generation of hydrogen. This is true for the early stages of cycling where the only gas found inside the cell is oxygen. However, continued cycling of the cell results in hydrogen gas beginning to be evolved, and a noted increase in the proportional hydrogen within is observed. The reason for this behavior is the result of oxygen recombination on the surface of the metal hydride negative electrode, an exothermic reaction that causes localized heating of the metal hydride alloy. This heating in turn affects the equilibrium pressure of the alloy resulting in the release of hydrogen and increased pressure during charging. The charge current must then be controlled at the end of charge and during overcharge to limit the generation of oxygen to below the rate of recombination to prevent the buildup of gases and pressure.

A factor in the design of NiMH batteries is the negative to positive ratio (N/P). It is based on the use of a negative electrode (the metal hydride electrode) that has a higher effective capacity than the positive (or nickel oxyhydroxide electrode). Overall, as shown in Fig. 22.1, having an excess of metal hydride (MH) capacity allows for gas recombination reactions to occur during overcharge (oxygen recombination) and overdischarge (hydrogen recombination, see Sec. 22.10.11). In addition, excess MH electrode capacity is provided to inhibit oxidation and corrosion of the MH alloy. N/P ratios vary by cell design and for a given manufacturer but are typically within the range of 1.3 to 2.0. The lower N/P values are used to maximize energy while higher values are used in power and cycle life designs. The useful capacity of the battery is thus determined by the positive electrode.

22.3.2 Metal Hydride Alloy

NiMH batteries are an unusual battery technology in that the metal hydride active material is an engineered alloy made up of many different elements, and the MH alloy formulas vary to a significant degree.^{3,4} The negative electrode contains either an AB_2 (LaCePrNdNiCoMnAl), an A_2B_7 ($\text{LaCePrNdMgNiCoMnAlZr}$), or an AB_2 (VTiZrNiCrCoMnAlSn) disordered type metal hydride

active material.^{5,6,7,8} AB_5 type alloys are more common, despite significantly lower hydrogen storage capacity as compared to A_2B_7 (320 vs. 380 mAh/g) and AB_2 (320 vs. 440 mAh/g). The advantages of the AB_5 alloys include low raw-material cost, easy activation and formation, flexibility in electrode processing, and high discharge-rate capability. On the other hand, there has been significant ongoing development to improve the properties of A_2B_7 and AB_2 materials to take advantage of their inherently higher energy, which is especially important for cost reduction.

Acceptable electrochemical utilization of metal hydride materials as anodes in NiMH batteries requires that those materials meet a demanding list of performance attributes, including hydrogen storage capacity, suitable metal-to-hydrogen bond strength, acceptable catalytic activity, discharge kinetics, and acceptable oxidation/corrosion resistance. Multi-element, multiphase, disordered alloys of the $LaNi_5$, $LaMgNi$, and $VTiZrNiCr$ types are attractive development candidates for atomic engineering due to a broad range of elemental addition and substitution possibilities, availability of alternative crystallographic phases that form the matrix for chemical modification, and a tolerance for non-stoichiometric formulas. Through the introduction of modifier elements, easy activation and formation has been achieved. Special processing steps (such as alloy melting and size reduction) suitable for these metallurgically challenging materials have been developed.

The metal hydride active materials also have similar special design options. The active materials may be adjusted to obtain added capacity, power, or cycle life.

AB_5 Metal Hydride Alloys. For the AB_5 system, typical formulas include:

- $La_{5.7}Ce_{8.0}Pr_{0.8}Nd_{2.3}Ni_{59.2}Co_{12.2}Mn_{6.8}Al_{5.2}$ (atomic percent a/o)
- $La_{10.5}Ce_{4.3}Pr_{0.5}Nd_{1.3}Ni_{60.1}Co_{12.7}Mn_{5.9}Al_{4.7}$

While the capacity of the various AB_5 alloys is typically around 290 to 320 mAh/g, other overall performance attributes can be greatly influenced by changing the ratio of A to B elements in the alloy. It is common for the ratio of La/Ce to be reversed to emphasize cycle life and power. The total amount of Co, Mn, and Al significantly affect the ease of activation and formation, but increased cobalt has higher-cost implications. After production of the AB_5 alloy ingot, it is common to further refine the microstructure of the material by a post-anneal treatment at higher temperature for several hours. The annealing treatment can have a significant effect on capacity, discharge rate, and cycle life by adjusting crystallite size and grain boundaries, as well as by eliminating unwanted crystal structures that may be formed during ingot melting and casting. After annealing, the ingot is first crushed and then ground to the desired final particle size range. Additional special processing methods such as melt spinning and other rapid solidification techniques can also promote higher cycle life, although these processing methods are more expensive and there may be other trade-offs, such as discharge-rate capability.⁹

Commercial AB_5 alloys have a predominantly $CaCu_5$ crystal structure. However, within that structure, there are a range of lattice constants brought about by compositional disorder¹⁰ within the material that are important to catalysis, storage capacity, and stability to the alkaline environment and embrittlement. These materials also precipitate a nickel-cobalt crystal structure, which is important to high-rate discharge.^{11,12}

A_2B_7 Metal Hydride Alloys. A_2B_7 alloys also provide for compositional and processing choices. Popular A_2B_7 alloy formulas (a/o) include:

- $La_{4.8}Ce_{0.4}Pr_{9.1}Nd_{5.4}Mg_{1.7}Ni_{68.8}Co_{3.0}Mn_{0.2}Al_{5.5}Zr_{0.2}$
- $Nd_{18.7}Mg_{2.5}Ni_{74.7}Co_{0.1}Al_{3.6}Zr_{0.2}$

A_2B_7 alloy capacity may range from 335 to 400 mAh/g. Ce is often excluded from the alloy in an effort to reduce the tendency to form AB_5 crystal structures. The addition of Co helps reduce lattice expansion while Al forms a protective dense surface oxide, and together both improve the cycleability of the alloy. The addition of Mn has been shown to play a role in regulating the amount of the various crystal structures present, while the addition of Zr has been shown to improve the high-rate discharge capability of the alloys.

Alloy preparation using conventional methods results in a combination of PuNi_3 and CaCu_2 crystal structures within the alloy, but Mg is present only in the PuNi_3 crystal structure. After production of the A_2B_7 alloy ingot, further refinement of the material microstructure is required using a post-annealing treatment at a high temperature for several hours. The annealing treatment has been shown to be critical in reducing or eliminating the amount of AB_5 or other unwanted crystal structures that may be formed during ingot melting and casting. After annealing, the ingot is first crushed and then ground to the desired final particle size range. Additional, special processing methods such as melt spinning and other rapid solidification techniques may be required to completely eliminate unwanted AB_5 crystal structures depending on the alloy formulation.

AB_2 Metal Hydride Alloys. AB_2 alloys also provide for compositional and processing choices. Popular AB_2 alloy formulas (a/o) include:

- $\text{V}_{18}\text{Ti}_{15}\text{Zr}_{18}\text{Ni}_{29}\text{Cr}_5\text{Co}_7\text{Mn}_8$
- $\text{V}_5\text{Ti}_9\text{Zr}_{26.7}\text{Ni}_{38}\text{Cr}_5\text{Mn}_{16}\text{Sn}_{0.3}$
- $\text{V}_5\text{Ti}_9\text{Zr}_{26.2}\text{Ni}_{38}\text{Cr}_{3.5}\text{Co}_{1.5}\text{Mn}_{15.6}\text{Al}_{0.4}\text{Sn}_{0.8}$

AB_2 alloy capacity may range from 385 to 450 mAh/g. Higher vanadium-content alloys may suffer from higher rates of self-discharge due to the solubility of vanadium oxide and its consequent ability to form a special type of undesirable redox shuttle. The concentration of Co, Mn, Al, and Sn is important for easy activation, formation, and long cycle life. The ratio of hexagonal C_{14} to cubic C_{15} crystal structure is important for improving capacity or power.

Alloy preparation is done using conventional melting and casting methods to produce an ingot. After casting, the ingot is processed using a hydride/dehydride sequence to reduce the ingot into smaller pieces. These smaller pieces are then ground to the desired final particle size range. After grinding, oxygen is slowly introduced to allow for the growth of a protective oxide layer.

For all metal hydride alloys, the metal/electrolyte surface oxide interface is a crucial factor in discharge rate capability and cycle life stability. Original LaNi_5 and TiNi_2 ¹³ alloys extensively studied in the 1970s and 1980s for NiMH battery applications were never commercialized due to poor discharge rate and cycle life capability.^{14,15} Lack of catalytic activity at the surface oxide limits discharge, and lack of sufficient oxidation/corrosion resistance is a critical obstacle to long cycle life. The complicated chemical formulas and microstructures of present disordered AB_5 , A_2B_7 , and AB_2 alloys extend to the surface oxide. For the surface oxide, important factors include thickness, microporosity, and catalytic activity. Of importance to a high discharge rate was the discovery that ultrafine metallic nickel particles having a size on the order of 50 to 70 Å or less and dispersed within the oxide are excellent for catalyzing the reaction of hydrogen and hydroxyl ions.¹⁶

The other critical design factor within the surface oxide is to achieve a balance between surface oxide passivation and corrosion. Porosity with the oxide is important to allow ionic access to the metallic catalysts and therefore promote high-rate discharge. While passivation of the surface oxide is problematic for high-rate discharge and cycle life, unrestrained corrosion is equally destructive. Oxidation and corrosion of the anode metals consume electrolyte, change the state of charge balance, and create corrosion products that are sometimes soluble and capable of poisoning the positive electrode. Establishing a balance between passivation and corrosion for stability is a primary function of the compositional and structural disorder.

22.3.3 Nickel Hydroxide

Positive electrodes for use in NiMH batteries, whether cylindrical or prismatic, can be of the sintered or pasted type, which are also common to NiCd batteries. The nickel hydroxide for use in NiMH batteries is fundamentally the same as that used in NiCd and NiFe, and from a simple viewpoint, the basic compound is the same as that used by Edison and Junger 100 years ago. However, today's high-performance nickel hydroxide is more advanced and continues to improve in capacity, utilization, power and discharge rate capability, cycle life, high temperature charging efficiency, and cost.

Spherical Nickel Hydroxide. As mentioned previously, one type of nickel hydroxide is by far the most common—a high-density spherical type used in pasted electrodes which became commercial around 1990.^{17,18} High-density spherical nickel hydroxide is made in a precipitation reactor where metal salts such as nickel sulfate are reacted with a caustic such as NaOH in the presence of ammonia. The nickel source may have additives such as cobalt and zinc to enhance performance. The important physical parameters within this type of nickel hydroxide are:

- **Chemical formula:** The nickel hydroxide active material itself is most commonly a NiCoZn tri-precipitate; a common composition is $\text{Ni}_{94}\text{Co}_3\text{Zn}_3$. However, the amounts of cobalt and zinc, which are usually about 1 to 5% each, can be adjusted for conductivity, oxygen overvoltage, and microstructure refinement with some design trade-offs in terms of active material capacity and cost. Other more complicated multi-elemental precipitates such as NiCoZnCaMg offer higher capacity, cycle life, and high-temperature performance, but cannot be manufactured by conventional precipitation processes.
- **Tap density:** Usually around 2.2 g/cc, tap density is a measure of the dry nickel hydroxide powder packing efficiency and influences the amount of active material that can be loaded into the pores of the nickel foam current collector.
- **Particle size:** An average particle size of about 10 microns.
- **Surface area:** Measured by the BET method, surface area refers not to the geometric area of each nickel hydroxide sphere, but rather to the total surface area of each particle, which contributes to the charge-discharge reactions and can thus affect utilization and high-rate discharge capability. Typical BET surface area for high-density spherical nickel hydroxide is about 10 to 20 m^2/g .
- **Crystallinity:** Each nickel hydroxide sphere has an extremely high surface area corresponding to the nickel hydroxide crystallites themselves. Crystallinity is measured by x-ray diffraction, where the full width at half maximum (FWHM) of a reflection, such as the $\langle 101 \rangle$ plane, may yield a typical crystallite size of about 110 Å.

A variety of other factors contribute to performance, such as impurities from processing like residual sulfates, nitrates, sodium sulfate, and others.

The more common pasted nickel hydroxide positive electrode is typically produced by mechanically pasting high-density spherical nickel hydroxide into the pores of a foam metal substrate (Fig. 22.2). The foam metal substrate is typically produced by coating polyurethane foam with a layer of nickel either

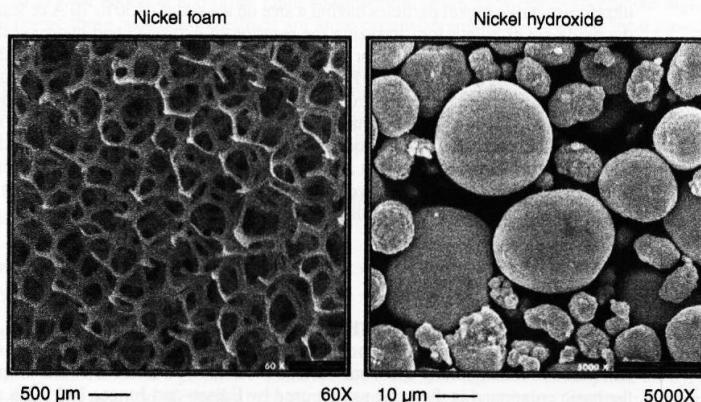


FIGURE 22.2 SEM micrographs of positive electrode nickel foam substrate and high-density spherical nickel hydroxide.

by electroplating or by chemical vapor deposition, followed by a heat treatment process to remove the base polyurethane. The pore size may be decreased from about 400 microns to 200 microns for better conductivity. The density of the foam may also be adjusted to promote conductivity and power versus capacity and utilization.

The foam¹⁹ is then physically loaded with nickel hydroxide having an average diameter of about 10 microns in a paste containing conductive cobalt oxides, which form a conductive network to compensate for the large distance from the nickel hydroxide to the metal current collector and for the fact that the nickel hydroxide itself is relatively low in conductivity. A cross-sectional comparison of sintered and pasted positive electrodes is presented in Fig. 22.3 under backscattered electron imaging, where the bright areas indicate metallic nickel current collection.

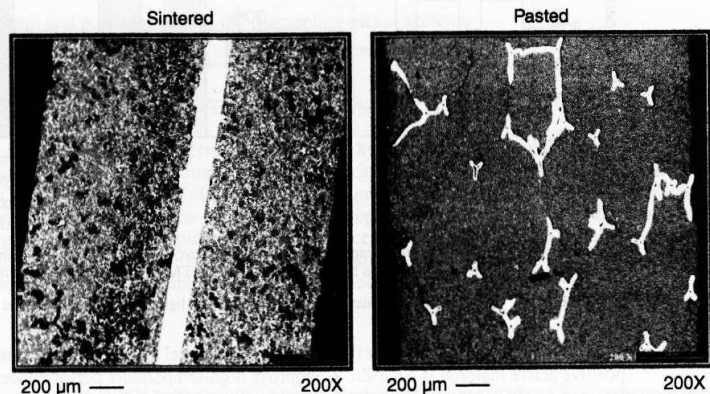


FIGURE 22.3 SEM micrographs under BEI imaging where bright areas indicate nickel metal current collection, illustrating the difference in active material distance to current collector for pasted and sintered positive electrodes.

The nickel hydroxide active material and electrode formula can be specially formulated for specific applications. For operation at temperatures above 35°C, some manufacturers may use other additives to the paste formula to inhibit premature oxygen evolution on charge (see "High-Temperature Nickel Hydroxide" below).²⁰ In addition, paste formula modifications may adjust the type and quantity of conductive network additives such as cobalt metal and cobalt monoxide.^{21,22,23} Usually, the paste additives are finely divided cobalt metal and cobalt monoxide that will dissolve and reprecipitate on the surface of the nickel hydroxide active material. However, the coating may not be uniform and complete in coverage.

For ultra-high-power discharge, it is possible to add metallic nickel fibers to the paste formula to enhance conductivity. In the case of calcium additives, the additive may cause a loss in power and/or cycle life. Cobalt metal and cobalt monoxide are relatively expensive battery materials, and increased use has cost implications. Addition of metallic nickel fibers lowers the amount of active material, resulting in reduced capacity and specific energy.

High-Temperature Nickel Hydroxide. To combat the premature oxygen evolution mechanism resulting from temperatures above ambient, manufacturers often introduce oxygen evolution suppressants such as $\text{Ca}(\text{OH})_2$, CaF_2 , or Y_2O_3 . As shown in Fig. 22.4, introduction of these additives can reduce capacity loss under 65°C charging from about 50% to below 20%. NiMH manufacturers must carefully select the oxygen suppressant type, amount, and location to avoid deleterious effects such as power loss and cycle life reduction due to the nonconductive nature of many of these materials.

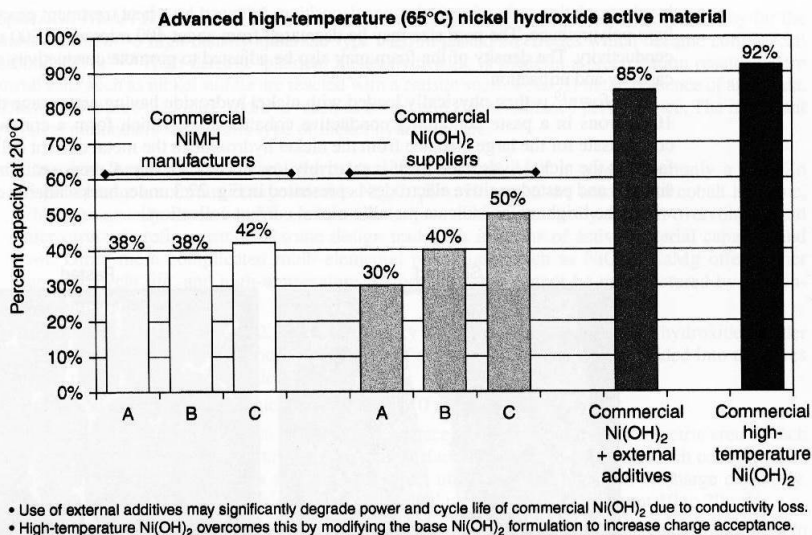


FIGURE 22.4 Temperature performance of cylindrical C-size batteries using commercial nickel hydroxide.

