CHAPTER 23
NICKEL-ZINC BATTERIES

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23.1 INTRODUCTION

Nickel-zinc batteries are the ideal choice when there is a need for a small, lightweight power source with excellent high-rate discharge capability at a cost point significantly lower than lithium-ion. It is an abuse-tolerant technology also capable of replacing both nickel-cadmium and nickel-metal hydride batteries in most high-volume applications. Portable applications with high current drains are well suited to nickel-zinc batteries because of their exceptional power density and the high specific energy values, currently ranging between 70 Wh/kg and 110 Wh/kg. Cycle lives that exceed 900 cycles at 80% depth of discharge are competitive with those of the best nickel-cadmium and lithium-ion technologies.

Nickel-zinc batteries are a member of a family of alkaline aqueous systems based on nickel positive electrodes that include nickel-iron, nickel-cadmium, and nickel-metal hydride. The common nickel electrode can achieve high cycle life under a wide variety of charge and discharge rates and is designed in all cases to be the ampere-hour (Ah) capacity limiting electrode under normal discharge conditions. The different counter electrodes establish the operating voltage, the size and weight of the battery, and influence the system cost and performance characteristics, such as rate capability, cycle life, and shelf life at various temperatures.

The distinctive characteristic of the nickel-zinc chemistry is the high open-circuit voltage of 1.73 V that enhances the energy density and reduces the number of cells required in higher voltage batteries. The latter factor reduces the cost of the battery with respect to other alkaline systems and proportionately lowers the internal impedance. Since the zinc electrode also demonstrates fast electrochemical kinetics, the battery is ideally suited to high discharge rate applications such as power tools and hybrid electric vehicles. Other applications include commercial AA cells that, under load, demonstrate close voltage compatibility with alkaline primary cells while, delivering superior runtimes at higher power levels.

23.1.1 History

Realization that the nickel-zinc electrochemical couple could be exploited as a rechargeable battery is documented in the patents of de Michalowski,[1] Junger,[2] and Edison[3] in 1899 and 1901. The first successful commercial demonstration of the technology did not occur until 30 years later in Ireland when Dr. James Drumm pioneered the electrification of the Bray to Dublin passenger rail cars in 1931 using large flooded electrolyte 440 V, 600 Ah batteries.[4,5] A total of four rail cars accumulated more than 700,000 miles during a service life that culminated in 1949, ostensibly due to the post–World War II availability of low-cost diesel fuel. Nickel-zinc batteries were used in a niche application as the power source in Russian mines,[6] but there was little further development until interest in electric

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vehicles was stimulated again during the gasoline shortages of the 1970s. At that time, the United States Department of Energy supported efforts from a number of companies to develop higher-energy alternatives to lead-acid electric vehicle batteries. The nickel-zinc battery was targeted as a high-energy-density battery that had the potential to meet aggressive cost goals provided that the cycle life of the zinc electrode could be significantly improved. General Motors Corporation engaged in one of the more ambitious programs to develop the battery for a small electric car based on the Chevrolet Chevette, but abandoned the program as enthusiasm for electric transportation abated in phase with the decrease in the price of oil.

Further development of the nickel-zinc couple was undertaken mainly in Japan between 1970 and 1990. However, despite substantial development efforts, the only product commercialized was a sealed, prismatic, maintenance-free battery of less than 10 Ah capacity from Yuasa. While the product was 60% lighter than an equivalent lead-acid battery, the cycle life at 100% depth of discharge was only 200 cycles at 2 h discharge rate.[7] Target markets were electric lawn mowers and light electric vehicles in direct competition with low-cost, maintenance-free lead-acid batteries.

After 2000, Evercel introduced a variety of larger prismatic cells and batteries[8] that achieved up to 600 cycles. The Evercel zinc electrode technology followed the development path of General Motors, but a customized electrode fabrication method ultimately proved difficult to commercialize. The batteries employed a starved electrolyte design and incorporated a gas recombination catalyst to help reduce pressure and minimize gas escape through the vent mechanism. While the technology appeared viable for the light electric vehicle and trolling-motor markets, sealed lead-acid batteries provided extremely cost effective competition.

In 2008, breaking the tradition of introducing prismatic nickel-zinc batteries in direct competition with lead-acid batteries, PowerGenix introduced the first sealed cylindrical nickel-zinc batteries for the power tool market.[9] These batteries were designed to directly compete with nickel-cadmium, nickel-metal hydride, and lithium-ion batteries. The company strategy adopted the manufacturing techniques and material development efforts of other alkaline battery manufacturers together with separator improvements from the lithium-ion industry. The combination delivers energy and power densities that have kindled renewed interest in this higher-voltage nickel battery as the competition between alkaline aqueous systems and lithium-ion batteries intensifies for market share.

23.2 NICKEL-ZINC CHEMISTRY

The chemistry of the nickel-zinc battery system is similar to that of nickel-cadmium, except that cadmium is replaced by zinc. The electrolyte is typically a 3 to 8 M alkali metal hydroxide solution in which specific additives are sometimes added to "manage" the charge–discharge behavior of the zinc electrode. The active material of the positive electrode is nickel (III) oxy-hydroxide and that for the negative electrode is high surface area metallic zinc. When discharged, the nickel (III) oxy-hydroxide is reduced to nickel (II) hydroxide and zinc is oxidized to zinc (II) species. The electrochemistry and mechanism of the reactions are quite complex[10] and for illustrative purposes, the simplified forms of the reactions are given below. Depending on the conditions, zinc hydroxide, zincate, or zinc oxide and their mixtures may constitute the final reaction product at the negative electrode on discharge. All may be reconverted to zinc during the charging process. The positive electrode reactions are provided below in a simplified form with more details found elsewhere.[11]

Negative electrode discharge reactions:

$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^- \qquad E^0 = -1.24\ V \tag{23.1}$$

$$Zn(OH)_2 + 2OH^- \rightarrow ZnO_2^{2-} + 2H_2O \tag{23.2}$$

$$ZnO_2^{2-} + H_2O \rightarrow ZnO + 2OH^- \tag{23.3}$$

Positive electrode discharge reactions:

$$2NiOOH + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^- \qquad E^0 = 0.49\ V \tag{23.4}$$

Overall reaction:

$$2NiOOH + 2H_2O + Zn \rightarrow Zn(OH)_2 + 2Ni(OH)_2 \tag{23.5}$$

or

$$2NiOOH + Zn + 2OH^- \rightarrow ZnO_2^{2-} + 2Ni(OH)_2 \tag{23.6}$$

or

$$2NiOOH + Zn + H_2O \rightarrow 2Ni(OH)_2 + ZnO \qquad E^0 = 1.73\ V \tag{23.7}$$

Although the above are the main charge-discharge reactions, the following reactions may also take place under various situations. For instance, when a nickel-zinc battery is overcharged, two reactions can take place. In general, toward the end of the charge process, both Reactions 23.8 and 23.9 occur simultaneously but not necessarily at equal rates. The combination of these reactions is equivalent to water electrolysis. As Reaction 23.10 shows, the oxygen so generated can be consumed at the metallic zinc electrode, if accessible. The reaction is known to be rapid.
Overcharge reaction at the negative electrode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^0 = -0.9 \tag{23.8}$$

Overcharge reaction at the positive electrode:

$$2OH^- \rightarrow \tfrac{1}{2}\ O_2 + H_2O + 2e^- \qquad E^0 = 0.3 \tag{23.9}$$

Recombination at the negative electrode:

$$Zn + \tfrac{1}{2}\ O_2 \rightarrow ZnO \tag{23.10}$$

Recombination of the hydrogen produced at the negative electrode can also occur at the positive electrode. The reaction is much slower than Reaction 23.10 and requires higher pressure or the presence of catalysts before there is significant impact on cell chemistry. In another instance, if a cell is overdischarged and the voltage is reversed, the following two reactions may occur.
Overdischarge at the negative electrode:

$$2OH^- \rightarrow \tfrac{1}{2}\ O_2 + H_2O + 2e^- \tag{23.11}$$

Overdischarge at the positive electrode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{23.12}$$

The overall reaction again constitutes water electrolysis.

$$H_2O \rightarrow H_2 + \tfrac{1}{2}\ O_2 \tag{23.13}$$

The following two reactions play important roles during cell storage where charge retention is affected by the stability of the two electrodes in the electrolyte. At the negative electrode, hydrogen is produced as a result of the thermodynamic instability of zinc in aqueous electrolyte.