Another method is to modify the formula of the nickel hydroxide itself. The most common NiMH positive active material is NiCoZn. To improve high-temperature performance, multi-element formulas such as NiCoZnCaMg have been developed, as shown in Fig. 22.5.

Sintered Nickel Hydroxide. Sintered electrodes have the best rate and power capability,²⁴ but sacrifice capacity on a weight and volume basis and are more expensive to manufacture. Sintered

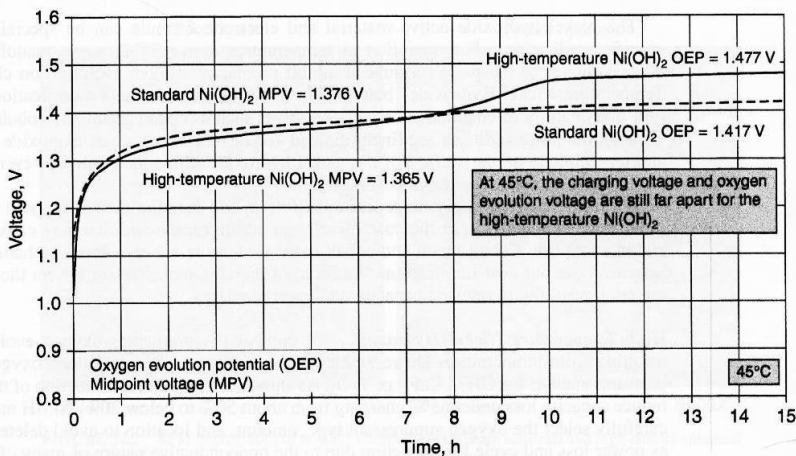


FIGURE 22.5 Charge characteristics of nickel hydroxide as a function of chemical formulation at 45°C.

electrodes involve an expensive and complicated sequence of manufacturing steps, and consequently it is typical that only companies with an existing capital investment for this kind of process would manufacture sintered electrodes. Sintered positives begin with the pasting of filamentary nickel²⁵ onto a substrate such as perforated foil, where the nickel fibers are then sintered under a high-temperature annealing furnace in a nitrogen/hydrogen atmosphere, and binders from the pasting process are burned away to leave a conductive skeleton of nickel having a typical average pore size of about 30 microns.

Nickel hydroxide is then precipitated into the pores of the sinter skeleton using either a chemical or electrochemical impregnation process. The impregnated electrode is then formed or preactivated in an electrochemical charge/discharge process. Important design variables in the manufacture of sintered nickel hydroxide electrodes include:

- Strength and pore diameter of the filamentary nickel skeleton
- Chemical composition of the nickel hydroxide active material
- Active material loading
- Amount of harmful impurities (e.g., nitrate, carbonate)

One aspect of sintered versus pasted nickel hydroxide technology is that sintered electrodes require the battery manufacturer to make a significant capital investment in facilities and equipment, and to have a great deal of internal expertise in processing. Pasted electrodes, conversely, place a great deal of emphasis on the expertise of the suppliers for both the nickel foam substrate and for the high-density spherical nickel hydroxide. Recent development in pasted electrode technology has brought about exceptional improvements in power and high-rate discharge capability to a level comparable to that of the sintered electrode technology.

22.3.4 Electrolyte

The electrolyte in NiMH batteries of all types is routinely a mixture of about 30% potassium hydroxide in water, providing high conductivity over a wide temperature range. It is most common for the electrolyte to have a lithium hydroxide additive at a concentration of about 17 g/L to promote improved charging efficiency at the nickel hydroxide electrode by suppressing oxygen evolution, the competing reaction to charge acceptance.

An important feature of the electrolyte is related to fill fraction. Essentially all NiMH batteries are of the sealed, starved electrolyte design. Similar to NiCd, the electrodes are nearly saturated with electrolyte, while the separator is only partially saturated to allow for rapid gas transport and recombination.

Special electrolytes are also used in NiMH batteries to enhance high-temperature operation. Instead of binary KOH/LiOH electrolytes, it is also possible to substitute a portion of the KOH with NaOH. The ternary KOH/NaOH/LiOH electrolyte is still at a high concentration of about 7M, but the contribution of NaOH promotes high-temperature charging-efficiency although it is typical for this electrolyte to decrease cycle life through increased corrosion of the metal hydride active materials.

22.3.5 Separator

The primary function of the separator is to prevent electrical contact between the positive and negative electrodes, while holding electrolyte necessary for ionic transport. Original separators for NiMH batteries were standard NiCd and NiH₂ separator materials. However, NiMH batteries proved to be more sensitive to self-discharge, especially when conventional nylon separators were used.²⁶ The presence of oxygen and hydrogen gas causes the polyamide materials in the nylon separator to decompose. The corrosion products from this decomposition allowed for poisoning of the nickel hydroxide, promoting premature oxygen evolution and also forming compounds capable of redox shuttle between the two electrodes, which further increases the rate of self-discharge.

In addition, the separator plays a crucial role relative to cycle life. In the starved electrolyte design, it is a common design principle to essentially saturate the electrodes with electrolyte at the assembly stage. The separator is designed to have a high electrolyte fill fraction in order to hold as much electrolyte as possible but not be overfilled so as to inhibit gas recombination. To the battery manufacturer, this means that during the first few charge/discharge cycles ("formation"), when the electrodes have not yet absorbed their full amount of intended electrolyte, charging must be initiated carefully to avoid venting.

The electrolyte design concept relates to capillary theory so that the electrolyte will migrate to the smallest pores. In the NiMH battery, this translates to the nickel hydroxide positive electrode having the smallest pores, followed by the metal hydride negative electrode, and finally the separator. At cell assembly, it is common for the separator to be about 90% filled, and then reduced to about 70% during the cell formation process of the first few charge/discharge cycles as both the positive and negative electrodes expand and contract, opening interior regions for electrolyte absorption. This process continues to some degree over many hundreds of charge/discharge cycles, where NiMH cell failure is common when the separator fill fraction has been reduced to about 10 to 15% of its original level. As a result, separators that can absorb larger quantities of electrolyte at cell assembly, have small pores able to compete for electrolyte, and retain surface wettability are highly desirable. Inspection of the separator in failed batteries shows even these types of separators undergo some degradation and loss of electrolyte absorption ability, although not nearly to the same degree as earlier generation separators.

Consequently, there was a need for a more stable NiMH separator material to reduce self-discharge while still retaining electrolyte crucial for maintaining cycle life. In NiMH batteries, there is now widespread use of what is termed "permanently wettable polypropylene." In fact, this separator is a composite of polypropylene and polyethylene where the base composite fibers require special surface treatments to make them wettable to the electrolyte. Currently there are two major types of surface treatments:

- **Acrylic acid:** This process involves the grafting of a chemical such as acrylic acid to the base fibers to impart wettability and is accomplished using a variety of techniques such as UV or cobalt radiation.²⁷
- **Sulfonation:** This process imparts wettability to the polypropylene by exposing the base fiber material to fuming sulfuric acid. The separator surface is designed to be made hydrophilic to the electrolyte after completion of the treatment. Use of sulfonated separator materials is a key component in enabling "precharged" NiMH battery technology.

22.4 CELL CONSTRUCTION TYPES

Sealed nickel-metal hydride cells and batteries are constructed in cylindrical, button, and prismatic (both large and small) configurations, similar to those used for sealed nickel-cadmium batteries.

The electrodes are designed with highly porous structures having a large surface area to provide a low internal resistance and a capability for high-rate performance. The positive electrode in the cylindrical NiMH cell is a highly porous sintered or foam-nickel substrate into which the nickel compounds are impregnated, or pasted, and converted into the active material by electro-deposition. Foams have generally replaced sintered plaque electrodes. Expanded metals and perforated sheets are lower cost, but they have poor high-rate capability. Sintered structures are much more expensive. The negative electrode, similarly, is a highly porous structure using a perforated nickel foil or grid onto which the plastic bonded active hydrogen storage alloy is coated. The electrodes are separated with a synthetic nonwoven material, which serves as an insulator between the two electrodes and as a medium for absorbing the electrolyte.

22.4.1 Cylindrical Configuration

The assembly of the cylindrical unit is shown in Fig. 22.6. The electrodes are spirally wound, and the assembly is inserted into a cylindrical nickel-plated steel can. The electrolyte is added and contained within the pores of the electrodes and separator.

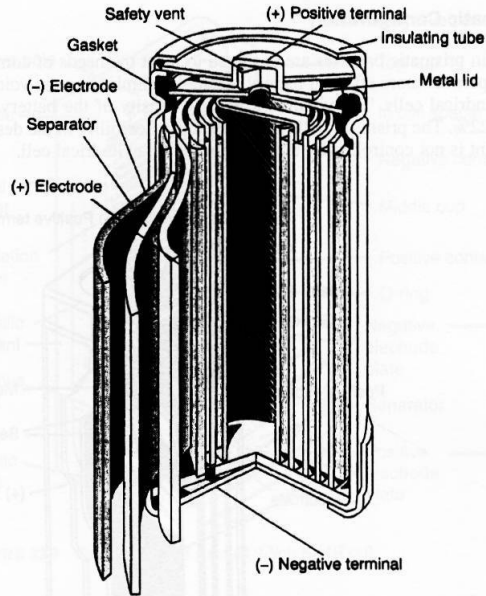


FIGURE 22.6 Construction of a sealed, cylindrical nickel-metal hydride battery.

The cell is sealed by crimping the top assembly to the can. The top assembly consists of a lid, which includes a resealable safety vent, a terminal cap, and a plastic gasket. The can serves as the negative terminal and the lid as the positive terminal, both insulated from each other by the gasket. The vent provides additional safety by releasing any excessive pressure that may build up if the battery is subjected to abuse.

22.4.2 Button Configuration

The button configuration is illustrated in Fig. 22.7. It is similar in construction to the nickel-cadmium button cell, except that the cadmium is replaced by the hydrogen storage alloy.

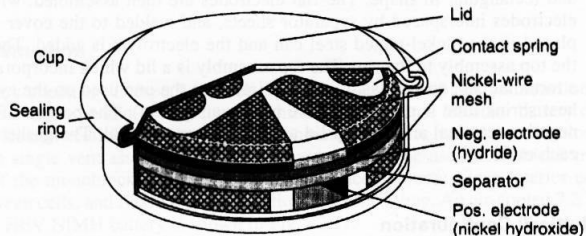


FIGURE 22.7 Construction of a sealed, nickel-metal hydride button cell.

22.12 SECONDARY BATTERIES

22.4.3 Small Prismatic Configuration

The thin prismatic batteries are designed to meet the needs of compact equipment. The rectangular shape permits more efficient battery assembly, eliminating the voids that occur within the assembly of cylindrical cells. The volumetric energy density of the battery can be increased by a factor of about 22%. The prismatic cells also offer more flexibility in the design of batteries, since the battery footprint is not controlled by the diameter of the cylindrical cell.

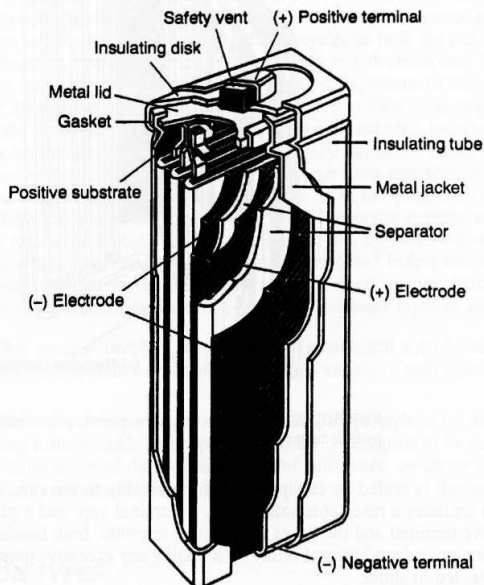


FIGURE 22.8 Construction of a sealed, thin, prismatic nickel-metal hydride button cell.

Figure 22.8 shows the structure of a prismatic battery. The electrodes are manufactured in a similar manner as the electrodes for the cylindrical cell, except that the finished electrodes are flat and rectangular in shape. The flat electrodes are then assembled, with the positive and negative electrodes interspaced by separator sheets, and welded to the cover plate. The assembly is then placed in the nickel-plated steel can and the electrolyte is added. The cell is sealed by crimping the top assembly to the can. The top assembly is a lid which incorporates a resealable safety vent, a terminal cap, and a plastic gasket, similar to the one used on the cylindrical cell. An insulating heat shrink tube is placed over the metal can (jacket). The bottom of the metal can serves as the negative terminal and the top lid as the positive terminal. The gasket insulates the terminal from each other.

22.4.4 9 V Multicell Configuration

The construction of a typical 9-Volt multicell battery is shown in Fig. 22.9.

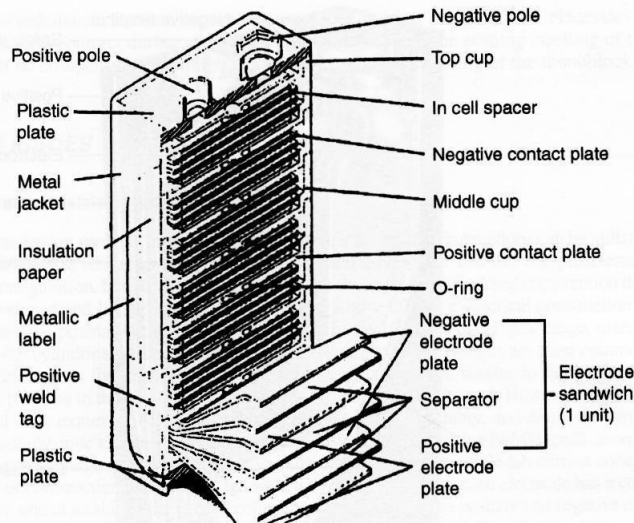


FIGURE 22.9 Cutaway view of a sealed 9-Volt NiMH cell.

22.4.5 Large Prismatic Configuration

The large prismatic configuration is similar in design to that of the small prismatic but with some exceptions, noted below.

Figure 22.10 shows the structure of a large prismatic battery. The electrodes are manufactured in a similar manner as the electrodes for the small prismatic cell. The electrodes are assembled with the positive and negative electrodes interspaced by separator sheets and welded to the individual terminals. The assembly is then placed into the can and the electrolyte is added. The cell is sealed by welding the top assembly to the can. The top assembly is a lid which incorporates a resealable safety vent, terminals, and plastic gaskets, similar to the one used on the cylindrical and small prismatic cell. The metal can (jacket) can be powder coated or taped with an insulating material to prevent cell to cell shorting. Two terminals projecting through the can lid serve as connections to the negative and positive electrodes, with a gasket insulating the terminals from the can.

22.4.6 Monoblock Construction

NiMH battery chemistry is especially well suited for HEV monoblock construction due to its high tolerance to overcharge and overdischarge, which pose problems for other battery chemistries. The monoblock design reduces cost by having a common pressure vessel construction and far fewer cell parts; a single vent assembly and shared hardware can be used in multicell modules. Further attributes of the monoblock construction include reduced volume, since interior cell walls can be shared between cells, and flexible choices of liquid or air cooling. An air-cooled 7.2 V 6.5 Ah plastic monoblock HEV NiMH battery is shown in Fig. 22.11.

Issues of monoblock construction include selection of the plastic casing material to avoid gas permeation and the need for individual cells to have well-matched capacity and impedance to avoid

22.14 SECONDARY BATTERIES

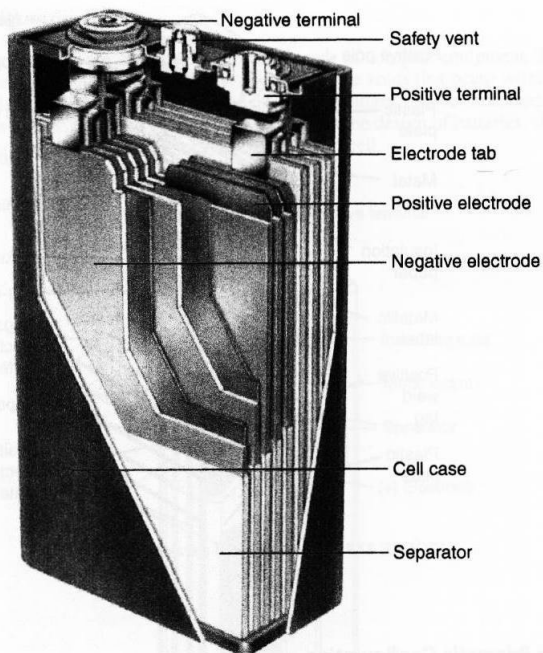


FIGURE 22.10 Cutaway view of a prismatic NiMH cell.

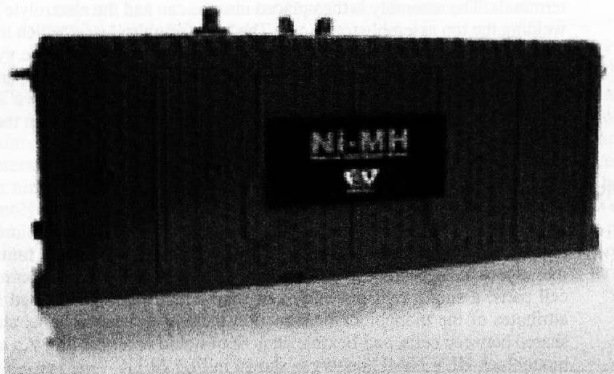


FIGURE 22.11 HEV plastic case prismatic module used in Toyota Prius.

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Ningde Amperex Technology Ltd.

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cell-to-cell imbalance. Further, monoblock construction must recognize that electrodes within each cell expand and contract during charge and discharge and that the ensuing swelling of the electrode stack must be compensated for in the mechanical design and loading of the monoblock.

22.5 CELL DESIGN ISSUES

22.5.1 Cylindrical versus Prismatic Configuration

NiMH batteries are versatile in that both cylindrical and prismatic constructions can be utilized. Each type of construction has advantages and disadvantages, and a particular end-use can predetermine the most suitable configuration. For NiMH applications below about 10 Ah, cylindrical construction dominates due to the lower cost and higher speed of manufacture. Above 20 Ah, cylindrical construction is extremely difficult, and the prismatic configuration dominates. In the 10 to 20 Ah cell size range, manufacturers are offering both cylindrical and prismatic designs, although prismatic designs are most common.

Cylindrical cells for industrial and propulsion applications are similar to high-volume production consumer batteries in that the well-known "jelly-roll" construction is used. However, most small portable cylindrical cells require only low to moderate discharge rate capability, and electrode terminal connections are usually quite simple. Conversely, since industrial and propulsion NiMH applications require high to ultra-high discharge rate capability and low internal resistance, multiple tab current collection is used. This type of construction is termed "edge welding" and requires that each electrode has a current collecting strip on one of its sides. The current collecting strips (both for the positive and negative electrodes) are disposed on opposite sides of the jelly-roll. After coil winding of the jelly-roll, the edge current collector is welded in multiple locations to each electrode. Other aspects of cell assembly are virtually identical to small consumer batteries. The net result of the enhanced current collection is a reduction in specific energy due to added weight, but an increase in specific power due to decreased cell AC impedance (usually around 8 to 12 m Ω for small portable batteries and around 1 to 2 m Ω for industrial cylindrical cells). For industrial applications such as HEV, motorcycle, and bicycle applications, the most popular cylindrical cell sizes are standard C and D sizes, although a multitude of height changes within that diameter are also used. Some work on larger size cells such as F size has also been reported.²⁸

Prismatic construction is conventional in that electrode stacks of alternating positive and negative electrodes with intermediate separators are used (as shown in Sec. 22.4.5). The main design alternatives involve the thickness and number of each of the electrodes and the aspect ratio (relative proportions of cell height to width to thickness). Key design variations include the ratio of active materials to inactive components (such as the cell can and terminal, and current collectors). In all cases, the cell designer has the objective of emphasizing one or more properties of performance characteristics such as energy versus power, while maintaining a minimum threshold of other performance parameter such as cycle life. One example is that for EV NiMH prismatic cells,²⁹ a specific power of about 200 W/kg is acceptable for most vehicles. Consequently, relatively thick positive and negative electrodes can be used to increase the ratio of active material to inactive cell components, thereby providing specific energy in the 63 to 80 Wh/kg range. Alternately, HEV prismatic NiMH batteries typically must deliver a specific power greater than 1300 W/kg, and therefore electrode thickness is reduced as compared to the electrode thickness used for EV applications. NiMH batteries for HEV use have a typical specific energy ranging from about 42 to 68 Wh/kg.

22.5.2 Metal versus Plastic Cell Cases

NiMH cylindrical cells exclusively use metal cell cases. One important reason for this is that the can itself is electrically connected to the metal hydride negative electrode and serves as the negative terminal. Another important reason is that many applications require fast charge in which gas recombination can cause considerable internal pressure and only the strength of a metal container would suffice without significant volumetric penalties. Finally, the metal crimp seal to the cover plate assembly with a polysulfone seal ring is inexpensive, fast, and reliable.

Both metallic and plastic cell cases are common for the prismatic NiMH batteries used in automotive applications such as electric vehicles. Unlike cylindrical cells where the can itself is the negative terminal, prismatic designs have both a positive and negative terminal at the top cover plate. Key decision criteria for selecting metal cell cases include excellent thermal conductivity, inexpensive prototyping costs for changing cell dimensions, and small volumetric penalties.

The primary advantage of plastic cell cases are cost and electrical isolation in the ≥ 320 V battery packs common to today's electric vehicles, where even high resistance leakage currents must be considered. Further design considerations for plastic cell cases include development costs for permanent molds, gas permeation, thermal conductivity, and sufficient plastic thickness for gas pressure containment without wall bulging. NiMH battery modules using plastic cell cases are shown in Fig. 22.12.

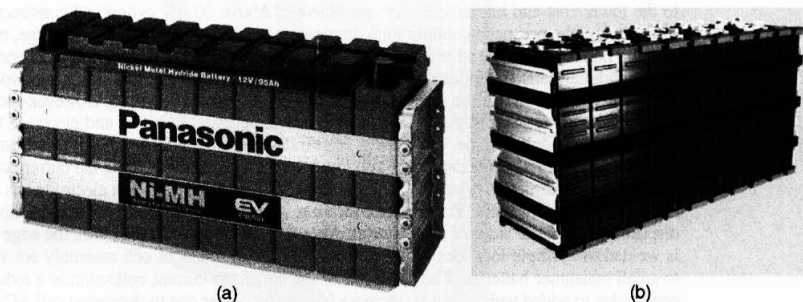


FIGURE 22.12 NiMH battery modules using (a) plastic cases; (b) metal cases.

22.5.3 Energy versus Power Design Trade-offs

Similar to other rechargeable battery technologies, NiMH batteries can be designed to emphasize energy, power, or some combination of the two. The application itself may dictate the choice, but perhaps not for obvious reasons. In electric vehicle applications, a certain threshold power such as 200 W/kg is required for adequate vehicle performance, and once the power requirement is met, competing designs usually tout specific energy in the range of 62 to 80 Wh/kg. The motivation for the higher energy is of course longer vehicle range, but can be attained only with added cost. The typical figure of merit for electric vehicle battery cost is \$/kWh, where the USABC/PNGV goal of \$150 per kWh has proven to be one of the most challenging development targets. NiMH cost is mainly controlled by the amount, cost, and utilization of raw materials rather than processing labor, assembly, packaging, etc. Consequently, an important development activity for many NiMH manufacturers is to obtain higher utilization of less expensive active materials on a mAh/g basis and therefore reduce battery costs.

For HEV applications, specific energy is of far less importance since the battery has a vastly different function than in pure electric vehicles. For HEVs, the main purpose of the battery is to accept and utilize the energy from regenerative braking and assist in acceleration at startup. The battery is commonly exposed to very-high-current pulses during both charge and discharge, but energy extraction is usually limited to relatively small depths of discharge. The crucial requirement for the NiMH HEV battery is therefore specific power, and the USABC/PNGV goal for battery developers is greater than 1000 W/kg. NiMH batteries available today are in the 1000 to 1300 W/kg specific power range, with development reports approaching 2000 W/kg. Besides performance required for HEV operation, an important figure of merit for NiMH battery developers is power cost in \$/kW, and the PNGV goal is below \$12 per kW. In this case, the specific energy for a typical HEV battery may be in the 32 to 56 Wh/kg range combined with specific power in the 1000 to 1300 W/kg range.

22.5.4 Cell, Module, and Pack Design

A typical 5.0 Ah C-size NiMH portable cell has an AC impedance on the order of 8 to 15 m Ω , and a $\Delta V/\Delta I$ resistance of 15 to 30 m Ω . In contrast, a 100 Ah NiMH EV cell has an impedance on the order of 0.4 m Ω , and a $\Delta V/\Delta I$ resistance of 0.9 m Ω . Despite the low resistance, heating is still a concern due to the extremely high current pulses resulting from regenerative braking and during vehicle acceleration. Even the I^2R heating effects at these high currents are small in comparison to heating due to overcharge. Consequently, an essential aspect of NiMH EV and HEV battery design involves thermal management.

Proper thermal management begins at the metal hydride negative electrode, understanding that overcharge heat is generated at the surface of the hydride electrode where oxygen is recombined. Heat must migrate from the negative electrode to the cell case and therefore good thermal conductivity within the electrode and electrode stack bundle is important. Cells are usually packaged into 12 V modules, with cells bound together in a back-to-back arrangement. An important design feature is that the cells at each end will have a much higher exposed surface area available for convective cooling. This raises concerns of thermal imbalance within a module and a resultant state-of-charge imbalance which will lead to premature failure. Therefore, proper module design must include end-plate and heat sink considerations.

Modules are packaged in a variety of configurations. Within the various packaging arrangements, important design considerations are distance between modules, air or water flow channels, and battery tray heat sink characteristics to equalize cooling from module to module.

22.5.5 Thermal Management—Water Cooling versus Air Cooling

A first step in NiMH EV, PHEV, and HEV thermal management is to decide whether to use water cooling or air cooling. There has not yet been a clear-cut consensus on which approach will dominate. At present, all hybrid electric vehicles use air-cooled batteries, including the Toyota Prius, Honda Insight, Ford Escape, and Fusion. Currently, demonstration models using other battery technologies for plug-in hybrids and pure electric vehicles require water-cooled batteries to more closely control temperature variations. The merits of each approach are highlighted in Table 22.2.

TABLE 22.2 Summary of the Merits for Thermal Management of HEV, PHEV, and EV Batteries

	Air cooling	Water cooling
Advantages	• Lightweight • Simple	• More effective heat transfer • Average fluid temperature more consistent • Integrated with vehicle cooling
Disadvantages	• Complicated distribution of air within pack • Incoming air must be free of dirt and water from road • Variable ambient temperature	• Increased weight • Elaborate module design • Higher average fluid temperature

22.6 EV BATTERY PACKS

22.6.1 USABC Performance Targets

It is interesting to review the USABC technical performance requirements, (see Table 22.3) and then evaluate why NiMH batteries led in virtually all worldwide EV battery demonstration and development programs before most manufacturers abandoned EV work in favor of HEVs.

TABLE 22.3 Primary USABC Midterm Performance Goals for the EV Battery and Actual Performance of the Commercial and Advanced NiMH Battery

Property	NiMH		
	USABC	Commercial	Prototype
Specific energy (Wh/kg)	80 (100 desired)	63–75	85–90
Energy density (Wh/L)	135	220	250
Power density (W/L)	250	850	1000
Specific power (W/kg) (80% DOD in 30 s)	150 (>200 desired)	220	240
Cycle life (cycles) (80% DOD)	600	600–1200	600–1200
Life (years)	5	10	10
Environmental operating temperature	–30° to 65°C	–30° to 65°C	–30° to 65°C
Recharge time	< 6 hours	15 min (60%) <1 h (100%)	15 min (60%) <1 h (100%)
Self-discharge	<15% in 48 h	<10% in 48 h	<10% in 48 h
Ultimate projected price (\$/kWh) (10,000 units at 40 kWh)	<\$150	\$220–400	\$150

Despite the complicated appearance of the USABC requirements, the actual development targets were quite simple. In 1991, there were only two types of automotive-size rechargeable batteries that could be used for electric vehicles: lead-acid and nickel-cadmium. Lead-acid batteries simply did not have sufficient specific energy and cycle life to be viable for EV use. NiCd batteries, while somewhat higher in specific energy and with good cycle life, were not high enough in energy and still faced the environmental issues inherent in the use of cadmium, operation in a flooded electrolyte configuration requiring maintenance, and with the memory effect.

NiMH dominated early EV applications over Na-S, Ni-Zn, and other advanced systems due to excellent overall performance, environmental friendliness, and safety factors. Essentially, an advanced battery technology for EV applications had to satisfy all minimum performance requirements and then compete on energy and cost. NiMH EV batteries demonstrated:

- **High energy:** Commercial electric vehicles (such as GM's EV1) achieved a range of over 200 mile when using NiMH batteries with a specific energy of 70 Wh/kg. Prototype vehicles (such as Solecia Force) using NiMH batteries demonstrated a 350 mile range.
- **High power:** Commercial electric vehicles using 220 W/kg specific power NiMH batteries had demonstrated acceleration comparable to ICE powered vehicles. Advanced EVs using NiMH routinely set race and demonstration range and speed records.
- **Flexible packaging:** EV NiMH batteries operated well in 320 V AC propulsion or 180 V DC propulsion systems and had a wide variety of cell capacities. The volumetric performance of NiMH was exceptional, offering vehicle designers a small size battery package.
- Long life (600 to 1200 cycles to 80% DOD).
- Wide operating temperature range (–30°C to + 65°C).
- Fast charge and simple normal charging.
- Maintenance-free operation.

The main developmental activity for NiMH EV batteries was to reduce cost. Because only prototype production volumes existed, the initial cost of manufacture for NiMH batteries was relatively high. Significant investment was made to decrease cost, with highlights including:

- **Pilot manufacturing capability:** Increased volume production allowed reduced overhead and labor, and the incorporation of automated and semi-automated manufacturing.
- **Increased specific energy:** By raising specific energy from 56 to 80 Wh/kg through increased utilization of active materials, the battery cost in \$/kWh had decreased significantly (>\$1000/kWh to <\$350/kWh, even at relatively low production volumes).
- **Lower cost nickel hydroxide:** From 1995, where high-density spherical nickel hydroxide prices were around \$30 per kg, new lower cost suppliers and manufacturing processes allowed nickel hydroxide prices to drop to about \$20 per kg.
- **Lower cost metal hydride materials:** Improved efficiency melt/cast processes, scrap recycle, elimination of costly sintering, versatile use of inexpensive substrate materials and significantly reduced battery formation.

22.7 HYBRID BATTERY PACKS

22.7.1 Hybrid Electric Vehicle Types

The crucial targets for HEV, as compared to PHEV or EV goals, include a much greater emphasis on power, both on charge and on discharge, and less emphasis on energy. For HEV applications, typical NiMH batteries have a specific energy in the 45 Wh/kg range and have attained a specific power of about 1000 to 1300 W/kg. HEV cycle life is measured at low depth of discharge (approximately 2 to 5% DOD) compared to 50 to 80% for PHEV and 80% DOD for EV. Even cost is calculated on available power in \$/kW. Car makers essentially want to use the smallest energy battery capable of supplying the required power. An important figure of merit target for the HEV car makers is a power to energy ratio (P/E) of 40. Present NiMH HEV batteries have attained P/E ratios of about 25.

In this context, the Partnership for the Next Generation Vehicles (PNGV) was established to enable automakers and the government to meet an equivalent fuel economy of 80 miles per gallon of gasoline. For many car manufacturers, development efforts focused on a variety of different hybrid electric vehicles of a variety of concepts.³⁰ For example, several types of HEVs were based on how the internal combustion engine (ICE) and electric drive are cooperatively incorporated into the system and, in a parallel design, how the ICE and the electric motor drove the wheels.

In all cases, the electric motor can also be used to recharge the battery. There are several different types of hybrids on the market today. The various operating modes for each type of vehicle make the size of the battery extremely wide ranging, anywhere from 0.5 to 20 kWh. The main difference between such operating modes is the degree of electrification (purely electric drive) involved. Below is a brief breakdown of these operating modes based on increasing levels of electric motor usage. More detailed information is found in Chap. 29.

Micro Hybrid. A micro hybrid uses start/stop technology where the ICE shuts down upon braking thereby reducing fuel consumption and emitting less pollution while stopped. The electric motors are incapable of providing the vehicle with any level of propulsion without ICE help and can recapture some energy through regenerative braking. The system consists of a 42 V battery and electric motor, with most manufacturers opting for lead-acid technology due to cost concerns. This type of hybrid operates in a charge-sustaining mode and is widely used by European automotive manufacturers.

Mild Hybrids. A mild hybrid, like the micro hybrid, uses stop/start technology, shutting down the engine for stops; is incapable of providing the vehicle with any level of propulsion without ICE help; and can recapture some energy through regenerative braking. Unlike the micro hybrid, a mild hybrid can provide some level of power assist to the ICE and operate at a higher voltage—140 to 160 V. This type of hybrid operates in a charge-sustaining mode and is used by automotive manufacturers such as GM, Mercedes, and BMW.

Full Hybrids (HEV). A full hybrid incorporates the same features as the micro and mild hybrids, i.e., start/stop and regenerative braking, and adds a limited range of pure electric propulsion—typically less than 5 miles at speeds under 35 mph. These full hybrids operate in a charge-sustaining mode and are used by automotive manufacturers such as Toyota, Honda, and Ford. The systems vary from automaker to automaker, but the batteries operate in the 200 to 300 V range with less than 2.0 kWh of energy storage.

Plug-in Hybrids (PHEV). A plug-in hybrid is a full hybrid but with a larger pure electric driving range—typically 10 to 40 miles at speeds up to 35 mph. The batteries for PHEVs operate in the same voltage range as the full hybrid and contain more energy, 5 to 20 kWh depending on vehicle size. They are equipped with a power cord and are designed to be recharged either at home or at public charging stations. This type of hybrid operates both in a charge-sustained mode and a charge-depletion mode, as shown in Fig. 22.13. This dual mode operation places a high degree of stress on the battery, making cycle life a determining factor in the choice of battery chemistry. Lithium-based PHEVs are currently in prototype production and testing by most major automotive manufacturers, such as Toyota, GM, Mercedes, BMW, and Ford, while Plug-In Conversions Corporation (PICC) is presently providing a 6.4 kWh NiMH battery for the aftermarket conversion of HEVs to PHEVs.