Self-discharge at the negative electrode:

$$Zn + 2H_2O \rightarrow ZnO + H_2 \tag{23.14}$$

At the positive electrode, the charged nickel oxy-hydroxide electrode can also react with the electrolyte to produce oxygen and nickel hydroxide.
Self-discharge at the positive electrode:

$$2NiOOH + H_2O \rightarrow 2Ni(OH)_2 + ½\ O_2 \quad (23.15)$$

23.2.1 The Zinc Electrode

Zinc metal is abundant, relatively harmless to the environment, and comparatively inexpensive. It has a low redox potential that provides a high electromotive force when used in combination with suitable positive active materials. Zinc is used as the negative electrode for primary battery systems such as alkaline-manganese dioxide and zinc/air, however, its use in secondary batteries has been limited. This is due to the fact that the discharge products of the zinc electrode, i.e., zinc oxide, hydroxide, or zincate, can dissolve in alkaline electrolyte, making their site-specific recharge difficult. Additionally, zinc is not thermodynamically stable in aqueous electrolyte, and significant measures must be taken to minimize self-discharge.

The individual problems of the zinc electrode are listed below.

Formation of Zinc Dendrites. This may occur during recharging when zinc preferentially plates onto electrode high points rather than uniformly over the electrode surface. Eventually the gradual progression of nonuniform zinc plating results in zinc penetration of the separator and contact with the positive electrode to create an internal electronic short and nonfunctioning cell. Various methods have been employed to inhibit dendrites, including the use of microporous separators with small tortuous pores. A meandering electrolyte pathway can prove so difficult for the zinc to navigate that significant gains in cycle life can be achieved.

Zinc Shape Change. Zinc dissolves in the electrolyte during discharge as a result of reactions 23.1 and 23.2 and may move away from its original location. During charge, the zinc may deposit at locations remote from the point of origin, causing the phenomenon known as "shape change."

Zinc Agglomeration. As zinc dissolves during discharge, the charging process may not restore the original high surface area. The redistribution and loss of surface area can compromise the high-rate capability and eventually lead to some zinc isolation with an associated loss in active material utilization.

Passivation of Zinc. Passivation of zinc occurs when a compact film of discharge product is formed on the surface of zinc during discharge, effectively shutting down the discharge process. This occurs when the concentration of discharge products reaches a solubility limit and zinc oxide or hydroxides precipitate onto the zinc surface. Passivation is a strong function of current density, the solubility of zinc, and temperature. At lower temperatures, where both solubility and diffusivity are reduced, passivation at the negative electrode may control the delivered capacity of the cell.

Corrosion of Zinc. The instability of zinc in aqueous media is a result of the zinc redox potential being less than that of hydrogen (see reaction 23.14 above). Pure zinc has a relatively high overpotential for hydrogen evolution lending a kinetic stability to the metal and a low inherent corrosion rate. The presence of any hydrogen evolution catalyst such as iron or cobalt can dramatically change this situation, and it is critical to limit the exposure of zinc to such materials. This can be particularly challenging when zinc is coupled with a nickel electrode that includes cobalt as a key constituent. Rechargeable zinc electrodes inhibit zinc corrosion by using alloying elements and selected organic inhibitors. Similar techniques are also extensively used in primary batteries, but the larger active zinc particle size of 100 to 300 microns generates significantly less gas than the 0.2 to 0.3 micron particles associated with rechargeable zinc electrodes. The correspondingly high corrosion rate must be reduced and controlled by a combination of chemical, mechanical, and cell design considerations.

The issues of dendrite formation, shape change, agglomeration, and zinc passivation are all associated with the solubility of zinc oxide in the alkaline electrolyte. Approaches to reduce zinc solubility

have focused on modifications to the negative electrode and the electrolyte that often accelerate zinc passivation and inhibit high-rate capability and low-temperature performance.

There have been a large variety of chemicals added to the negative electrode to improve cycle life and aid electrode manufacturing. The more common additives and their function are listed below. A more complete listing has been published previously.[12]

- Reduction of shape change, agglomeration, and dendrite formation: calcium hydroxide, calcium zincate, fluoride, phosphate, calcium titanate
- Corrosion reduction: bismuth, indium, lead, cadmium added as oxide
- Conductivity enhancement: bismuth, lead, conductive ceramic, metallic zinc powder
- Internal wicking of electrode: cellulose, chopped newsprint, inorganic fibers
- Electrode binder for integrity and handling: PTFE

Although lead and cadmium additions may help zinc cycle life, they are no longer environmentally acceptable and have been replaced with less hazardous materials.

The alkaline electrolyte used in the nickel-zinc battery is usually a combination of hydroxides of alkali metals such as potassium, sodium, and lithium. Unfortunately, the conflicting electrolyte requirement of the nickel and the zinc electrodes usually necessitates compromise. Nickel electrode capacities are maximized by higher hydroxide concentrations, but this can significantly increase zinc solubility and reduce cycle life.[13] Acids with buffering capability have been used in the electrolyte to reduce free alkalinity and improve zinc cycle life while maintaining nickel electrode efficiency.[14,15] Other anions such as fluoride and silicate have been used in the electrolyte and in the negative electrode to reduce the zinc solubility.

Examples of negative electrode and electrolyte compositions used by various organizations are given in Table 23.1

TABLE 23.1 Examples of Critical Components in Various Nickel-Zinc Designs

Organization	Typical negative electrode composition	Typical electrolyte composition	Reference
PowerGenix	ZnO 85 to 95% Bi_2O_3 1 to 10% KF 0.05 to 4.5%	Total excess OH^- 2.5 M to 5 M Borate 0.6 M to 1.3 M	21
S.C.P.S.	Contains $(M_2O)_n$ $(TiO_2)_m$ xH_2O; M is an alkali metal, where 0.5<n<2 and 1<m<10, 0<x<10, typical Zn =5% TiN = 10% CaTitanate = 1.25% CaAluminate = 3% Bi_2O_3 = 5% $Ni(OH)_2$ = 5% Rest is ZnO Plasticizer = PTFE	OH^- = 7 M to 15 M; typically 7 M with saturated ZnO	18
Massey University	Ratio of Znstearate to ZnO = 0.075 to 0.25 Ratio of Castearate to ZnO = 0.03 to 0.15 Graphite = 15 to 35% Some amounts of lead and/or copper salt	KOH solution with saturated ZnO and tetrabutyl ammonium hydroxide	23
Evercell or Energy Research Corporation	CaZincate = 30 to 60% PTFE = 1 to 4% ZnO, $Ca(OH)_2$, PbO	KOH = 31 to 35%	25
Lawrence Berkeley Laboratory	ZnO = 93% Lead oxide = 2% Newsprint = 1% PTFE = 4%	KOH = 3.2 M KF = 1.8 M K_2CO_3 = 1.8 M	24, 15

23.2.2 Important Considerations of Pairing Nickel with Zinc Electrodes

The beneficial effects of the inclusion of zinc ions into the rechargeable positive nickel hydroxide electrode lattice structure have been established.[16] A corresponding benefit may be derived from the zinc ions present in the nickel-zinc cell electrolyte. However, a secondary effect of the presence of zinc ions close to the positive electrode is the precipitation of zinc oxide in the pore structure, with a resulting restriction of ionic flow. More severe plugging can result in capacity loss that may happen at the early stage of cycling,[12] but the severity is highly dependent on the conditions that control the zinc solubility in the electrolyte. These include the temperature and hydroxyl ion concentration as well as the rates of charge and discharge of the battery. During the charging process, hydroxyl ions are consumed at the positive electrode and generated at the negative electrode. These changes in hydroxyl ion concentration can precipitate zinc oxide directly within the pores of the positive electrode.