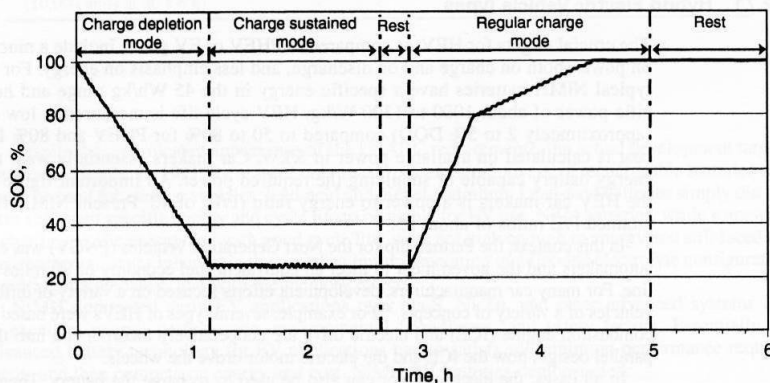


FIGURE 22.13 A simplified representation of a PHEV duty cycle.

22.7.2 Charge Depletion

Charge depletion concept hybrid vehicles are designed to have a certain vehicle range when driven solely in the electric vehicle mode. The motivation is that in heavily congested urban areas where air quality is a vital concern, the vehicle operates with zero emissions. Therefore, in the charge depletion mode the specific energy of the battery remains important, and a specific energy above 60 Wh/kg may be required. For example, a Toyota Prius HEV uses a 1.3 kWh NiMH prismatic comprised of 28 6-cell modules and has a pure electric vehicle range of less than 6 miles. However, when replaced with a 6.4 kWh, 30 Ah NiMH battery pack, the vehicle range on electric drive can be extended to over 25 miles.

22.7.3 Charge Sustained

The more common HEV concept is termed charge sustained, where the vehicle is designed to be operated under the various modes giving the greatest overall fuel economy. In this case, a primary function of the battery is to utilize the otherwise wasted energy of braking, and another main function is to assist the

vehicle during acceleration. This concept essentially embraces the fact that ICE engines are very efficient on the highway at constant speed but very inefficient under start-and-stop city traffic conditions. It is a common strategy for the engine to be shut off while the vehicle is stopped at a traffic light, and for the battery to supply the energy needed for the initial vehicle acceleration while the ICE is restarted.

22.8 FUEL CELL STARTUP AND POWER ASSIST

Fuel cells are a significant developmental focus for many companies worldwide, offering the potential for fuel economy exceeding the equivalent of 100 miles per gallon. The most commonly discussed fuel cell is the proton exchange membrane (PEM) type.

The relevance to NiMH batteries is that fuel cell vehicles will still require a substantial (approximately 1 to 10 kWh) battery for several reasons:

- **Startup:** The PEM fuel cell and reformer may operate at a temperature of about 100°C, and the battery must supply sufficient energy for the vehicle to operate until the system comes up to that operating temperature.
- **Acceleration:** A critical obstacle for a PEM fuel cell will be cost, due to its use of expensive catalysts and an expensive membrane. The fuel cell will be sized for an average required vehicle power, not for peak power conditions where the battery will dominate. Essentially, the fuel cell in a fuel cell hybrid electric vehicle is used to charge the battery and operate the vehicle, while the battery is used for power load-leveling.
- **Efficiency:** The fuel cell can be operated under close to steady state conditions in an optimum region of fuel utilization.
- **Regenerative braking:** Similar to ICE powered hybrid vehicles; the fuel cell has no mechanism to take advantage of the otherwise wasted energy of braking without the battery.

22.9 CONSUMER BATTERIES—PRECHARGED NiMH

NiMH technology continues to expand into new markets. Consumer products such as digital cameras and RC toys that were previously the exclusive domain of alkaline primary cells are now beginning to use rechargeable NiMH batteries with “ready to use” capability that provides the consumer a choice with equal or better performance than alkaline in some applications (see Chap. 32). Hence, “precharged” NiMH batteries are achieving wide market acceptance.

The key to this NiMH technology advancement has been the improvement in charge retention to a remarkable 85% for 1 year (comparable to alkaline). Much work has gone into reducing self-discharge mechanisms, resulting in two distinct classes of NiMH technology:

- **Conventional NiMH:** The rate of self-discharge is dependent on storage temperature and time—the higher the temperature, the greater the rate of self-discharge. This is illustrated in Fig. 22.14, which shows charge retention for conventional sealed cylindrical NiMH batteries following storage at different temperatures for varying periods of time. The comparison is for a battery discharged at the rated discharge load (approximately the 1C rate) at the stated temperature. Note that conventional, NiMH technology has a charge loss in the range of 20% for 30 days.
- **Advanced precharged NiMH:** This class of NiMH technology is often referred to as “ready to use.” These batteries are sold in the precharged state similar to alkaline primary cells and can be stored for up to 1 year with less than 20% loss in capacity. In order to achieve this low level of self-discharge, manufacturers typically use sulfonated separators, cobalt encapsulated Ni(OH)₂ with little added cobalt to the positive paste, and low corrosion AB₅ or A₂B₇ metal hydride alloys. This is illustrated in Fig. 22.15.

22.22 SECONDARY BATTERIES

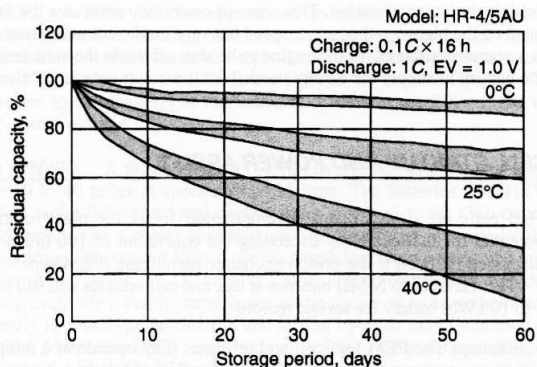


FIGURE 22.14 Charge retention characteristics of conventional NiMH cylindrical batteries at various temperatures.

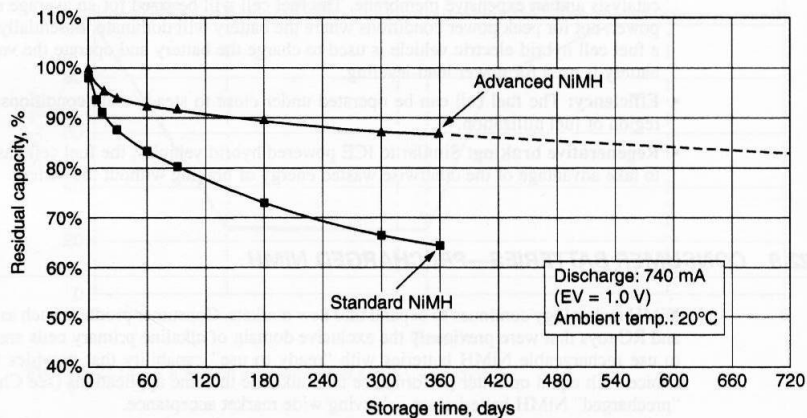


FIGURE 22.15 Charge retention characteristics of advanced vs. conventional NiMH cylindrical batteries.

Storage of the NiMH cell in a charged condition has no permanent effect on its capacity. Any capacity loss due to self-discharge is reversible, and batteries can recover to full capacity by simply recharging. However, storage at high temperatures, similar to operation at elevated temperatures, may deteriorate seals, MH alloys, and separators, leading to permanent damage, such as loss of capacity, cycle life, and overall battery lifetime. Hence, it is recommended that the temperature range for storage of NiMH cells be maintained at 20 to 30°C .

22.10 DISCHARGE PERFORMANCE

22.10.1 General Characteristics

The discharge characteristics of sealed NiMH batteries are very similar to those of sealed nickel-cadmium batteries. Several comparisons are illustrated in Chap. 15. The open-circuit voltage of the

batteries of both systems ranges from 1.25 to 1.35 V, the nominal voltage is 1.2 V, and the typical end voltage is 1.0 V.

(Note: All batteries were recharged between 20° and 25°C under conditions shown, unless specified otherwise.)

22.10.2 Discharge Characteristics

Cylindrical Batteries. Typical discharge curves for a cylindrical sealed NiMH battery under various constant current loads and temperatures are shown in Fig. 22.16. (The data are based on the rate performance at 20°C at the 0.2C discharge rate to 1.0 V.) A flat discharge profile is a characteristic. The discharge voltage, as expected, is dependent on the current and temperature. Typically, with higher currents or lower temperatures, one will observe a lower operating voltage in the battery. This is due to a higher IR drop resulting from increasing current or increasing resistance from the lower temperatures. However, because of the relatively low resistance of NiMH batteries (as well as nickel-cadmium batteries), this drop in voltage is less than experienced with other types of portable primary and rechargeable batteries.

Button Batteries. Typical discharge curves for button-type sealed NiMH batteries at room and other temperatures are shown in Fig. 22.17.

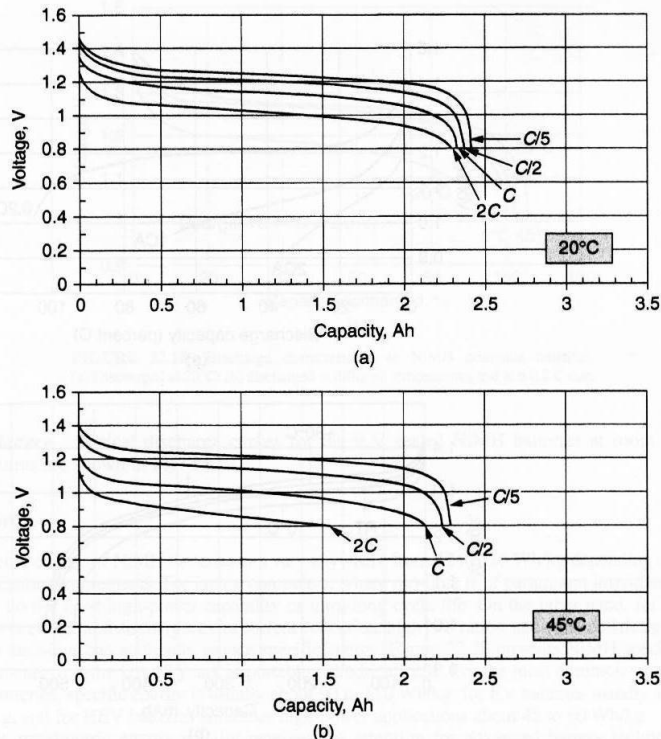


FIGURE 22.16 Discharge characteristics of NiMH cylindrical batteries. (a) Discharged at 20°C; (b) discharged at 45°C; (c) discharged at 0°C.

22.24 SECONDARY BATTERIES

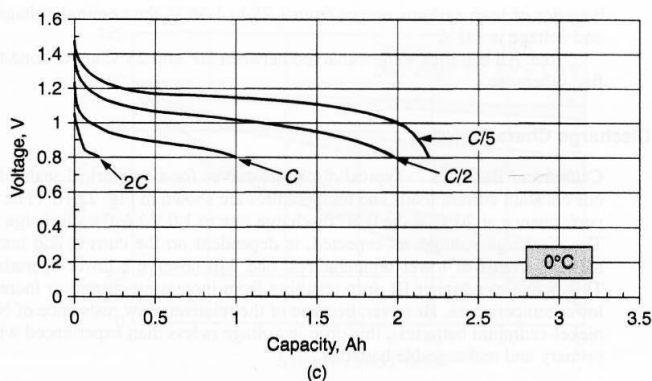


FIGURE 22.16 (Continued)

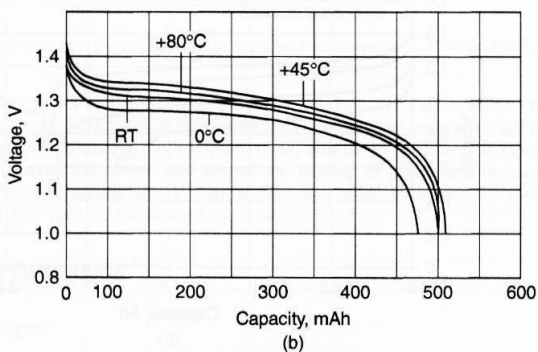
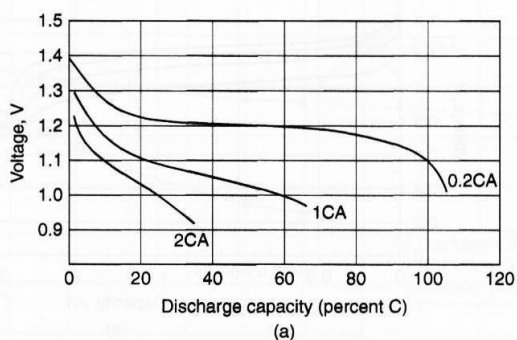


FIGURE 22.17 Discharge characteristics of NiMH button batteries. (a) Discharged at 20°C; (b) discharged at different temperatures and at a 0.2 C rate.

Prismatic Batteries. Typical discharge curves for the prismatic sealed NiMH batteries at room and other temperatures are shown in Fig. 22.18.

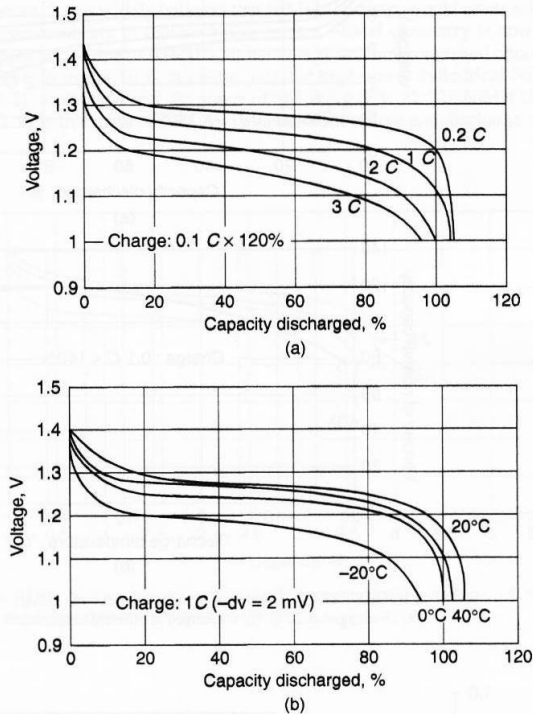


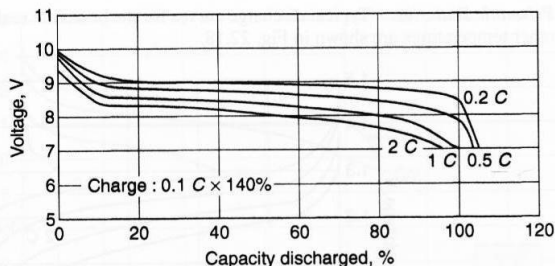
FIGURE 22.18 Discharge characteristics of NiMH prismatic batteries. (a) Discharged at 20°C; (b) discharged at different temperatures and at a 0.2 C rate.

9-Volt Battery. Typical discharge curves for the 9 V sealed NiMH batteries at room and other temperatures are shown in Fig. 22.19.

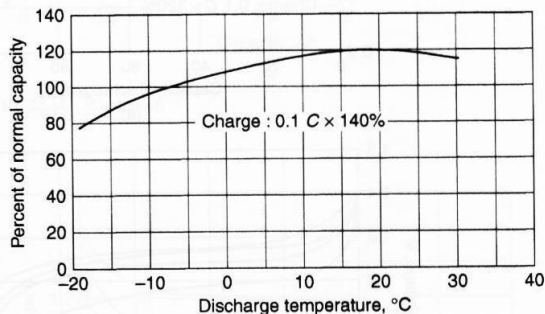
22.10.3 Specific Energy

The specific energy of NiMH batteries can vary anywhere from 42 to 110 Wh/kg depending on particular application requirements. For laptop computers, where run-time is of paramount importance, NiMH batteries do not need high-power capability or ultra-long cycle life. On the other hand, for extremely high-power charge and discharge, extra current collection, high N/P ratios, and other cell design and construction decisions can additively reduce specific energy. Figure 22.20 presents NiMH specific energy improvements over the last 18 years in portable cylindrical cells. For the most common small portable NiMH batteries, specific energy is usually about 90 to 110 Wh/kg, for EV batteries usually about 65 to 75 Wh/kg, and for HEV batteries and other high-power applications about 45 to 60 Wh/kg.

While gravimetric energy usually receives the attention for advanced battery technologies, in many cases volumetric energy density (in watt-hours per liter) is more important. NiMH has exceptionally high energy density, having achieved 430 Wh/L.



(a)



(b)

FIGURE 22.19 Discharge characteristics of NiMH 9 Volt batteries. (a) Discharged at 20°C; (b) discharged at different temperatures and at a 0.2 C rate.

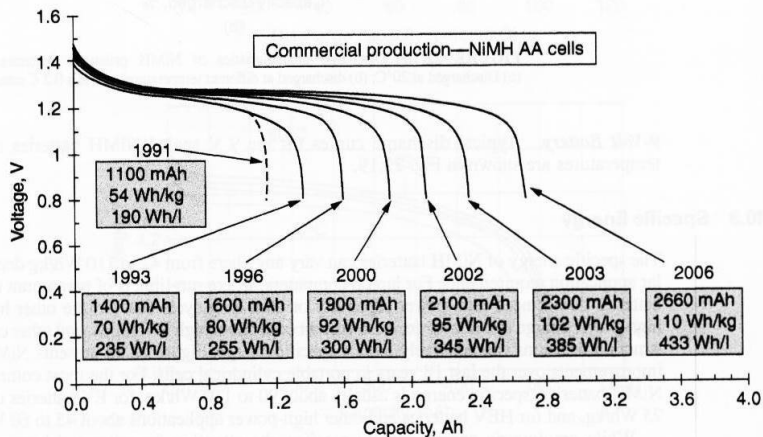


FIGURE 22.20 Evolution of specific energy for NiMH cylindrical AA-size batteries.