A second problem with nickel-zinc cells is the disparity in charge efficiency of the positive and negative electrodes. At the positive electrode, oxygen evolution (reaction 23.9) competes with the nickel hydroxide charging reaction such that an additional 20% overcharge may be required before the electrode is fully charged. Techniques to improve charge efficiency include the addition of oxides, such as calcium oxide or zinc oxide to the nickel hydroxide, or simply charging to less than full capacity. The latter approach unfortunately reduces the cost advantage of the technology over competitive batteries. In contrast, the charging process at the zinc electrode is 99% efficient with small amounts of hydrogen being produced as in reaction 23.8. In vented cell configurations, the disparity in electrode charge efficiencies results in the rapid conversion of all of the zinc oxide in the negative electrode to zinc metal. This promotes the evolution of hydrogen during charge with resulting dry-out and premature failure. One solution to this problem is to operate the cell with a starved electrolyte to encourage the reaction of gaseous oxygen with the negative electrode. The immediate effect of "oxygen recombination" is to both proportionately reduce the charging efficiency of the negative electrode and to equalize charging efficiencies at both electrodes. While the microporous separator may block the access of oxygen to the central area of the negative electrode, the edges can often provide sufficient recombination for charge efficiency equalization. If differences in charging efficiencies can be moderated, then gas recombination catalysts can be used effectively to maintain low cell pressure and allow oxygen recombination to occur at a lower rate at the negative electrode.

23.2.3 The Separator System

The choice of the separator system is a key element in the life of a nickel-zinc battery. The separator is present to electronically insulate the nickel and the zinc electrodes while minimally restricting passage of ions to allow efficient electrochemical discharge and charge of the active materials. Achieving these goals requires a robust separator that resists mechanical penetration while providing a sufficiently open structure for low electrical resistance. In nickel-zinc cells, the separator also inhibits the growth of metallic zinc dendrites that may bridge the positive and negative electrodes. This requirement normally defines a pore size that is both small and tortuous but necessarily at odds with a requirement for ease of ion flow associated with low resistance. Achieving the balance between these requirements is particularly difficult for higher discharge rate applications where there is a greater need to minimize cell resistance for efficient high-power discharge without excessive temperature buildup. Combining a highly conductive electrolyte with less conducting, dendrite inhibiting separators may deliver good high-rate performance. However, the highly conducting electrolytes that provide low resistive losses are the most effective in dissolving the zinc oxide to promote failure modes such as shape change, densification, and dendrite growth. It is therefore very important to address the zinc failure modes from the perspective of separator, electrolyte, and the negative electrode composition so that high-rate charge and discharge are enabled together with high cycle life. High-energy and high-power delivery from a nickel-zinc cell provides an incentive for the use of thin separator materials, but this must be achieved without compromising the safety of the cells. Polyolefin materials are favored as separators since they can be fabricated in high-strength thin films with small, tortuous pores. Unfortunately, these materials are not easily wetted by an aqueous alkaline solution and must be treated either with a surfactant or by

chemical grafting of surface groups. Even with such treatment, the wicking ability of the polyolefin separator alone is insufficient to promote good uniform electrolyte distribution without the help of an additional separator such as a high-porosity nonwoven polyamide, a wetting capable polyolefin, or an electrolyte absorbent PVA/cellulose mix.

Parameters normally used to characterize separators are porosity, ionic resistance, air permeability, pore size, mechanical strength, chemical stability, dimensional stability, and wetting ability. Most out-of-cell separator evaluations are based on characterization of resistance and air permeability since these properties are determined by the aggregate of porosity, pore size, pore tortuosity, and wetting ability. The other physical properties such as mechanical strength and thermal stability govern the issues of manufacturability, reliability, and safety. Even using these criteria as guidelines, it is often difficult to predict the suitability of various separator combinations in the nickel-zinc system without extensive in-cell testing.

23.2.4 The Positive Electrode

The positive electrode is very similar to that used in nickel-metal hydride and nickel-cadmium systems. The most widely used nickel electrode is a high porosity nickel foam pasted with spherical nickel hydroxide particles with additions of binder and conductivity enhancing material such as nickel powder and cobalt oxide. Commercially available nickel hydroxide contains 0 to 3% cobalt hydroxide and 0 to 3% zinc hydroxide as co-precipitated material. These additives improve charge acceptance and stabilize the preferred beta crystal structure of nickel hydroxide.

The pasted alkaline nickel electrode demonstrates a mild memory effect or voltage depression if repetitively discharged to the same state of partial charge. However, one or more full discharges to 1.1 V in the case of nickel-zinc batteries will restore the discharge voltage curve to its original condition.

23.3 CELL CONSTRUCTION

Nickel-zinc batteries have traditionally followed the construction guidelines set up for nickel-cadmium and nickel-metal hydride batteries in prismatic and cylindrical formats. The most significant differences lie in the separator system used and the choice of negative electrode substrate. Normally a high cycle life nickel-zinc cell will employ a multilayer separator consisting of one or more layers of a microporous membrane together with a single more highly porous "wicking" separator that promotes good electrolyte distribution and is capable of buffering the electrolyte volume changes that occur during charge and discharge of the cell. The microporous membrane separator plays an important role in preventing electrical short conditions resulting from zinc forming a conducting bridge between the positive and negative electrodes. A secondary consequence of using a less open separator system is a significant reduction in the oxygen and hydrogen gas recombination rates as compared to other alkaline systems. Particular attention must be given to the charging procedures to prevent undue gas pressure buildup in overcharge with resulting vent operation and shortening of cycle life.

The choice between cylindrical and prismatic designs depends on the application. Smaller capacity cells below around 20 Ah favor the cylindrical format because there are fewer individual parts and ease of construction on a jelly-roll winder. This format becomes more challenging for higher capacity cells as plate widths and lengths increase and manufacturing becomes more difficult. Under higher-rate discharges, there are also thermal management issues associated with the difficulty in heat removal from larger diameter jelly-rolls. At lower discharge rates and high ampere-hour requirements, the prismatic cells gain favor on the basis of the easier assembly of thicker plates and the superior packing density of this configuration.

23.3.1 Prismatic Construction

Whether in single cell or monoblock configuration, the prismatic construction has been the most common format for nickel-zinc batteries. The zinc electrodes are individually tabbed before being bagged in one, two, or even three layers of microporous polyolefin film. A manual or automatic stack and wrap

machine can alternate these zinc electrodes with tabbed positive electrodes between a web of nonwoven wicking separator that may be based on nylon or grafted polyolefin. The negative and positive tabs are individually grouped and bolted, or resistance welded to the terminals of the cell. Sealing through the lid of the cell is generally accomplished using O-ring seals that resist the creeping of alkaline electrolyte. The cell stack is compressed and inserted into the case before the lid is welded or glued in position. After cell sealing, the electrolyte is introduced under vacuum and is allowed to soak for several hours prior to applying the first charge to the cell. Figure 23.1 shows a typical prismatic construction for a 20 Ah cell. Energy densities range from 60 to 100 watthours per kilogram and 110 to 200 watthours per liter. Most designs are maintenance-free and use sufficient electrolyte to wet the separators without saturation and without electrolyte outside of the cell stack. Because of the low pressure tolerance of the prismatic design, safety vents normally do not exceed 100 psi. Recombination has less driving force at lower ambient pressures, and for long life, it is commonplace to include free-standing recombination catalysts that can promote the production of water from gaseous hydrogen and oxygen present in the cell.

23.3.2 Sealed Cylindrical Construction

A jelly-roll construction can provide very uniform current density if current collection take place at either ends of the jelly-roll. This configuration is thus well suited to high-power applications such as power

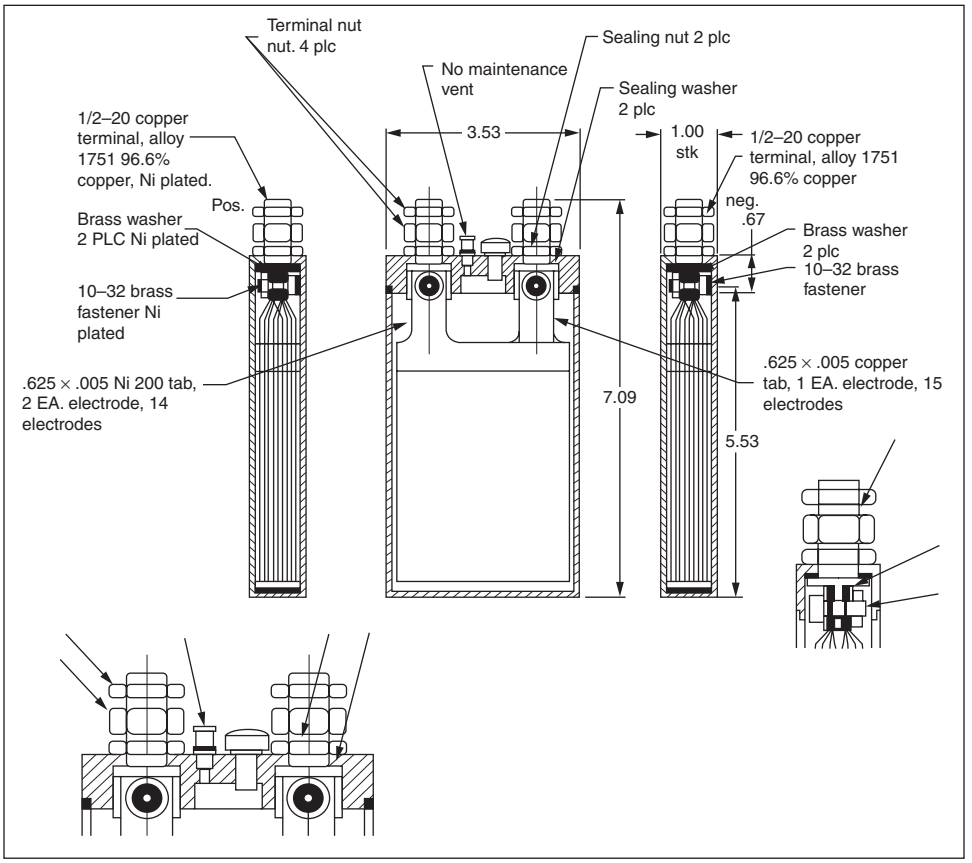

FIGURE 23.1 A prismatic cell construction.

tool and hybrid electric vehicle batteries. A rapid winding process can achieve 5 to 8 jelly-rolls per minute from one machine and can guarantee cost competitive production and throughput. After the jelly-roll is wound, one or more contacts may be attached to the electrodes before it is inserted into the can where welds may be made between the can surface and tabs or discs attached to the jelly-roll. The can containing the jelly-roll is then filled under vacuum with an appropriate amount of electrolyte, and the cell is capped and allowed to soak before the application of the first charge. Figure 23.2 is an exploded view of a typical nickel-zinc spiral-wound construction where a spring that is welded to the cap provides contact to the zinc current collector and a nickel "spiked" disc welded to the can base provides a similar function for the positive electrode.

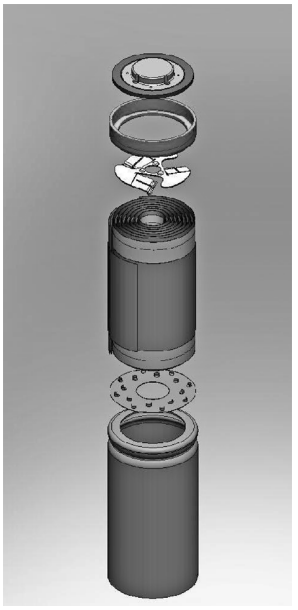

FIGURE 23.2 Exploded view of sealed sub *C* nickel zinc cell (*Courtesy of PowerGenix, Inc.*)

The design differs from the prismatic cell in several key respects. The microporous separator is wound such that the edges are open with free access to the electrodes from either end of the jelly-roll. This allows contacts to be made either by welding or simple pressure contact. Unlike the prismatic design, the vent should not open unless there is an abnormal pressure buildup. Excessive opening of the vent may result in electrolyte fouling and ineffective subsequent closure with oxygen ingress eventually discharging the zinc electrode. Vent opening pressures must be high enough to remain closed at all operating conditions yet low enough to guarantee safety under abuse. The polarity of the can may be either positive or negative, but hydrogen catalysts such as iron should not be exposed to electrolyte at the zinc potential. General practice is to coat any metal in contact with the zinc electrode with material that can inhibit hydrogen release.

Small sealed cylindrical nickel-zinc cells exhibit higher specific energy and energy density (70 to 110 Wh/kg and 200 to 360 Wh/L) than the prismatic cell. This is primarily a result of an efficient bussing design and minimal electrolyte amounts in the totally sealed configuration. In multicell batteries, the less efficient volumetric packing capability of cylindrical designs sometimes may eliminate this advantage.

23.3.3 Nickel Electrode

The active material of the positive electrode, nickel hydroxide, has little electronic conductivity in either the charged or discharged state. Electronic conductivity to the active material is provided by the supporting electrode substrate and other conducting additives that provide "micro" conductive elements within the bulk active material.

Nickel electrode technologies[11] have been incorporated with minimal changes from nickel-cadmium and nickel-metal hydride cells. The most robust nickel hydroxide electrode incorporates a porous, sintered nickel substrate as the current carrying backbone. The highly porous nature allows nickel hydroxide active material to be chemically or electrochemically impregnated into the structure along with small amounts of cobalt hydroxide that help active material conductivity and promote efficient charging. While the sintered nickel electrode is capable of thousands of cycles, it is an expensive electrode to manufacture with a requirement for strict environmental controls during the solution processing and washing. The high nickel-metal content provides good overdischarge tolerance, good current distribution, and excellent high-power performance. However, such robustness exacts a gravimetric and volumetric energy penalty.

An alternate pasted-positive electrode does offer significant cost and energy density advantages that enable nickel-zinc technology to compete effectively with existing commercial lithium-ion batteries. The electrode substrate is a highly porous nickel foam that functions as a three-dimensional electronic conductor. The basis weight may vary from 300 to 600 g/m^2 with the choice mainly being determined by the current carrying requirement of the plate. The active nickel hydroxide is manufactured as 10 micron diameter spherical particles containing approximately 2% co-precipitated cobalt hydroxide. Additions of

nickel and cobalt metal to the positive mix improves electronic conductivity, and promotes high active material utilization particularly at high discharge currents. Unfortunately, the cobalt additions to the positive electrode can be extremely detrimental to the negative zinc electrode if the ions are allowed to diffuse or migrate across the separator barrier. The offending material is generally soluble cobalt (II) that is reduced in contact with zinc metal to produce cobalt metal sites capable of catalyzing hydrogen evolution. The more recent use of spherical nickel hydroxide particles with a conductive cobalt (III) layer has proved more beneficial to the nickel-zinc cell. Without the need for excessive additions of cobalt metal or cobalt oxide, the contamination of the negative electrode has been minimized. Specific treatments of oxidized cobalt-treated nickel hydroxide have proved even more beneficial to the nickel-zinc battery by optimizing conditions of high cobalt stability with high positive electrode efficiency and minimal expansion over the cycle life of the cell.[17] These continuous improvements have gradually enhanced the reliability and abuse tolerance of the nickel foam/spherical nickel hydroxide based electrode technology and allowed a continuous production pasting process to be easily incorporated into the nickel-zinc manufacturing process.

Other nonsintered positive electrodes such as the roll-bonded positive method have been described as lower-cost alternatives to the pasted foam technology. In the former technique, nonaqueous fluids are used to fibrillate dry Teflon particles in the creation of rubberized active material sheets that are pressed onto either side of a nickel-plated steel substrate to create the three-dimensional electrode. As a further cost reduction step, graphite or carbon is employed as a low-cost substitute for nickel-metal conductive diluents, but invariably there is gradual oxidation of the carbon to create carbonates that slowly destroy the alkalinity of the electrolyte over time with a resulting degradation of the midpoint discharge voltage and power capability. A major disadvantage of this type of electrode is the loss in volumetric energy density from the use of such a low-density conductive material.

The most widely adopted positive electrode for the nickel-zinc system has proved to be the pasted nickel-foam variety. The electrode used readily available starting materials and delivered high energy density and good current carrying capability. In addition, the pasting technique provided a clean continuous electrode processing method at low capital cost for high volume production.

23.3.4 The Zinc Electrode

The rechargeable zinc electrode normally contains 50 to 200% ampere-hour excess of zinc and zinc oxide as compared to the positive nickel hydroxide electrode. The electrode is prepared in a fully discharged state although zinc metal or alloy may be present for enhanced electrode conductivity and additional active discharge material. Methods of preparation of the electrode include slurry coating and pasting as well as less widely used methods such as roll bonding and simple pressing. The most common current collector substrates are perforated or expanded sheets of copper or brass, although substantial advantage is claimed from the use of a copper foam that creates a three-dimensional conducting matrix.[18] Substrates have generally incorporated a surface layer that inhibits hydrogen evolution at the zinc potential and is stable under conditions where the negative electrode undergoes polarization. This may occur during high-rate or low-temperature discharge. The necessity for more "green" batteries has eliminated lead plating as the preferred surface layer in favor of silver or tin. A more recent approach created a corrosion resistant alloy[19] by heat treating a tin-plated copper current collector.