22.10.4 Specific Power

The power capability is a main strength of NiMH batteries relative to other advanced battery chemistries. For many years, it was widely believed that NiMH chemistry would never achieve a sufficiently high-rate discharge capability to replace NiCd. In fact, NiMH chemistry is now quickly replacing NiCd in these applications due to NiMH's higher energy and environmental concerns.

Voltage profiles up to the 10 C discharge rate for high-power cylindrical NiMH cells are presented in Fig. 22.21, attaining a specific power of 865 W/kg (Fig. 22.22). NiMH HEV module power shown in Fig. 22.23 is in excess of 1300 W/kg under both charge and discharge conditions.

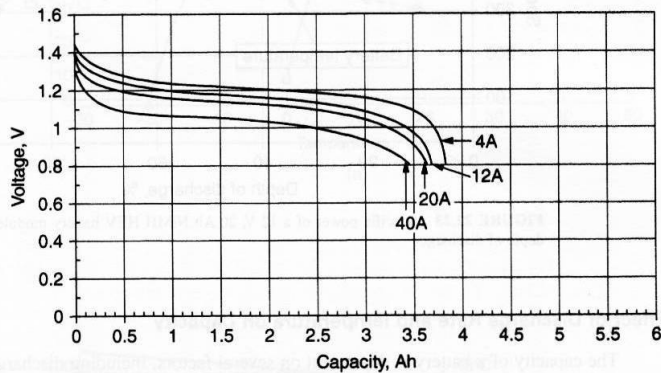


FIGURE 22.21 Voltage-capacity profiles for high-power NiMH cylindrical 3.5 Ah C-size batteries at different rates on continuous discharge.

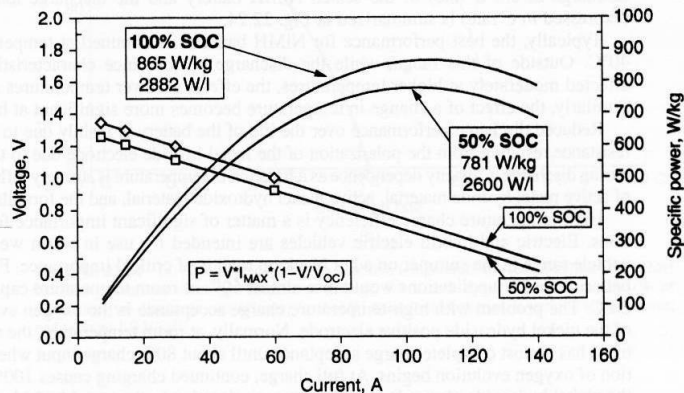


FIGURE 22.22 Specific power for ultra-high power NiMH cylindrical 3.5 Ah C-size batteries.

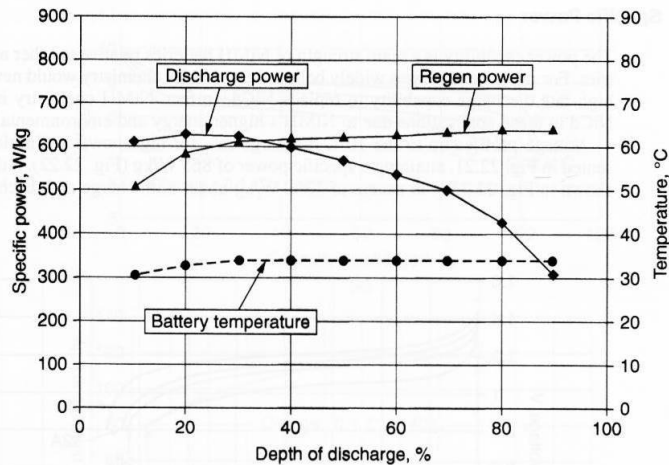


FIGURE 22.23 Specific power of a 12 V, 20 Ah NiMH HEV battery module as a function of depth of discharge.

22.10.5 Effect of Discharge Rate and Temperature on Capacity

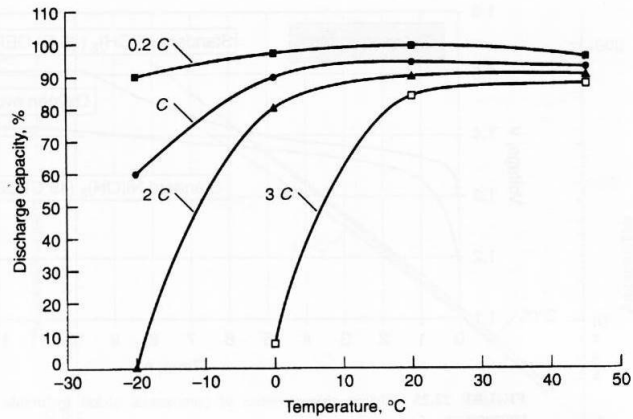
The capacity of a battery is dependent on several factors, including discharge current, temperature, and the cutoff or end voltage. The capacity can be increased by continuing the discharge to the lower end voltages, particularly at the higher current drain rates and lower temperatures, where the voltage drops off more rapidly than at the lighter drain rates. However, it should be noted there is a risk to the battery by discharging to too low a cutoff voltage as the cells may be permanently damaged (see Sec. 22.10.11). Hence, the cutoff or end voltage for the NiMH battery is typically 1.0 V per cell.

The relationship between the capacity (expressed as a percentage of the capacity at 20°C on discharge at 0.2 C rate) of the sealed NiMH battery and the discharge temperature and current (expressed in C rate) is summarized in Fig. 22.24.

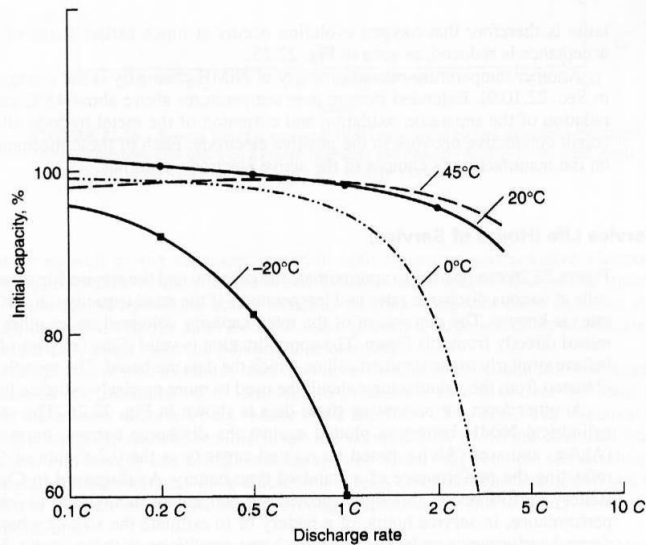
Typically, the best performance for NiMH batteries is obtained at temperatures between 0 and 40°C. Outside of this range, while the discharge performance characteristics of the battery are affected moderately at higher temperatures, the effects at lower temperatures are more pronounced. Similarly, the effect of a change in temperature becomes more significant at higher discharge rates.

Reduced discharge performance over the life of the battery is mainly due to an increase in internal resistance resulting from the polarization of the metal hydride electrode due to the generation of water during discharge. Capacity dependence as a function of temperature is strongly influenced by the selection of active metal hydride material, active nickel hydroxide material, and the formulation of the electrolyte.

High-temperature charge efficiency is a matter of significant importance for propulsion applications. Electric and hybrid electric vehicles are intended for use in warm weather climates, where vehicle range in the summer on a hot blacktop road is of critical importance. First-generation NiMH batteries for EV applications would lose almost 50% of room temperature capacity when charged at 60°C. The problem with high-temperature charge acceptance is the oxygen evolution characteristics of the nickel hydroxide positive electrode. Normally, at room temperature, the nickel hydroxide electrode has almost complete charge acceptance until about 80% charge input when the competing reaction of oxygen evolution begins. At full charge, continued charging causes 100% oxygen evolution at the nickel hydroxide electrode, and the oxygen migration to the metal hydride or cadmium electrode forms the well-known oxygen recombination overcharge mechanism. At elevated temperatures, the



(a)



(b)

FIGURE 22.24 (a) Discharge capacity vs. ambient temperature for sealed cylindrical NiMH batteries at various discharge rates; end voltage 1.0 V/cell. (b) Discharge capacity (% of 0.2 C rate) vs. discharge rate (C rate) for NiMH cylindrical batteries at various temperatures; end voltage 1.0 V/cell.

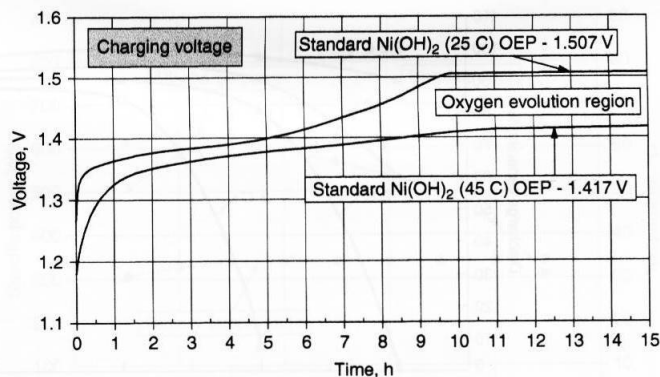


FIGURE 22.25 Charge characteristics of commercial nickel hydroxide as a function of temperature.

issue is therefore that oxygen evolution occurs at much earlier states of charge, and total charge acceptance is reduced, as seen in Fig. 22.25.

Another temperature-related property of NiMH chemistry is the storage effect on life (discussed in Sec. 22.10.9). Extended storage over temperatures above about 45°C can reduce life due to degradation of the separator, oxidation and corrosion of the metal hydride alloy, and disruption of the cobalt conductive network in the positive electrode. Each of these mechanisms is highly dependent on the manufacturer's choices of the active electrode materials.

22.10.6 Service Life (Hours of Service)

Figure 22.26 can be used to approximate the capacity and the service life of standard cylindrical NiMH cells at various discharge rates and temperatures if the rated capacity (at 20°C and the 0.2 C discharge rate) is known. The percentage of the rated capacity delivered under other conditions can be determined directly from this figure. The approximation is valid if the cells are of similar construction and behave similarly to the standard cell on which the data are based. The specific data for a given cell type obtained from the manufacturer should be used to more precisely estimate the performance.

Another form for presenting these data is shown in Fig. 22.26. The service life, in hours, of a cylindrical NiMH battery is plotted against the discharge current, normalized to the unit weight (Ah/kg) and size (Ah/L), based on a rated capacity at the 0.2 C rate of 60 Ah/kg and 200 Ah/L, reflecting the performance of a standard type battery. As discussed in Chap. 3 "Factors Affecting Battery Performance," this figure provides a convenient monograph to determine the approximate performance, in service hours, of a battery or to estimate the size of a battery that will deliver the desired performance under specified discharge conditions, with the caveat that the battery has similar construction and characteristics to the "standard" battery on which the data are based and an energy density close to the one specified.

22.10.7 Charge Retention

Charge retention is an area where NiMH manufacturers compete and the end-user must be careful to compare all performance properties for a given design. It is understood that the state-of-charge of a NiMH battery decreases during storage due to self-discharge and is highly dependent on

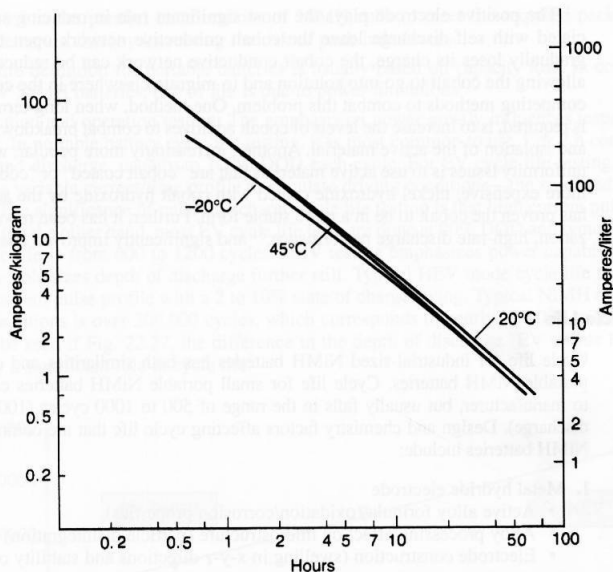


FIGURE 22.26 Service life of a standard NiMH cylindrical battery at various discharge rates and temperatures based on a specific capacity and capacity density under rated conditions at 20°C of 60 Ah/kg and 200 Ah/L; end voltage 1.0 V/cell.

temperature as well as the separator material, active positive and negative electrode materials employed. The specific formula of the metal hydride active material, separator material, and the quality of the nickel hydroxide active material all play important roles in either decreasing or increasing the self-discharge rate. Because there is such a large selection of materials for use in NiMH batteries, charge retention performance can vary.

For example, advanced separator materials have the ability to reduce self-discharge from about a 30% loss in one month at room temperature to about a 15% loss over the same time period. However, these same materials may reduce cycle life from 15 to 50%. The chemical mechanisms for how the separator reduces self-discharge are complicated, involving chemical grafting agents that can bind and thereby inactivate chemical species which may promote self-discharge. However, these separator treatments may have deleterious effects on electrolyte absorption and the ability of the separator to retain electrolyte during cycling. Separator dry-out is a very common mechanism of battery failure.

The choice of the metal hydride alloy can provide similar design trade-offs. Higher capacity AB_2 alloys also have higher rates of self-discharge compared to lower capacity AB_5 or A_2B_7 alloys discussed previously. The mechanisms for the effect of the MH alloy on self-discharge are two-fold. First, corrosion products from the hydride alloy may migrate to the nickel hydroxide positive electrode and promote oxygen evolution during storage. Second, other corrosion products such as vanadium with its multivalent oxides may form redox shuttle mechanisms similar to nitrate ions. Likewise, the quality of the nickel hydroxide material, the use of encapsulated nickel hydroxides as well as residual impurities such as nitrates and carbonates can influence the above-cited self-discharge mechanisms. However, ultra-low impurity levels and added encapsulation may add to processing costs.

The positive electrode plays the most significant role in reducing self-discharge. Losses associated with self-discharge leave the cobalt conductive network open to degradation. As the cell gradually loses its charge, the cobalt conductive network can be reduced to Co (2+) or Co metal, allowing the cobalt to go into solution and to migrate elsewhere in the cell. Currently, there are two competing methods to combat this problem. One method, when long-term storage over several years is required, is to increase the levels of cobalt additives to combat breakdown of the conductive network and isolation of the active material. Another, increasingly more popular, way to avoid cobalt loss and uniformity issues is to use active materials that are "cobalt coated" or "cobalt encapsulated." Although more expensive, nickel hydroxide coated with cobalt hydroxide by the active material manufacturer has proven the cobalt to be in a more stable form. Further, it has been reported to offer increased utilization, high-rate discharge performance,³¹ and significantly improved charge retention.

22.10.8 Cycle Life

Cycle life for industrial-sized NiMH batteries has both similarities and differences to that of small portable NiMH batteries. Cycle life for small portable NiMH batteries can vary from manufacturer to manufacturer, but usually falls in the range of 500 to 1000 cycles (100% DOD under 2 h charge/discharge). Design and chemistry factors affecting cycle life that are common to both large and small NiMH batteries include:

1. Metal hydride electrode
 - Active alloy formula (oxidation/corrosion properties)
 - Alloy processing effect on microstructure (particle disintegration)
 - Electrode construction (swelling in x-y-z directions and stability of conduction pathways)
2. Nickel hydroxide electrode
 - Active material formula (swelling and poisoning resistance)
 - Conductive network stability (amount and type of cobalt oxides)
 - Substrate (pore size, strength, and resistance to fracture)
3. Cell design
 - N/P ratio (amount of excess negative electrode capacity to influence cell pressure, MH corrosion, disintegration)
 - MH discharge reserve (overdischarge protection)
 - Separator (stability to corrosion, electrolyte absorption and retention, thickness, and resistance to short circuit)
 - Electrolyte (composition, amount, and fill fraction)
 - Vent pressure (weight loss, charge imbalance)
 - Electrode stack design (compression, electrode thickness, aspect ratio of height to width)

Factors affecting cycle life in industrial-sized NiMH batteries that differ from those factors affecting cycle life in portable NiMH batteries include:

- Significantly higher battery voltages (42 to 320 V versus 12 V) increases risk of abusive overcharge and overdischarge due to capacity or state-of-charge mismatch.
- Overall higher energy (0.1 kWh versus 33 kWh) increases heat generation and therefore the criticality of thermal management (which can be further influenced by battery pack enclosure heat transfer limitations).
- Typically higher operating temperature: Air-cooled and water-cooled vehicle batteries usually operate at a temperature of 35°C or higher, whereas operating temperatures for portable batteries may experience transient high temperatures, but on average are at or near room temperature.
- Series/parallel strings: In portable batteries, there are a large number of cell sizes available, ranging from 100 mAh button cells to 7 to 12 Ah D and F cells. There is a much smaller availability of cell sizes for HEV and EV NiMH batteries. Consequently, vehicle propulsion applications may

have to use series/parallel combinations of NiMH cells to meet the required pack voltage and energy demands, thereby increasing the risk of pack imbalances.