The composition of the negative electrode precursor mix includes conductive elements, anticorrosive additives as well as the fine particle (<1 micron) zinc oxide active material. Other additives such as cellulose[20] and aluminum fiber[21] can provide electrolyte irrigation, while other ceramic materials such as aluminum oxide are useful in trapping soluble zinc hydroxides before they migrate away from their original location. As with most battery electrodes, there is always the need for one or more binders to provide electrode integrity and prevent powder generation during processing. In aqueous pasting or slurry coating techniques, additional processing additives such as carboxymethyl cellulose and various oxide dispersants may be added as an aid to paste stability and flow characteristics. The conductive elements may include metal oxides with redox potentials positive of the zinc potential or zinc metal itself. Other electronically conductive materials such as carbon, conductive polymers, and ceramic materials have also been used.

Perhaps one of the most extensively used oxide additives has been calcium oxide. This material has the benefit of combining with zinc oxide to create calcium zincate that is a much less soluble

discharge product than the normal zinc hydroxides. The weight of calcium oxide added may be as much as 25 wt % of the active zinc. This significantly increases the weight of the negative electrode and decreases cell energy density. There may also be electrode kinetic factors that restrict the effectiveness of this additive to lower rate discharges and charges. Studies have determined the kinetics of calcium zincate formation is relatively slow, indicating that as discharge rates increase, there may be less benefit to the calcium addition.[22]

From an electrode fabrication perspective, calcium oxide additions normally restrict electrode processing to nonaqueous techniques such as roll bonding where rubberized sheets of the zinc electrode are pressed into or onto the substrate. Attempts to form the zincate during aqueous paste mixing invariably failed as the exothermic reaction between zinc and calcium oxides resulted in an unworkable mixture. Pasting or slurry coating a zinc electrode containing calcium oxide from an aqueous medium required the preformation of calcium zincate.

In summary, the application and current drain requirements may determine the type of negative zinc electrode that may be included in the cell. High-current drain favors copper foam current collection and zinc oxide containing compositions. Lower-current drains may favor the copper foil current collector with calcium zincate additives. Both types of electrode must work in tandem with specific electrolytes and separator systems to reduce dendrite formation and electrode active material redistribution.

23.3.5 Separator and Electrolyte Design Considerations

Most nickel-zinc cell designs employ a multicomponent separator that includes a thin microporous polyolefin dendrite penetration barrier combined with a more highly porous material capable of absorbing and retaining electrolyte. Traditionally, at least one layer of microporous polyolefin is wrapped around the zinc electrode to limit electrolyte access and reduce the dissolution of zinc oxide. Since this separator is a major cost element of the cell, it is prudent to minimize the number of layers necessary to achieve the desired cycle life. Although one layer is often all that is necessary to provide several hundred charge-discharge cycles, two layers can provide the necessary insurance against separator defects or mechanical damage during the manufacturing process. Of particular concern in cylindrical cells is the winding process, where the thin polyolefin separator sheets may be damaged as components slide against one another during jelly-roll assembly. Some simplification in the assembly process can be achieved by laminating the separators, particularly when using more than two individual layers. High-power and high-energy applications will seek to minimize these separator layers and reduce resistive losses by the choice of a highly conductive electrolyte.

To meet the demand for even higher-energy-density nickel-zinc batteries in the future, one of the most probable approaches will be to use thinner microporous separator materials that have been developed for high-power, high-energy-density lithium-ion cells.

23.4 PERFORMANCE CHARACTERISTICS

The general characteristics of nickel-zinc batteries are given in Table 23.2. Relevant parameters are given value ranges that encompass both cylindrical and prismatic versions of the technology. The higher volumetric energy density and power density figures correspond to small, cylindrical cells optimized for small size and high power. Cycle life figures are highly variable and dependent upon the design, discharge and charge conditions, as well as the defined capacity level at which the test is terminated. Nickel-zinc batteries generally show a gradual loss in Ah capacity during cycling, with end of life being determined when the value reaches 60 to 80% of the initial rated capacity. At higher discharge rates, original equipment manufacturers frequently specify an end of life capacity that is less than the normally accepted 80%.

One of the most important advantages of the nickel-zinc battery is the low impedance, which is a direct consequence of the reduced cell count necessary to achieve battery voltage. A 14.4 V battery will require approximately 30% fewer cells than an equivalent nickel-cadmium or nickel-metal hydride version. While this has a significant impact on the weight and size, there is an immediate 30% reduction in the impedance if the individual cells have comparable impedance values. In general, the nickel-zinc cell will have lower impedance than similar size alkaline cells because of the use of a

TABLE 23.2 The Range of Characteristics of Nickel-Zinc Batteries

Parameters	
Cathode electrochemistry	$Ni(OH)_2$ /NiOOH
Anode electrochemistry	ZnO/Zn
Electrolyte (% potassium hydroxide)	20 to 35
Separator	Microporous + wicking
Nominal cell voltage (volts)	1.65
Operating temperature range (°C)	–20 to 50
Theoretical specific energy (watthour per kilogram)	334
Specific energy (watthour per kilogram)	70 to 110
Energy density (watthour per liter)	130 to 350
Specific power (watts per kilogram)	280 to 2500
Power density (watts per liter)	420 to 7000
Charge retention (percent loss per month at 25°C)	20
Cell cycle life (cycles at 100% DOD)	300 to 900

low resistivity copper current collector and the inherently fast electrochemical kinetics of the zinc electrode. The room-temperature voltage profile of a PowerGenix 48 g sub *C* size cylindrical cell is shown in Fig. 23.3 for differing discharge rates as a function of the delivered capacity. The AC impedance of this cell measured at 1 kHz is under 4 mΩ and the direct-current impedance calculated from the midpoint voltage is less than 8 mΩ. Even at a 20 A discharge current, the midpoint voltage is 1.55 V and the difference in delivered capacity from cells discharged at 400 mA is less than 100 mAh. The temperature rise during the discharge as measured by a thermocouple located on the side of the cell case is below 50°C when the cell is completely discharged at the 15 *C* rate.

Extremely high currents can be delivered by a nickel-zinc sub *C* size cell under constant voltage load. At the 1 V level, currents in excess of 140 A can be delivered with calculated power densities greater than 2.5 kW/kg over a 20 s time period (Fig. 23.4).

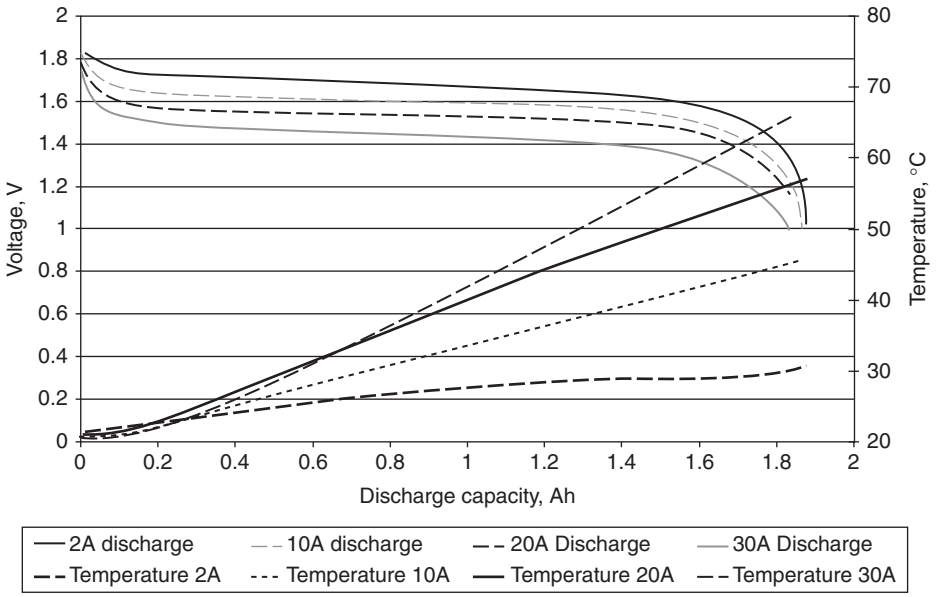

FIGURE 23.3 The voltage-capacity curves for a 1.9 Ah sub *C* cell and associated temperature rise. (*Courtesy of PowerGenix, Inc.*)

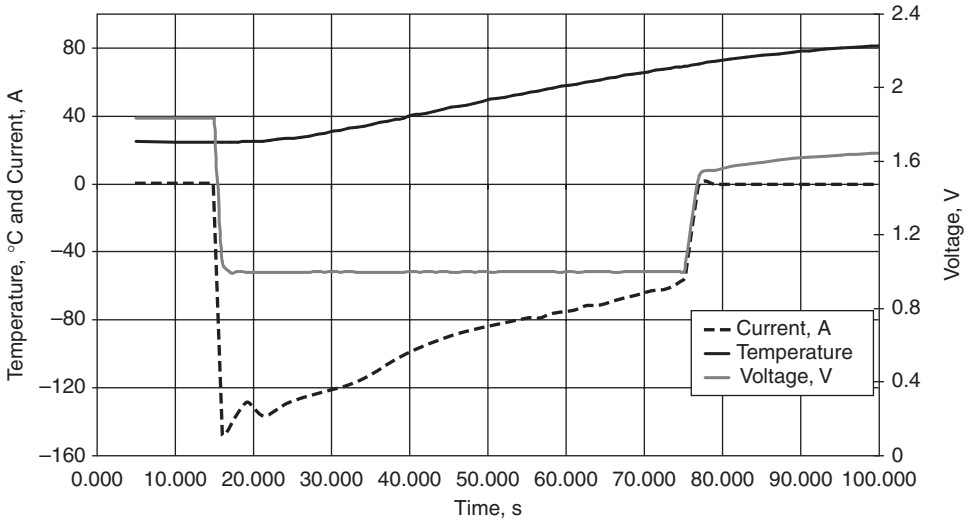

FIGURE 23.4 Current and temperature response of sub *C* size cell held at 1 V. (*Courtesy of PowerGenix, Inc.*)

Ambient temperature affects both the delivered capacity and the discharge voltage level of the cell. The discharge curves of the high-rate sub *C* size cell at the 5 *C* discharge rate and various temperatures are shown in Fig. 23.5 after charging was completed at room temperature.

The high-rate, room-temperature cycle life of both the single cell and a 19.2 V battery encased in plastic is shown in Fig. 23.6. The battery consists of 12 sub *C* size cells connected in series. The discharge current is maintained at 10 A to 1.1 V per cell with a 20 A current being applied periodically every 50 cycles as a check of power degradation. In the case of the single cell and the battery pack, power degradation was minimal over the period of the test and no soft shorts were detected by periodic open-circuit voltage decay checks. The single cells achieved approximately 900 cycles to

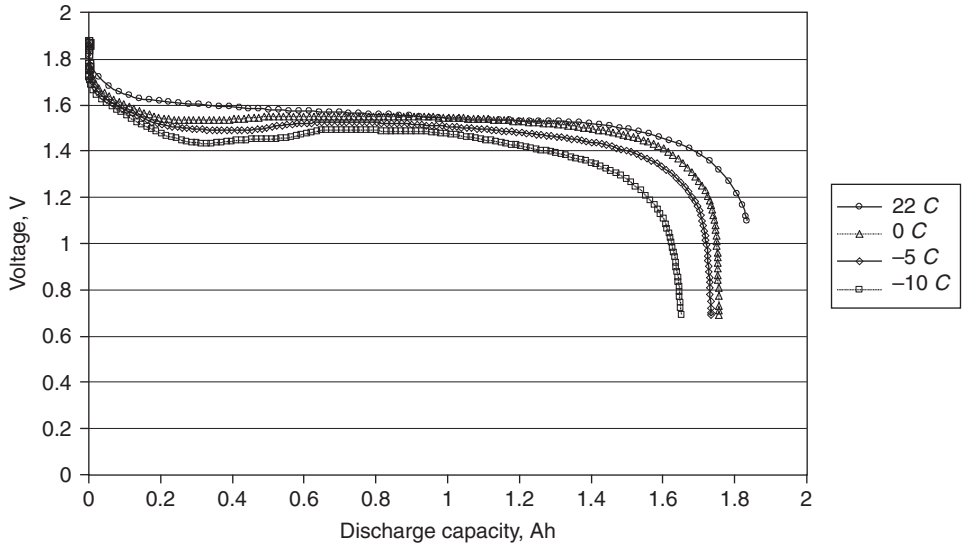

FIGURE 23.5 The effect of temperature on the voltage response of a nickel-zinc sub *C* size cell discharged at the 5 *C* rate. (*Courtesy of PowerGenix, Inc.*)

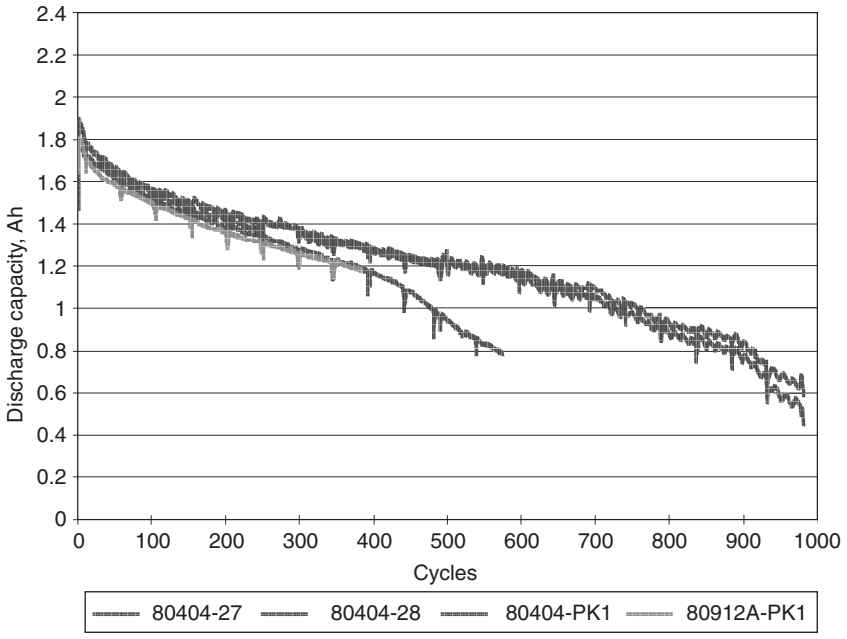

FIGURE 23.6 10 A cycling of single sub *C* size cells and the 19.2 V plastic encased battery. (*Courtesy of PowerGenix, Inc.*)

a capacity value of 0.8 Ah. There is a faster degradation in the pack capacity versus the single cell, probably as a result of the increased temperature within the pack and the inevitable overdischarge and overcharge of some of the closely packed cells with differing thermal environments.

Figure 23.7 shows the voltage curves at different discharge rates for a 1500 mAh AA-size cell and Fig. 23.8 illustrates how the discharge curves are affected by temperature at a fixed discharge rate of 1 *C*.

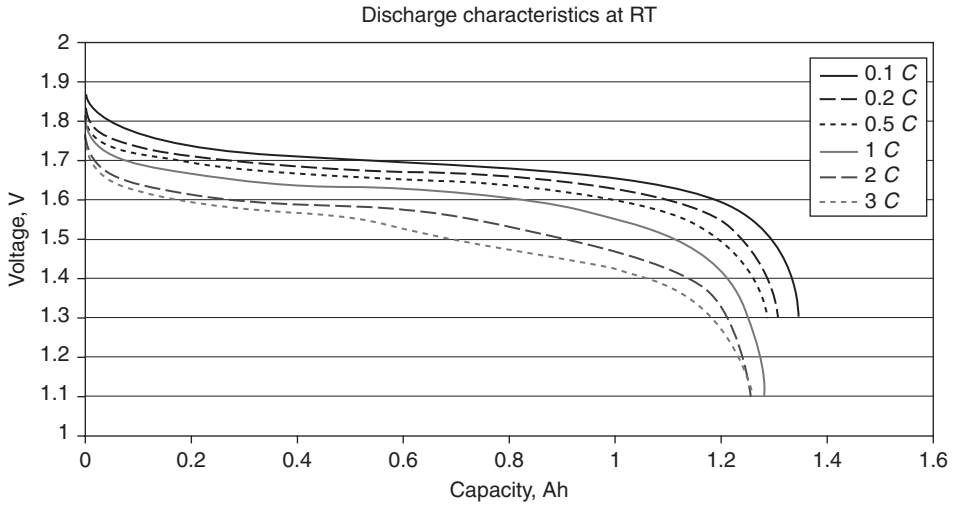

FIGURE 23.7 The voltage-capacity curves of the 1500 mAh AA-size cell. (*Courtesy of PowerGenix, Inc.*)