- End of life definition for portable batteries is usually based on capacity loss. In contrast, in EV and HEV NiMH batteries, end of life is due to power limitations.
- Qualification and operation testing: The emphasis on power greatly influences testing and methodology. In portable battery cycle life testing, it is most common to use 1 or 2 h constant current charge and discharge, usually to 100% DOD each cycle. For EV cycle life testing, discharge is usually a variable current/time profile to simulate driving conditions—the so-called “DST” drive profile. The significance of pulsed discharge cycle life testing is that high current pulses dominate the test. On the other hand, most EV cycle life tests are done at 80% DOD and typical NiMH module cycle life is from 600 to 1200 cycles. HEV testing emphasizes power capability even more, and de-emphasizes depth of discharge further still. Typical HEV mode cycle life testing is under a high current pulse profile with a 2 to 10% state of charge swing. Typical NiMH cycle life under these conditions is over 300,000 cycles, which corresponds to nearly 150,000 miles in a vehicle. As can be seen in Fig. 22.27, the difference in the depth of discharge (EV versus HEV cycling) can play a significant role in cycle life.

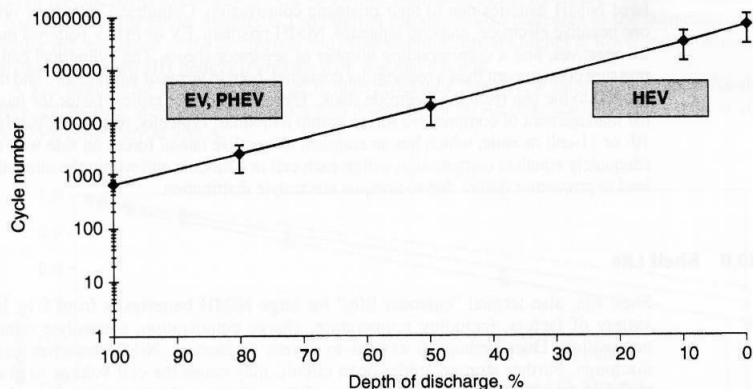


FIGURE 22.27 Relationship between depth of discharge (DoD) and cycle life for NiMH batteries.

Failure modes for EV, PHEV, and HEV batteries included short circuit due to mechanical penetration through the separator. The frequency of such events is usually small based on sound cell and electrode engineering and if manufacturing quality control is sufficient. Another failure mode may be due to abusive overcharge where excessive venting results in insufficient electrolyte within the separator. Abusive overcharge may result from charge imbalances caused by thermal differences from one part of the large battery to another. The problem may be compounded by the sophistication of the charger, where voltage and temperature sensing may not be on an individual module or cell basis. Another failure mode stems from overdischarge, where a cell or module within a high-energy PHEV or EV battery is discharged below the minimum recommended cell voltage of 1.0 V. Overdischarge is likely caused by state-of-charge imbalance within a high voltage string due to thermal gradients within a battery. Another source of abusive overcharge and overdischarge is the “weak cell or weak module” concept. This involves the statistical predictability within a large number of cells as to the decay rate of capacity, power, and resistance as a function of cycle.

A common feature of the above-cited EV/PHEV/HEV failure modes is the importance of maintaining state-of-charge balance within a battery pack that may contain several hundred individual

cells. The method used to maintain equalized state-of-charge within an industrial NiMH battery is in effect to routinely bring all the cells to the same state-of-charge. This method of using overcharge to equalize state-of-charge is corrupted if the cell temperature within a battery pack is extreme or if cell-to-cell temperature gradients are too large. One of the biggest factors in replicating the excellent cycle life of small portable NiMH batteries in EV, PHEV, and HEV applications is proper thermal management, which was discussed in Sec. 22.12.2.

If premature failure due to short circuit and abusive overcharge/overdischarge is prevented, the principal failure mode in industrial EV, PHEV, and HEV NiMH batteries is increasing internal resistance with cycling. The EV or PHEV user will observe that top acceleration will diminish after long-term use, or that vehicle range will gradually decrease. To the HEV end-user, battery failure due to increasing internal resistance and resultant power loss will be observed as an inability of the battery to assist acceleration during drive and the inability of the battery to utilize regenerative braking energy due to excessive heating caused by the high charging currents being supplied during braking.

This primary failure mode of increasing internal resistance and power loss during cycling is caused by the same mechanisms as observed in small portable NiMH batteries; namely, separator dry-out as a result of electrolyte redistribution due to swelling of the metal hydride and nickel hydroxide electrodes, consumption of electrolyte due to oxidation of the separator, metal hydride active material, and positive electrode materials, and loss of electrolyte through venting.³² These mechanisms may be exaggerated for large NiMH batteries due to their prismatic construction. Cylindrical cells have one positive electrode, one negative electrode, and one separator. NiMH prismatic EV or PHEV batteries may have 20 positives, 21 negatives, and a corresponding number of separator sheets. The cylindrical can is more effective in pressure containment than a rectangular container, both in terms of gas pressure and the mechanical forces applied to the can from the electrode stack. Therefore, another critical factor for large NiMH batteries is the management of compressive forces within a module. Typically, restraining bands are used to secure a 10- or 11-cell module, which has an endplate to equalize lateral forces on side wall of the can. Failure to adequately equalize compression within each cell in a module and within the internal cell stack itself will lead to premature failure due to unequal electrolyte distribution.

22.10.9 Shelf Life

Shelf life, also termed "calendar life," for large NiMH batteries is from 5 to 10 years based on a variety of factors, including temperature, charge equalization, electrolyte compensation, and gas permeation. Over perhaps 6 months to a year of storage, NiMH batteries may completely self-discharge. Further storage, under open circuit, may cause the cell voltage to gradually decline to 0 to 0.4 V, which can cause a breakdown of the cobalt conductive network in the positive electrode and/or increased surface oxidation of the metal hydride active material.³³ The length of time the battery is stored under this low voltage condition, the temperature of low voltage storage, and cell design influence the ease and degree of recovery of the battery. For example, a few cycles of low rate charge and discharge may be needed to recover cell capacity and power. If the degree of low voltage degradation is severe, the battery may not be recoverable.

Design factors that must be considered for good shelf life are the oxidation and corrosion resistance of the metal hydride alloy, the amount of precharge on the metal hydride electrode, the formula of the nickel hydroxide active material, and the quality of the cobalt conductive network in the positive electrode.

Considering the cost of industrial NiMH batteries, most users leave the battery on low-current trickle charge if the battery will not be used for extended periods. Alternately, the battery may receive a periodic top-off charge designed to compensate for normal self-discharge capacity losses.

22.10.10 Coulombic/Voltaic Efficiency and Internal Resistance

The NiMH battery has a low internal resistance because of the use of thin plates with large surface areas and low resistance and an electrolyte having a high conductivity. Figure 22.28 shows the change in internal resistance with the depth of discharge. The resistance remains relatively constant during

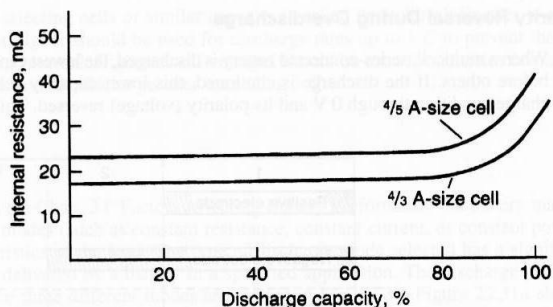


FIGURE 22.28 Internal resistance vs. discharge capacity of NiMH cylindrical batteries.

most of the discharge cycle. Toward the end of the discharge cycle, the resistance also increases due to conversion of the active materials. The internal resistance also increases as the temperature drops because the resistance of the electrolyte and other components are higher at lower temperatures. The resistance of the NiMH battery increases with use and cycling.

A key strength of NiMH technology is high efficiency due to low internal resistance. As shown in Fig. 22.29, over 90% voltaic efficiency was observed for 60 Ah prismatic NiMH EV cells at 100 A; over 75% efficiency at 300 A.

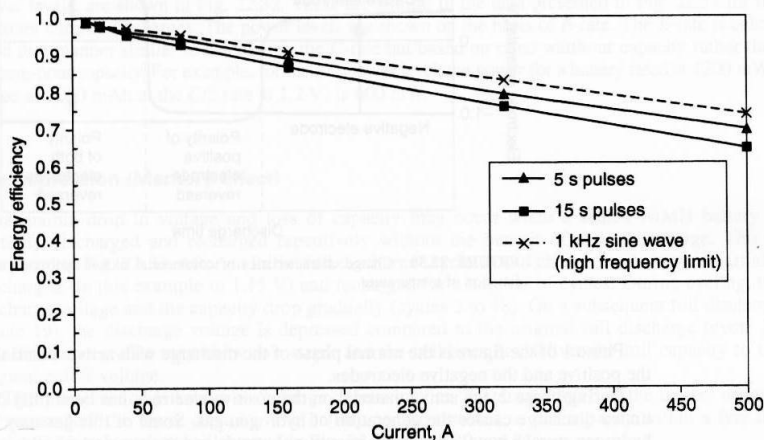


FIGURE 22.29 Energy efficiency of a 60 Ah NiMH HEV battery module as a function of discharge rate.

Voltaic efficiency is largely determined by the linear resistance components in the cell, the electronic and ionic resistances, which can be lowered by further engineering changes. Coulombic efficiency was determined to be 99% at 50% state of charge under an aggressive simulated HEV driving cycle, which is a typical operating point for charge-sustaining HEVs. Under the EPA combined city-highway FTP driving schedule, energy efficiency is about 93 to 95%.

22.10.11 Polarity Reversal During Overdischarge

When a multicell, series-connected battery is discharged, the lowest capacity cell will reach full discharge before others. If the discharge is continued, this lower capacity cell can be driven into an overdischarge condition through 0 V and its polarity (voltage) reversed. This is illustrated in Fig. 22.30.

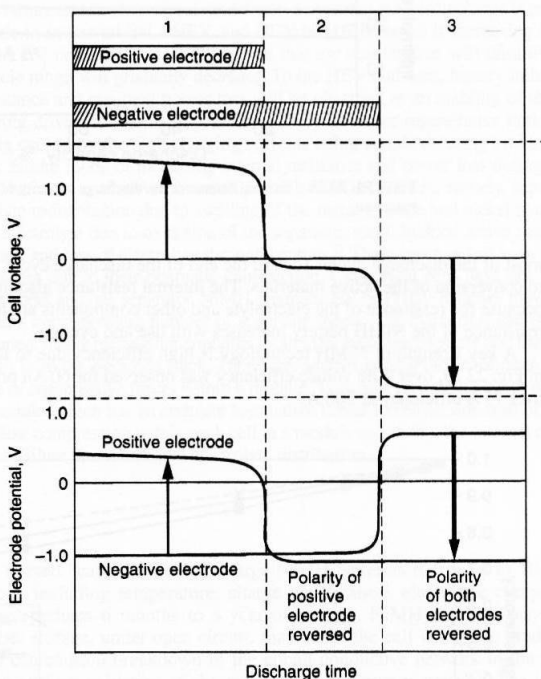


FIGURE 22.30 Charge characteristics of commercial nickel hydroxide as a function of temperature.

Phase 1 of the figure is the normal phase of the discharge with active material remaining on both the positive and the negative electrodes.

During phase 2, the active material on the positive electrode has been fully discharged and continued discharge causes the generation of hydrogen gas. Some of this gas may be absorbed by the hydrogen storage metal alloy in the negative electrode and the remainder builds up in the cell. Active material, however, still remains on the negative electrode and the discharge continues. The cell voltage is dependent on the discharge current, but remains within -0.2 to about -0.4 V.

In phase 3, the active materials on both electrodes have been depleted and oxygen is produced at the negative electrode. Prolonged overdischarge leads to gassing, higher internal cell pressure, venting, and deterioration of the cell.

The greater the number of cells in series (in a multicell battery), the greater the possibility a reversal of polarity will occur. To minimize the effect, whenever three or more cells are connected in series, the cell selection method employed should group cell capacities within a narrow range of $\pm 5\%$.

The process of selecting cells of similar capacity is called "matching." Further, a cutoff voltage of 1.0 V per cell or higher should be used for discharge rates up to 1 C to prevent the possibility that any cell goes into reversal. Higher cutoff voltages should be used for batteries containing more than 10 cells in series and for discharge rates exceeding 1 C.

22.10.12 Type of Discharge

As discussed in the Chap. 3 ("Factors Affecting Battery Performance") a battery may be discharged under different modes (such as constant resistance, constant current, or constant power), depending on the characteristics of the load. The type of discharge mode selected has a significant impact on the service life delivered by a battery in a specified application. The discharge profiles of a NiMH battery under the three different modes are plotted in Fig. 22.31. Figure 22.31a shows the voltage profile, Fig. 22.31b shows the current profile, and Fig. 22.31c shows the power profile during discharge of the battery. As an example, the data are based on the discharge of a 1000 mAh battery such that, at the end of the discharge (1.0 V per cell), the power output is the same for all modes of discharge. In this example the power output at the 1.0 V cutoff is 100 mW. To discharge at the 100 mW at 1.0 V, the constant current discharge is 100 mA (C/10 rate) and the constant resistance discharge is 10 ohms. As shown, the longest service life is obtained under the constant power mode as the average current is the lowest under this mode of discharge.

22.10.13 Constant Power Discharge Characteristics

The discharge characteristics of the NiMH battery under constant power mode, at several different power levels, are shown in Fig. 22.32. These are similar to the data presented in Fig. 22.31 for the constant current discharges. The power levels are shown on the basis of *E*-rate. The *E*-rate is calculated in a manner similar to calculating the *C*-rate but based on rated watt-hour capacity rather than ampere-hour capacity. For example, for the *E*/2 power level, the power for a battery rated at 1200 mWh (rated at 1000 mAh at the C/5 rate at 1.2 V) is 600 mW.

22.10.14 Voltage Depression (Memory Effect)

A reversible drop in voltage and loss of capacity may occur when a sealed NiMH battery is partially discharged and recharged repetitively without the benefit of a full discharge. This is illustrated in Fig. 22.33. After an initial full discharge (cycle 1) and charge, the battery is partially discharged (in this example to 1.15 V) and recharged for a number of cycles. During cycling, the discharge voltage and the capacity drop gradually (cycles 2 to 18). On a subsequent full discharge (cycle 19), the discharge voltage is depressed compared to the original full discharge (cycle 1). The discharge profile may show two steps, and the cell does not deliver the full capacity to the original cutoff voltage.

This phenomenon is known as "voltage depression" or "memory effect," as the battery appears to "remember" the lower capacity. The battery can be restored to full capacity within a few full discharge-charge cycles, as illustrated in Fig. 22.33 (cycle 20 and 21).

The voltage drop occurs because only a portion of the active materials are discharged and recharged during shallow or partial discharging. The active material that has not been cycled changes in physical characteristics and increases in resistance. The active materials are restored to their original state by subsequent full discharge-charge cycling.

The extent of voltage depression and capacity loss depends on the depth of discharge and can be avoided or minimized by discharging to an appropriate end voltage. The effect is most apparent when the discharge is terminated at higher end voltages, such as 1.2 V per cell. A smaller loss occurs if the discharge is cut off between 1.15 and 1.10 V per cell. Discharging to an end voltage

22.38 SECONDARY BATTERIES

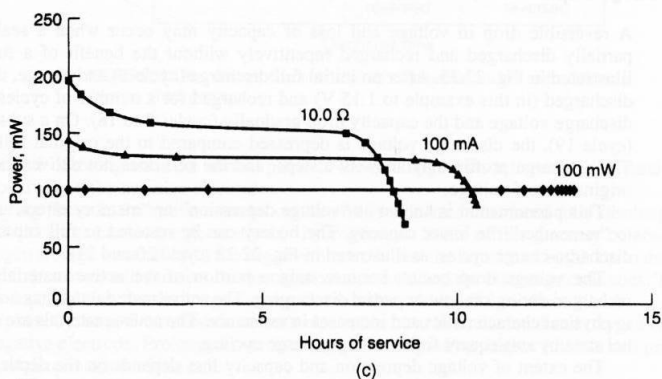
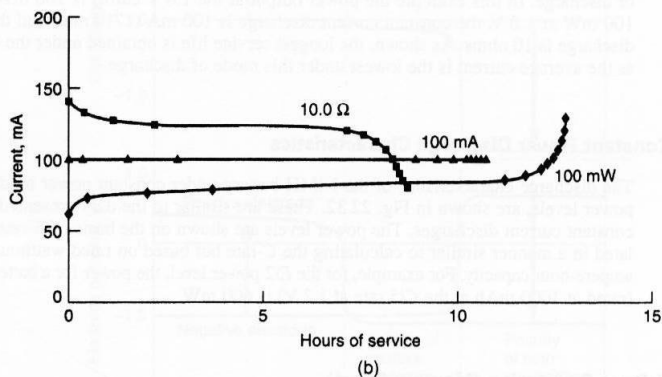
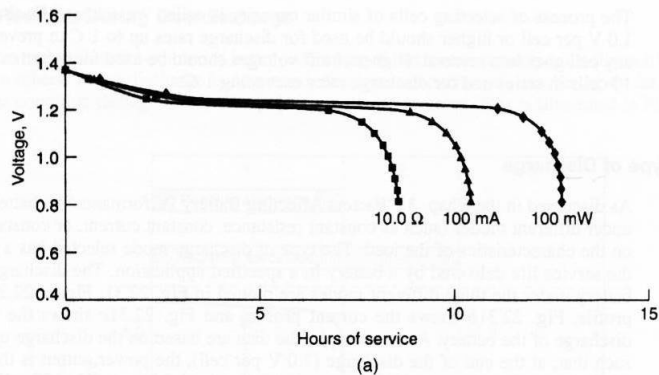


FIGURE 22.31 Discharge of NiMH cylindrical batteries—constant power vs. constant current vs. constant resistance: (a) voltage profile; (b) current profile; (c) power profile. All based on a battery rated at 1000 mAh.

Exhibit 2008

Ningde Amperex Technology Ltd.

IPR2023-00585, U.S. Patent No. 11,329,352

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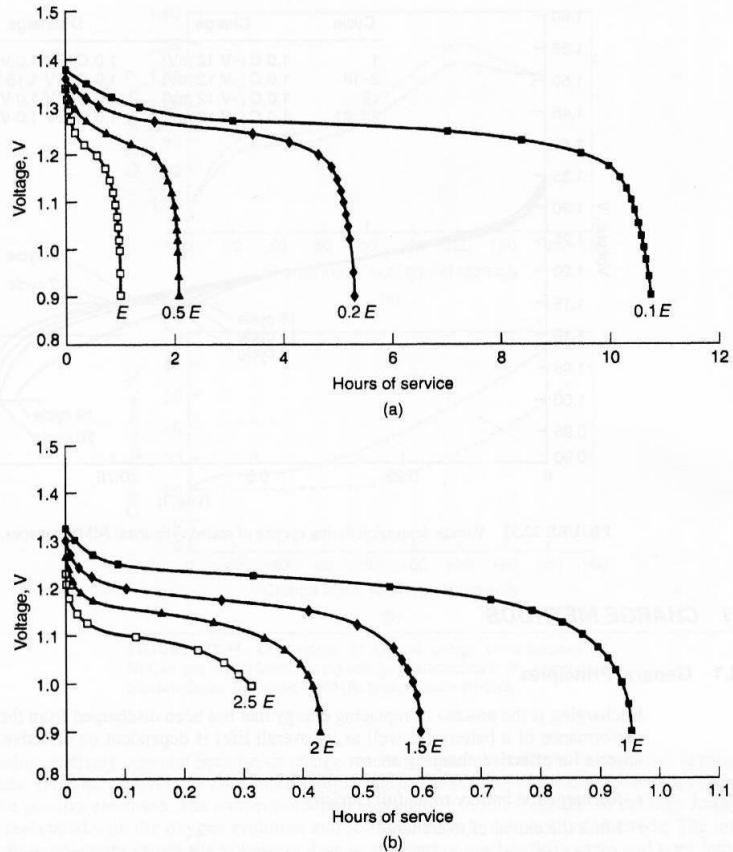


FIGURE 22.32 Constant-power discharge curves for NiMH cylindrical batteries at 20°C. (a) 0.1 E to 1 E discharge rate; (b) 1 E to 2.5 E discharge rate.

below 1.1 V per cell should not result in a significant voltage depression or apparent capacity loss on subsequent discharges. Discharging to too low an end voltage, however, should be avoided, as discussed in Sec. 22.10.11.

The effect is also dependent on the discharge rate. To a given end voltage, the depth of discharge will be less on discharges at the higher rates. This will increase the capacity loss as less of the active material is cycled.

While the memory effect may result in reduced battery performance, the actual voltage depression and capacity loss are only a small fraction of the battery's total capacity. Most users may never experience low performance due to this behavior. Often, the memory effect is used incorrectly to explain a low battery capacity that should be attributed to other problems, such as inadequate charging, overcharge, or exposure to high temperatures.

22.40 SECONDARY BATTERIES

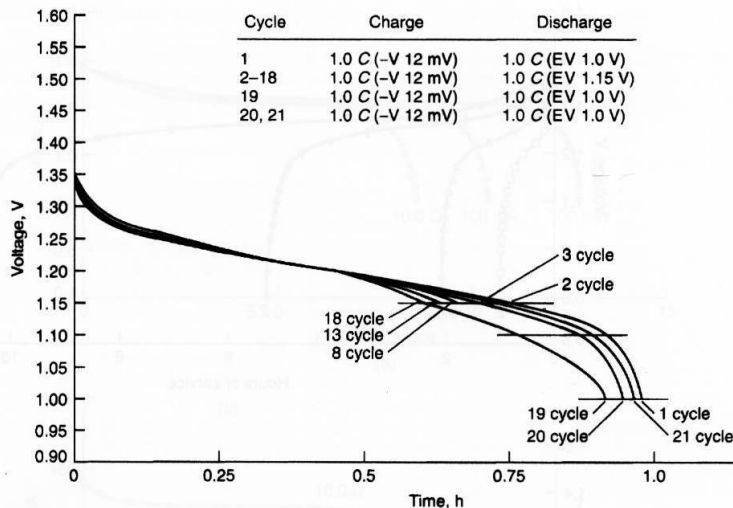


FIGURE 22.33 Voltage depression during cycling of sealed cylindrical NiMH batteries, 20°C.

22.11 CHARGE METHODS

22.11.1 General Principles

Recharging is the process of replacing energy that has been discharged from the battery. Subsequent performance of a battery (as well as its overall life) is dependent on effective charging. The main criteria for effective charging are to:

- Recharge the battery to its full capacity
- Limit the extent of overcharge
- Avoid high temperatures and excessive temperature fluctuations

Recharging characteristics of the NiMH battery are generally similar to those of the sealed nickel cadmium battery. However, there are some distinct differences, particularly on the requirements for charge control, as the NiMH battery is more sensitive to overcharge. Caution should be exercised before interchangeably using the same battery charger.

The most common charging method for the sealed NiMH battery is a constant current charge, but with the current limited to avoid an excessive rise of temperature or exceeding the rate of the oxygen recombination reaction.

The voltage profiles of NiMH and nickel cadmium batteries during charge at a moderate constant current rate are compared in Fig. 22.34. The voltage of both battery systems rises as the battery accepts the charge. During the first phase of the charge, the temperature of both batteries increases slightly due to Joule heating, which stems from the internal resistance of the batteries. Both battery chemistries are associated with endothermic charging processes ($Q_r = T\Delta S$ values are 27 KJ and 40 KJ for NiCd and NiMH batteries, respectively, where Q_r is the thermodynamic heat effect of the process related to the entropy change ΔS). An increase in the temperature of the battery indicates that the heating resulting from the Joule effect is larger than the cooling effect due to reversible heat ($T\Delta S$).

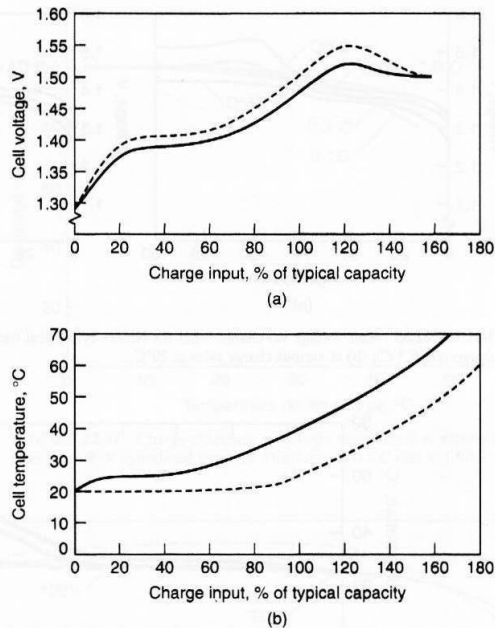


FIGURE 22.34 Comparison of typical charge characteristics of Ni-Cad and NiMH batteries: (a) voltage characteristics; (b) temperature characteristics. Solid line – NiMH; broken line – Ni-Cad.

remains relatively constant because its charge reaction is endothermic. As the batteries approach 75 to 80% recharge, the voltage rises more sharply due to the starting of the oxygen evolution reaction at the positive electrode. The temperature increases sharply at this stage due to the high Joule heating associated with the oxygen evolution and recombination at the negative electrode. The increase in cell temperature causes the voltage to drop as the battery reaches full charge and goes into over-charge due to the endothermic reversible heat effect ($T\Delta S$) of the charging process.

The voltage profile of the NiMH battery does not show as prominent a peak as that of the NiCd battery. The shallower drop in a NiMH battery may be due to a somewhat higher exothermic recombination reaction ($\Delta H = -572$ KJ/mol O_2 for NiMH versus $\Delta H = -550$ KJ/mol O_2 for NiCd), which compensates for the reversible endothermic effect of the charging reactions. Both the voltage drop after peaking ($-\Delta V$) and the temperature rise can be used to terminate the charge. However, while similar charge techniques can be used for both types of batteries, the conditions to terminate the charge may differ because of the different behavior of the two battery systems during charge.

The voltage of the sealed NiMH battery during charge depends on a number of conditions, including charge current and temperature. Figure 22.35 shows the voltage profile of the NiMH battery at different charge rates and temperatures. The voltage rises with an increase in charge current due to higher IR and overpotential during the electrode reaction. The voltage decreases with increasing temperature as the internal resistance and the overpotential during electrode reaction decreases. The voltage peak is not as evident at the low charge rates and at the higher temperatures.

The increase in battery temperature during charge at various charge rates is shown in Fig. 22.36. The internal cell pressure increases similarly. This rise in temperature and pressure at the higher

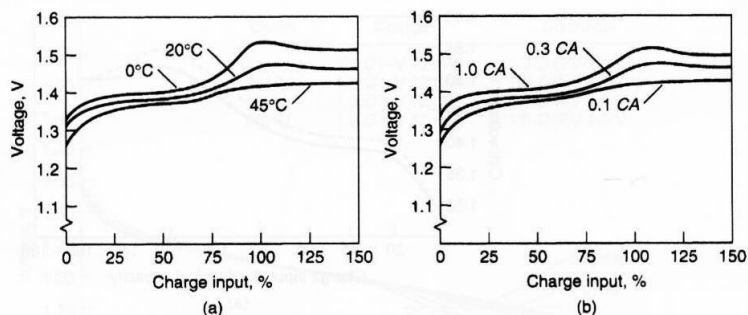


FIGURE 22.35 Cell voltage vs. charge input for NiMH cylindrical batteries: (a) at various temperatures (charge rate 0.3 C); (b) at various charge rates at 20°C.

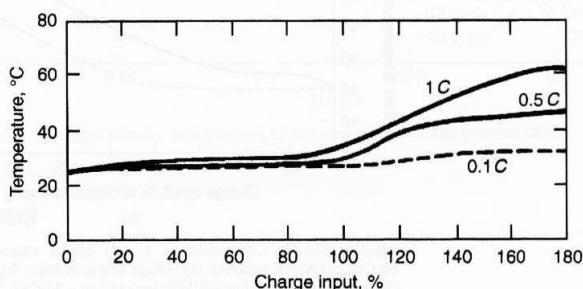


FIGURE 22.36 Battery temperature during charge of NiMH cylindrical batteries.

charge rates emphasizes the need for proper charge control and effective charge termination when "fast charging" to avoid venting and other deleterious effects.

The charge efficiency is also dependent on temperature. It decreases at the higher temperatures due to increasing evolution of oxygen at the positive electrode. At lower temperatures, oxygen recombination is slowed and a rise in internal cell pressure may occur depending on the charge rate. Figure 22.37 shows the available discharge capacity following charging at various temperatures and several charge rates. As shown, the battery capacity is reduced after high temperature charging. The extent of this effect is also dependent on the conditions of the discharge following the charge, as well as on other charge conditions.

Proper recharging is critical not only to obtain maximum capacity on subsequent discharges, but also to avoid high temperatures, overcharge, and other conditions that could adversely affect battery life.

22.11.2 Techniques for Charge Control

Characteristics of the NiMH battery define the need for charge control to terminate the charge, thereby preventing the battery from being overcharged or exposed to high temperatures. The advantage of employing proper charge control to maximize the life of the battery is illustrated in Fig. 22.38. The highest capacity levels are achieved with the 150% charge input, but at the expense of cycle life. The longest cycle life is attained with the 120% charge input, but with lower capacity due to

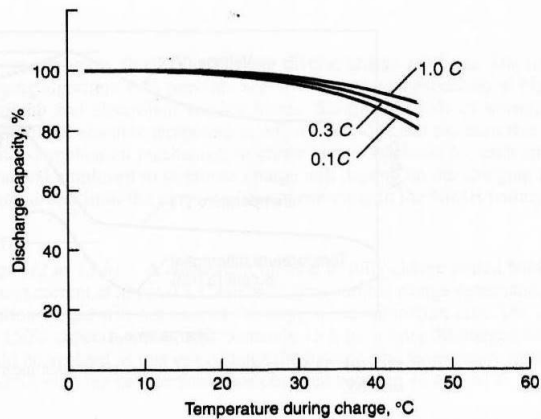


FIGURE 22.37 Charge efficiency vs. charge temperature at various charge rates for NiMH cylindrical batteries. Discharge at 0.2 C rate to 1.0 V.

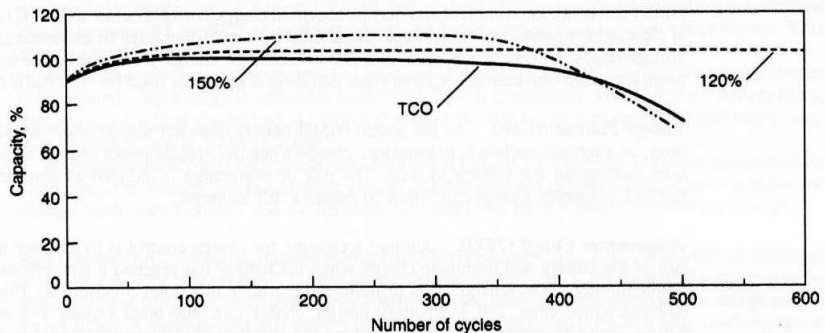


FIGURE 22.38 Effect of charge control on cycle life of NiMH cylindrical batteries. 1 C charge rate, discharge at 1 C to 1.0 V. TCO—charge termination at 40°C; 120%—charge termination at 120% charge input; 150%—charge termination at 150% charge input.

insufficient charge input. Thermal cutoff charge control may reduce cycle life because the battery is usually allowed to reach higher temperatures during charge. This method, however, is useful as a backup control in the event that the maximum temperature is exceeded during charge.

Some popular methods for charge control are summarized hereafter. The characteristics of these methods are illustrated in Fig. 22.39. In many cases, several methods are used during a single charge, particularly to control high-rate charging.

Timed Charge. Under this charge control method, charge is terminated after the battery has been charged for a predetermined amount of time. This method should only be used for charging at low rates to avoid excessive overcharge because the state-of-charge of the battery, prior to charging, cannot always be determined. This procedure is also used as a "topping" charge to other charge termination methods to ensure a complete recharge.

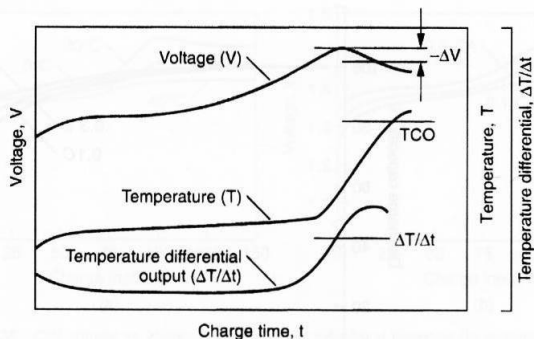


FIGURE 22.39 Comparison of charge termination methods: TCO, $\Delta T/\Delta t$, and $-\Delta V$.

Voltage Drop ($-\Delta V$). With this technique, widely used with sealed nickel cadmium batteries, the voltage during charge is monitored and charge terminated when the voltage begins to decrease. This approach can be used with the NiMH battery, but as noted in Sec. 22.10.1, the peak voltage with the NiMH cell is not as prominent and may be absent in charge currents below the 0.3 C rate, particularly at elevated temperatures. The voltage signal must be sensitive enough to terminate charge when the voltage drops, but not so sensitive that it will terminate charge prematurely due to noise or other normal voltage fluctuations. A 10 mV per cell drop is generally used for the NiMH battery.

Voltage Plateau (0 ΔV). As the sealed NiMH battery does not always show an adequate voltage drop, an alternate method is to terminate charge when the voltage peaks and the slope is zero rather than waiting for the voltage to drop. The risk of overcharge is reduced as compared to the $-\Delta V$ method. A topping charge can follow to ensure a full recharge.

Temperature Cutoff (TCO). Another technique for charge control is to monitor the temperature rise of the battery and terminate charge when the battery has reached a temperature that indicates the beginning of overcharge. It is difficult to determine this point precisely as it is influenced by ambient temperature, cell and battery design, charge rate, and other factors. For example, a cold battery may be overcharged before reaching the cutoff temperature, while a warm battery may be undercharged. Usually this method is used in conjunction with other charge control techniques and mainly to terminate the charge in the event the battery reaches excessive temperatures before the other charge controls activate.

Delta Temperature Cutoff (ΔT). This technique measures the battery temperature rise above the ambient temperature during charging and terminates charge when this rise exceeds a predetermined value. In this way, the influence of ambient temperature is minimized. The cutoff value is dependent on several factors, including cell size, configuration and number of cells in the battery, and the heat capacity of the battery. Therefore, the cutoff value must be determined for each type of battery.

Rate of Temperature Increase ($\Delta T/\Delta t$). In this method, the change in temperature with time is monitored and charge is terminated when a predetermined incremental temperature rise is reached. The influence of ambient temperature is virtually eliminated. A $\Delta T/\Delta t$ cutoff is a preferred charge control method for NiMH batteries because it provides long cycle life.

Note: Details on the design of batteries using protective devices and a description of the thermal protective devices that can be used for charge control are discussed in Chap. 5, "Battery Design."