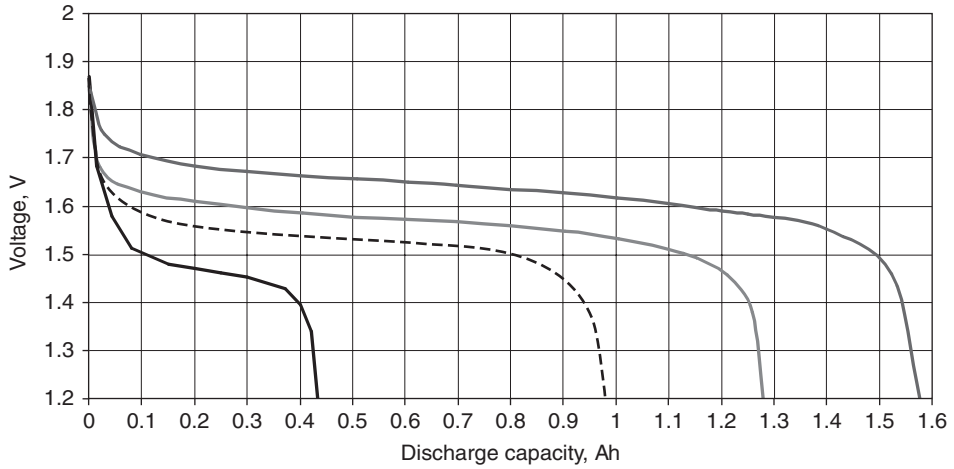

FIGURE 23.8 The 1 *C* discharge behavior of 1500 mAh AA-size cells at 25 *C*, 0 *C*, –10 *C,* and –18 *C* after charging at 0.5 *C* rate at room temperature. (*Courtesy of PowerGenix, Inc.*)

The 1500 mAh AA-size cell is a general-purpose, medium-rate cell with an internal impedance of 12 mΩ for target applications such as digital cameras and electric toothbrushes. Figure 23.9 shows the cycle life when charged within 2 h and discharged completely over a 1 h period. For higher-power applications, a 1300 mAh AA-size cell is available with an AC impedance of 6 mΩ. Figure 23.10 shows a relatively flat voltage response during discharges between 0.25 A and 10 A. The cycle life of a high-power AA-size 10.4 volt pack discharged at 10 A is shown in Fig. 23.11.

The largest cylindrical cells currently available are D size with capacities of 6.5 and 8 Ah. This cell size is specifically designed for light electric vehicles where periodic high-pulse currents are required for acceleration and hill climbing. Figure 23.12 shows the voltage response to various current levels up to 80 A.

Larger capacity prismatic nickel-zinc cells have been produced by Evercel and S.C.P.S. in France. The latter company has demonstrated 30 Ah cells with an excellent cycle life of over 900 cycles to

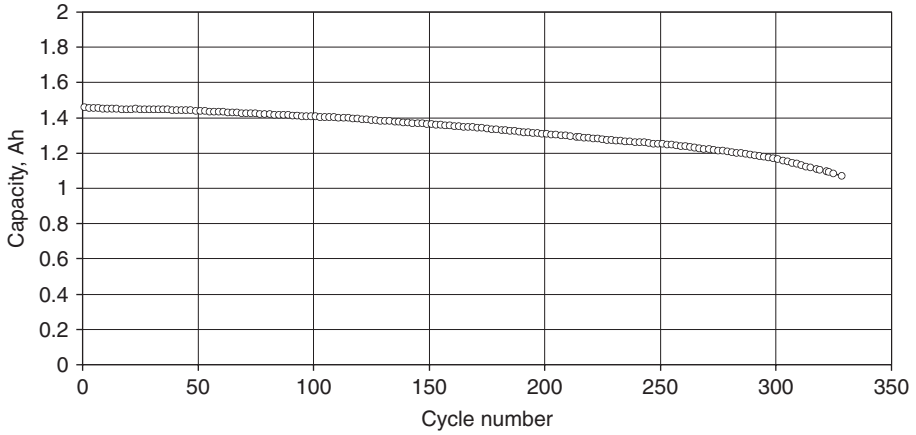

FIGURE 23.9 The capacity-cycle number graph for the 1500 mAh AA-size cell discharged at the 1 *C* rate and charged at the 0.5 *C* rate. (*Courtesy of PowerGenix, Inc.*)

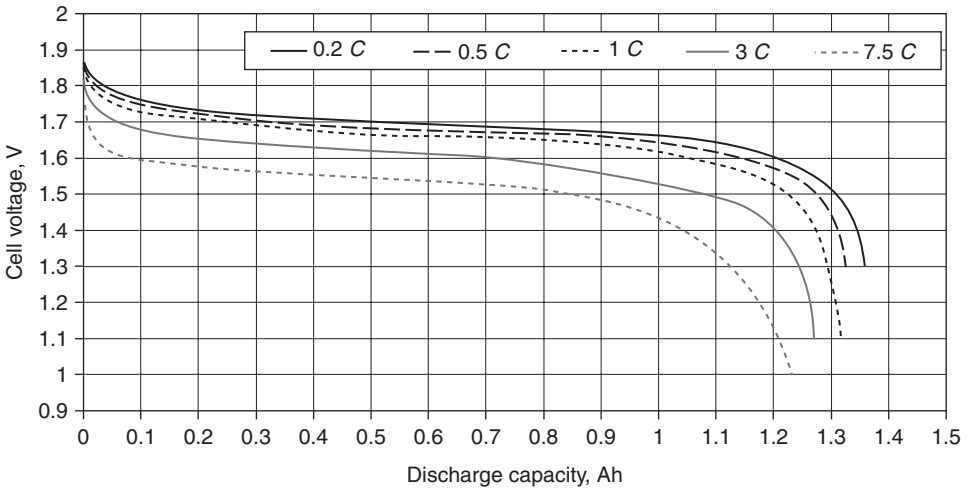

FIGURE 23.10 The cell voltage vs. discharge capacity for the 1300 mAh high rate AA-cell at various discharge rates. (*Courtesy of PowerGenix, Inc.*)

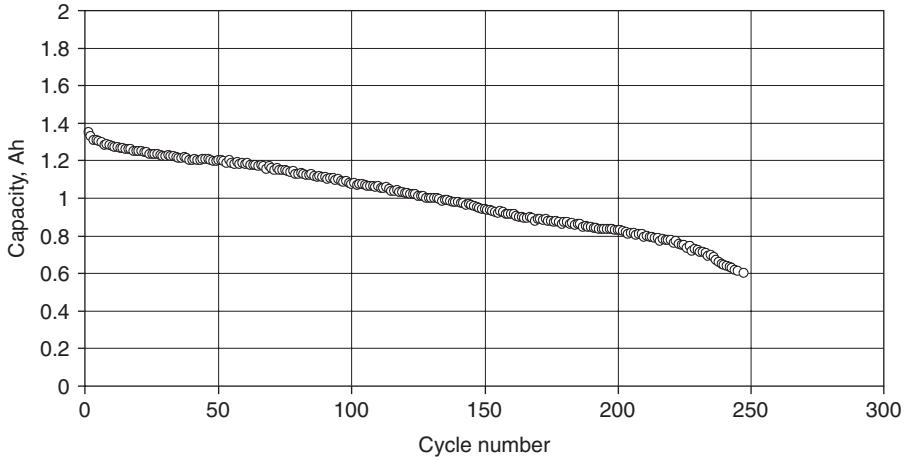

FIGURE 23.11 The capacity-cycle number graph for a 6-cell 10.4 V pack of 1300 mAh high-power AA-size cell discharged at 10 A and charged at 600 mA. (*Courtesy of PowerGenix, Inc.*)

80% depth of discharge at the *C*/3 discharge rate with specific energy values between 70 and 80 Wh/kg and energy density values of 130 Wh/L. Figures 23.13 and 23.14 illustrate the discharge rate dependence of the capacity and the cell cycling performance. Special design features focus on improving the zinc electrode conductivity by inclusion of copper foam as the negative current collector together with the use of conductive ceramic additives to suppress dendrite formation. These cells extend service life by including gas recombination electrodes and a charging method that limits the oxygen generated by the positive electrode.