22.11.3 Charging Methods

NiMH batteries are extremely flexible and accept diverse charge methods. The principal factor in designing a charging algorithm is to prevent excessive overcharge, especially at high rates, in order to avoid heat buildup and electrolyte venting losses. Several methods of sensing overcharge are common, including time, absolute temperature, ΔT , $\Delta T/\Delta t$, $-\Delta V$, and pressure rise. In all cases, the oxygen evolution/recombination mechanism to create heat is the basis for each charge termination approach. The method employed to terminate charge will depend on the charging rate (slow to fast charging) and should best limit the amount of heat generation in the NiMH battery in order to prevent damage.

Low Rate Charge (12 to 15 h). A convenient method to fully charge sealed NiMH batteries is to charge at a constant current at about 0.1 C rate with time limited charge termination. At this current level, the generation of gas will not exceed the oxygen recombination rate. The charge should be terminated after 150% capacity input (approximately 15 h for a fully discharged battery). Excessive overcharge should be avoided as this can damage the battery. The temperature range for this charge method is 5 to 45°C, with the best performance obtained between 15 and 30°C.

Quick Charge (4 to 5 h). NiMH batteries can be recharged efficiently and safely at higher rates. Charge control is required in order to terminate the charge when the rate of oxygen recombination is exceeded or the battery temperature rises excessively. The fully discharged battery can be charged at a 0.3 C rate for a charge time equivalent to a 150% charge input (approximately 4.5 to 5 h). In addition to the timer control, a thermal cutoff device should be used as a backup control to terminate charge at about 55 to 60°C to avoid exposing the battery to excessively high temperatures. This charging method may be used in an ambient temperature range of 10 to 45°C.

As a further precaution, the decrease in voltage ($-\Delta V$) should also be sensed to ensure that charge is terminated early enough to minimize overcharge. This is particularly advisable if the battery being charged was not fully discharged. A "topping" charge at the 0.1 C rate, as described previously, may then be used to assure 100% recharge.

Charging sealed NiMH batteries at rates between 0.1 and 0.3 C generally is not recommended. At these rates, the voltage and temperature charge profiles may not exhibit characteristics suitable for voltage-based cutoff control and the batteries may otherwise be exposed to harmful overcharge.

Fast Charge (1 h). Another method of charging NiMH batteries in an even shorter time is to charge at constant current at the 0.5 to 1 C rates. At these high charge rates, it is essential that the charge be terminated early during overcharge. Timer control is inadequate as the time needed for charge cannot be predicted. A partially charged battery could easily be overcharged, while a fully discharged one could be undercharged, depending on how the timer control is set.

With fast charging, the decrease in voltage ($-\Delta V$) and the increase in temperature (ΔT) can be used to terminate the charge. For better results, termination of fast charge can be controlled by sensing the rate of temperature increase ($\Delta T/\Delta t$) with a thermal cutoff (TCO) backup.

Figure 22.40 shows the advantage of using a $\Delta T/\Delta t$ method compared to $-\Delta V$ in terminating a fast charge. The $\Delta T/\Delta t$ method can sense the start of the overcharge earlier than the $-\Delta V$ method. The battery is exposed to less overcharge and overheating, resulting in less loss of cycle life. A temperature increase of 1°C/min should be used for $\Delta T/\Delta t$; a temperature of 60°C is recommended for the TCO.

In the case of multicell batteries of three cells or more, $-\Delta V$ termination with TCO backup may be adequate. The $-\Delta V$ value usually is 10 to 15 mV per cell and 60°C for the TCO.

While the infrastructure to fast charge EV batteries is not fully in place, a strength of NiMH battery technology is the ability to accept fast charge when it is required and the proper power is available. As an example, a typical EV cell capacity may be approximately 100 Ah. Therefore, if 15 min charging is desired, currents of approximately 400 A (at 360+ V) must be available.

NiMH batteries can accept from 60 to 80% charge within 15 min, at which point current must be reduced. Temperature rise due to internal resistance heating is small, on the order of 15°C for

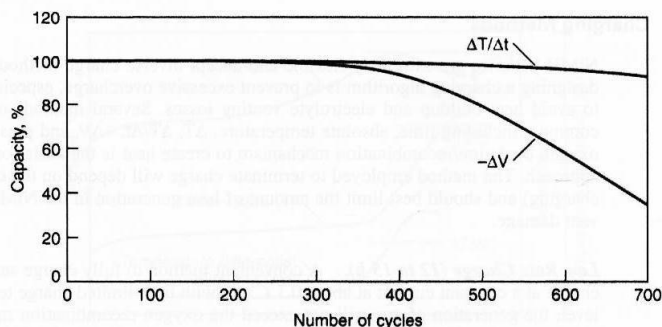


FIGURE 22.40 Cycle life and capacity as a function of charge termination method for NiMH cylindrical batteries. Charge 1 C, rest 30 min, discharge 1 C to 1.0 V, rest for 2 h.

a 33 kWh battery, whereas heating due to oxygen recombination is very large. Again, the crucial aspect of fast charge is proper sensing of the onset of overcharge.

Trickle Charge. A number of applications require the use of batteries that are maintained in a fully charged condition. This is done by trickle charging—charging at a rate that will replace the capacity loss due to self-discharge. A trickle charge at a current of between 0.03 and 0.05 C rates is recommended. The preferred temperature range for trickle charging is between 10 and 35°C. Trickle charge may be used following any of the previously discussed charging methods.

Three-Step Charge Procedure. A three-step procedure provides a means of rapidly charging a sealed NiMH battery to full charge without excessive overcharge or exposure to high temperatures.

1. The first step is a charge at a 1 C rate terminated by using the $\Delta T/\Delta t$ method or the $-\Delta V$ method.
2. This is followed by a 0.1 C topping charge, terminated by a timer after ½ to 1 h of charge.
3. The third step is a maintenance charge of indefinite duration at a current of between the 0.05 and 0.02 C rates. The battery should also be protected with a thermal cutoff device to terminate the charge so that the temperature does not exceed 60°C.

22.11.4 Regenerative Braking

Regenerative braking is a vehicle characteristic that helps NiMH dominate EV and HEV applications. Vehicle range is an area of competition for EV and HEV manufacturers, and a method of extending vehicle range from 5 to 20% is to utilize the energy lost during conventional braking to charge the battery. Regenerative braking energy is available to the battery at extremely high power (approximately 500 W/kg), and many rechargeable battery technologies cannot efficiently utilize the energy supplied at such a high power. NiMH batteries are able to accept regenerative braking energy over a wide state of charge range and over a wide temperature range.

Figure 22.41 shows a plot of voltage-current measurements on an Ovonic NiMH 13-HEV-60 (13 V, 60 Ah) module during an aggressive simulated HEV driving cycle. In contrast to results of a typical high-power lead-acid battery, also shown, the V-I slope is relatively constant. The lead-acid battery shows a significantly higher resistance for charge. For the Ovonic 13-HEV-60 module, the effective resistance on charge and discharge were the same, about 6 mΩ. This provides a substantially higher capability for acceptance of regenerative braking energy.

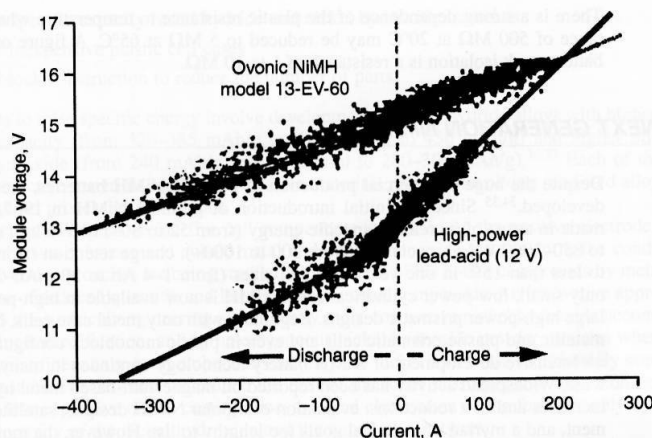


FIGURE 22.41 A comparison of the high-rate charge-discharge performance for HEV applications between NiMH and lead-acid batteries.

22.11.5 Charge Algorithms

Charge algorithms refer to the programming used to charge the NiMH HEV battery. Conceptually, the battery can accept charge input at extremely high rates until the battery is about 80% fully charged, at which point the charge current must be reduced. In overcharge, the charge current should not exceed the 10 h charge rate, and generally, the total charge input should be below about 110 to 120%.

An inherent virtue of NiMH batteries is that simple charging methodology can be used, with inexpensive equipment, and that it is not necessary to monitor the voltage of each cell in the high voltage string.

One method used to reliably charge NiMH EV batteries utilizes constant current steps to a temperature compensated voltage limit. Practically, this means that charging is done at high current until a predetermined voltage is reached which is an indication of a certain state-of-charge. At this voltage, the current is reduced or stepped down, until another predetermined voltage is reached. An important aspect of the charge algorithm is that the prescribed voltage set points are variable, based on temperature and current.

22.12 ELECTRICAL ISOLATION

Isolation of the EV and HEV battery from the vehicle is essential due to the high voltages involved. Isolation begins at the cell level, where plastic cell cases are preferred from an electrical isolation perspective, and metal cased cells must have some kind of insulative coating that is stable and free of pinholes.

The battery module (usually 12 V) must also be isolated from the battery tray, usually done with plastic isolation mounts. It is important that the cell and module interconnecting straps also be isolated from the battery tray.

In air-cooled battery packs, pack-to-vehicle resistance is strongly influenced by road contaminants such as dirt and salt, and pack case design must take this into consideration. For water-cooled designs, the issue is the resistance of the plastic casing materials to the coolant (e.g., ethylene glycol).

There is a strong dependence of the plastic resistance to temperature where a pack isolation resistance of 500 M Ω at 20°C may be reduced to 5 M Ω at 65°C. A figure of merit for HEV and EV battery pack isolation is a resistance of 1 to 10 M Ω .

22.13 NEXT GENERATION NiMH

Despite the huge commercial production of portable NiMH batteries, the technology is still being developed.^{34,35} Since the initial introduction of portable NiMH in 1987, great strides have been made in terms of increasing specific energy (from 52 to 80–110 Wh/kg), specific power (from 180 to 850–2000 W/kg), cycle life (from 300 to 1000+), charge retention (from 70% loss in one month to less than 15% in one year), and cell sizes (from 1–4 Ah to 30 mAh–250 Ah). Beginning with only small, low-power cylindrical cells, NiMH is now available in high-power cylindrical cells and large high-power prismatic designs. Beginning with only metal case cells, NiMH is now available in metallic and plastic prismatic cells and even in plastic monoblock configurations.

Intensive development of NiMH battery technology continues in many diverse locations worldwide. Widespread activity has been reported on magnesium-based metal hydride alloys for capacity increases and cost reductions, evaluation of bipolar NiMH designs, satellite NiMH battery development, and a myriad of technical goals too lengthy to list. However, the most intensive NiMH development at this time involves efforts to achieve “half the weight, half the cost” by continuing to reduce cost along with raising specific energy and specific power. R&D activity also focuses on increasing the depth of discharge under a given duty cycle while maintaining cycle life, thereby allowing for a smaller, less expensive battery to be employed. In addition, NiMH technology is looking at expanding into markets dominated by other battery chemistries.

22.13.1 Cost Reduction

Cost reduction continues to be at the forefront of NiMH development. High-volume portable battery production has seen NiMH cost reach or come below \$800/kWh, previously thought to be unobtainable. Key achievements in NiMH which have allowed this significant cost reduction include:

- Nickel hydroxide cost reduction from \$30 per kg to about \$20 per kg
- Nickel foam substrate cost reduction of about 50%
- Increased cell capacity and power by about 50% with virtually no additional cost
- Replacement of pure nickel wire mesh metal hydride electrode substrates with copper and nickel-plated steel on expanded metal and perforated sheet
- Use of pasted metal hydride electrodes
- Improved NiMH battery activation and formation

Despite these dramatic achievements, EV, PHEV, and HEV applications continue to demand even further cost reductions. Initial NiMH battery costs were above \$1500 per kWh at a prototype basis, and has steadily progressed to the \$800 to 1000 per kWh range (at projected production volumes of about 7,000 to 20,000 vehicles per year). At the \$800 per kWh level, and with a 1.6 kWh Prius HEV battery as an example, the vehicle battery cost is \$1280. Battery costs associated with PHEV and EV applications have most vehicle manufacturers placing a greater emphasis on hybrid electric vehicles where the battery may be only 10 to 25% of the EV battery size. However, there remains a tremendous development push for reduced NiMH cost to a target of \$150 per kWh.

Since NiMH costs are primarily driven by materials, important development activities to meet this goal include:

- Raising NiMH HEV specific energy from 45 Wh/kg to 65 Wh/kg
- Replacement of expensive inactive components such as nickel foam substrate and cobalt additives

- Higher specific capacity metal hydride and nickel hydroxide materials
- Use of inexpensive plastic cell cases
- Monoblock construction to reduce the number of parts

Efforts to raise specific energy involve development of metal hydride alloys with higher hydrogen storage capacity (from 320–385 mAh/g active material to 450 mAh/g) and higher utilization of nickel hydroxide (from 240 mAh/g active material to 280–300 mAh/g).^{36,37} Each of these higher utilization active materials requires innovative materials research involving modified alloy formulas and advanced processing techniques.

Reduction of expensive inactive cell components is focused on the positive electrode, including the nickel foam substrate and cobalt metal and cobalt monoxide used to form the conductive network. Several approaches are being studied: replacement of the cobalt compounds by metallic nickel fibers, use of reduced quantity, and less expensive cobalt compounds. An innovative approach being studied is the atomic engineering of inherently more conductive nickel hydroxide accomplished by multielement modification, and by heterogeneous nickel hydroxide powder particles where filamentary metallic fibers have been embedded into the base nickel hydroxide to ultimately connect to the outside conductive network. To reduce the cost of the foam substrate, cost reduction development includes less expensive nickel coating processes and elimination of the foam entirely by enhancing the conductivity of the nickel hydroxide and the conductive network.

Cell construction cost reduction involves development of novel plastic monoblock assemblies, reduction of parts through monoblock construction, lower cost plastic materials where possible, shared terminals and vents, and standardized sizes.

22.13.2 Ultra-High-Power Designs

For many years, it was thought that NiMH would never be able to completely replace NiCd in portable battery applications in which extremely high rates of discharge were required. In particular, power tools such as cordless drills require almost continuous discharge capability of 10 C rate. Today's NiMH cylindrical cells have exceeded the power of NiCd cells. Such high rate discharge capability has been accomplished through application of low-resistance current collection as in NiCd and through the use of improved surface catalytic activity metal hydride materials. High-power 3.5 to 7.0 Ah NiMH cylindrical cells for power tool and HEV applications have an AC impedance of about 1.7 mΩ and a $\Delta V/\Delta I$ internal resistance of about 4 mΩ. NiMH products in a variety of sizes (most commonly sub C, C, and D) are rapidly capturing portable power tool, scooter, and electric bicycle applications.

While NiMH chemistries for HEV applications have already demonstrated specific power in excess of 1300 W/kg, there is a worldwide development effort to achieve 2000 W/kg. NiMH cylindrical and prismatic prototype batteries have been announced with room temperature peak power in excess of 2000 W/kg and power over 2400 W/kg at 35°C. In some cases, power has been increased by sacrificing energy to about 44 Wh/kg, while in other designs inherently higher power active materials and casing construction have provided extremely high power without energy trade-offs. Figure 22.23 illustrates advanced HEV cell performance at 1050 W/kg. The concept is to reduce battery cost further by recognizing that for power-assist HEVs, the energy of the battery is not crucial, but rather the size of the battery is set to provide a predetermined power. Battery cost is primarily determined by the cost of battery components, and higher power utilization materials reduce the amount of material used.

A crucial factor in high-power NiMH batteries continues to be the development of highly catalytic metal hydride active materials. In particular, the interface between the bulk metal hydride and the electrolyte has been identified as essential for low voltage loss under pulse discharge. The surface oxide thickness and microporosity influence the reaction of H^+ and OH^- , and a critical observation was that within the high-power surface oxide metallic catalysts of enriched nickel regions having sizes less than 70 Å are especially important for reducing activation polarization.^{38,39}

22.13.3 Stationary Power

In North America, stationary power applications represent nearly a \$1B market. Today's existing applications—telecommunications, emergency lighting, and UPS systems—are dominated by lead-acid technology. Energy storage is considered by utilities as a means to reduce the economic and environmental impact associated with new plant construction. In addition, energy independence and energy security are driving increased investments in advanced forms of energy storage and the "Smart" grid. The adoption of renewables (solar and wind) that are intermittent in nature require new energy storage technologies in order to be integrated into the grid. Of the various energy storage technologies currently available, battery technology is considered to be the most proven and advanced form of energy storage to enable optimized power transmission and distribution from renewables.

Energy storage has long been dominated by lead-acid batteries of various different construction methods. Lead-acid at present dominates bulk energy storage due to its comparatively low initial cost. Routine maintenance can lead to high overall costs, including checking electrolyte level and adding water as necessary to each cell; keeping track of charge voltage; inspecting individual cases for leaks; periodic cleaning; and performing routine discharge tests. In addition, a growing need to add capacity to existing installations and a desire to utilize more "green" technology (wind and solar) are opening the door for other battery technologies.

For PV, telecom, and UPS (data centers, hospitals) systems integration, NiMH is well positioned against lead-acid due to its high energy, environmentally friendly, high durability, and long-life characteristics. This market will require high reliability, long life, and low maintenance to meet the demands of advanced energy storage technologies. NiMH battery technology can satisfy the needs of this application with proven high energy and power, cycle life, high temperature, float charge capability, reliability, and cost. Considering total cost of ownership (initial cost, operating costs, maintenance and life-cycle costs), NiMH may provide advantages over lead-acid.

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