A decrease in the depth of discharge during cycling will increase the number of cycles to a given capacity; however, for nickel-zinc cells, cycling to 100% depth of discharge may only decrease the cycle life by 20%. For multicell batteries, this factor will be greater and dependent on discharge rate, thermal environment, and the extent to which the cells have been capacity matched initially.

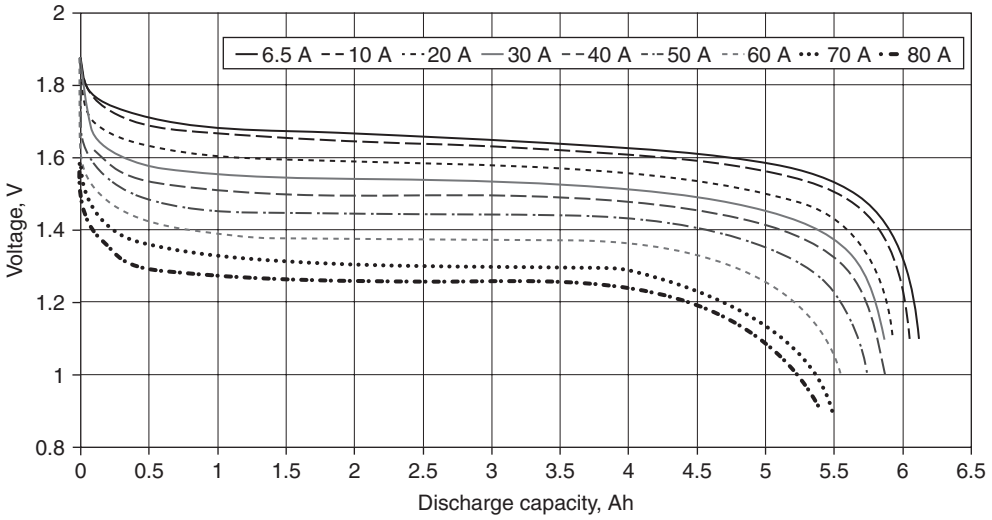

FIGURE 23.12 The voltage vs. discharge capacity for a 6.5 Ah D-size cell at various discharge rates. (*Courtesy of PowerGenix, Inc.*)

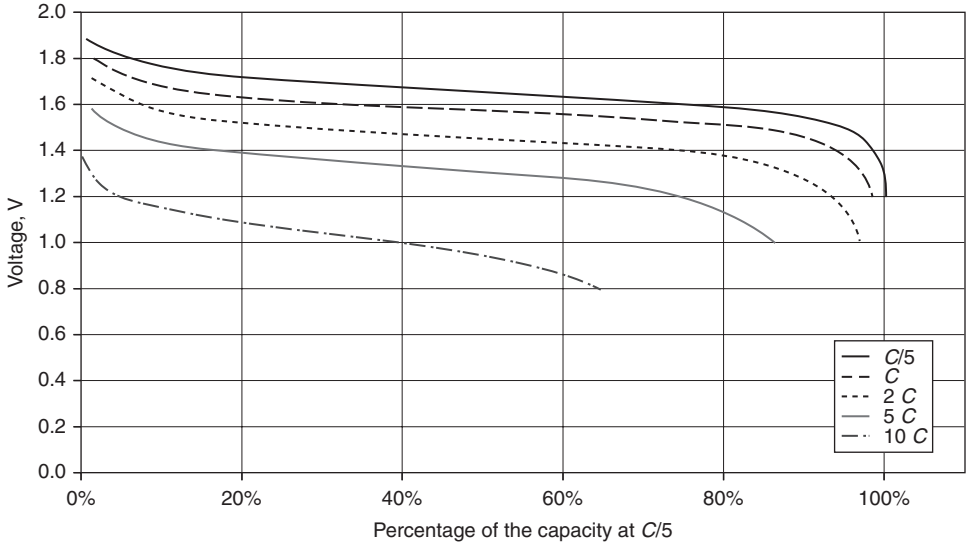

FIGURE 23.13 Discharge curves at various discharge rates for 30 Ah prismatic cell. (*Courtesy of S.C.P.S. France.*)

23.4.1 Storage Characteristics

The room temperature self-discharge rate of both the prismatic and cylindrical cells is approximately 1% of the ampere-hour capacity per day. As with all alkaline nickel batteries, long-term storage above 50°C is not recommended, however, accelerated testing is often performed at 60°C to establish the cells tolerance to extreme temperature conditions likely to be encountered during transportation. Fully charged cylindrical cells subjected to 60°C temperatures for a period of 30 days usually show capacity loss values of 20 to 30% under 5 *C* discharge conditions but do

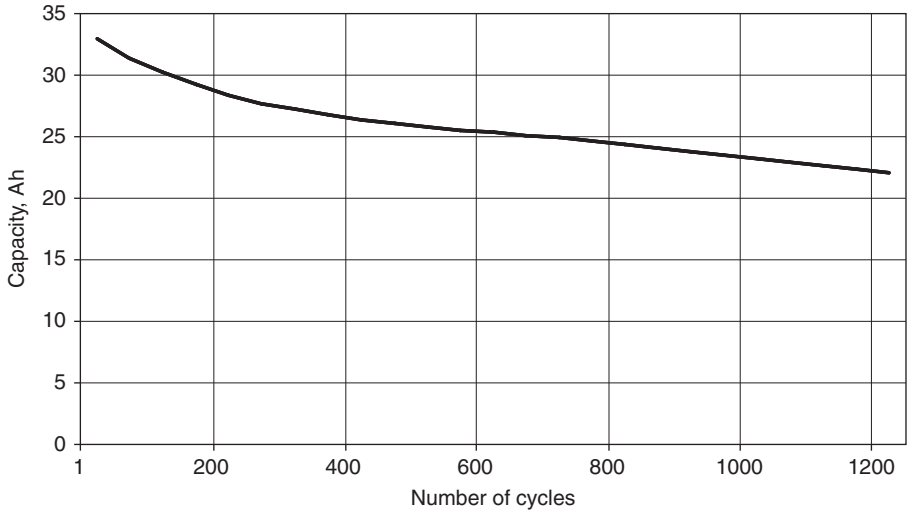

FIGURE 23.14 The cycle life of a 30 Ah prismatic cell under *C*/3 discharge and 80% depth of discharge. (*Courtesy of S.C.P.S. France.*)

experience approximately 5% loss in initial delivered capacity after recharging. Cycling performance is unaffected by the storage. For prismatic cells with incorporated recombination catalysts, the capacity retention may be higher since the evolved gases that recombine at electrode surfaces in cylindrical cells can contribute to the self-discharge of the electrode.

23.4.2 Safety Considerations

All commercially available cells and batteries should meet the minimum safety standards outlined in Underwriters Laboratories Inc. Document UL 2054 for Household and Commercial Batteries. This safety standard includes a series of mechanical tests that include shock and vibration and more severe crush tests. Various electrical tests that range from simple short-circuit tests to abnormal and abusive charge and discharge are defined with the purpose of creating standards that will reduce the risk of fire, explosion, and personal injury. All the PowerGenix cylindrical nickel-zinc cells described here pass these minimum standards and closely resemble the behavior of nickel-cadmium batteries. Any dangerous pressure buildup within the cell is released through a resealable vent designed to remain closed under all normal operating conditions. Testing above and beyond the UL standard has established nickel-zinc as exceptionally safe under the most abusive 5 *C* continuous overcharging and overdischarging. In both cases, the passage of current pressurizes the cell by breaking down the electrolyte into hydrogen and oxygen. Eventually the vent opens to release the pressure with resulting dry-out in less than 20 min (Fig. 23.15). Other extreme abuse tests such as a vertical crush test and screw and nail penetration tests have equally benign results to demonstrate a safety level that is necessary in the more abuse-prone power-tool industry.

23.4.3 Charging Nickel-Zinc Cells and Batteries

Figure 23.16 shows the voltage response at room temperature when a cylindrical sub *C* cell is charged continuously at 1 A. The internal pressure is also monitored using a strain gauge attached to the side of the cell. The voltage rises quickly above 1.8 V and maintains an efficient charge plateau with a midpoint

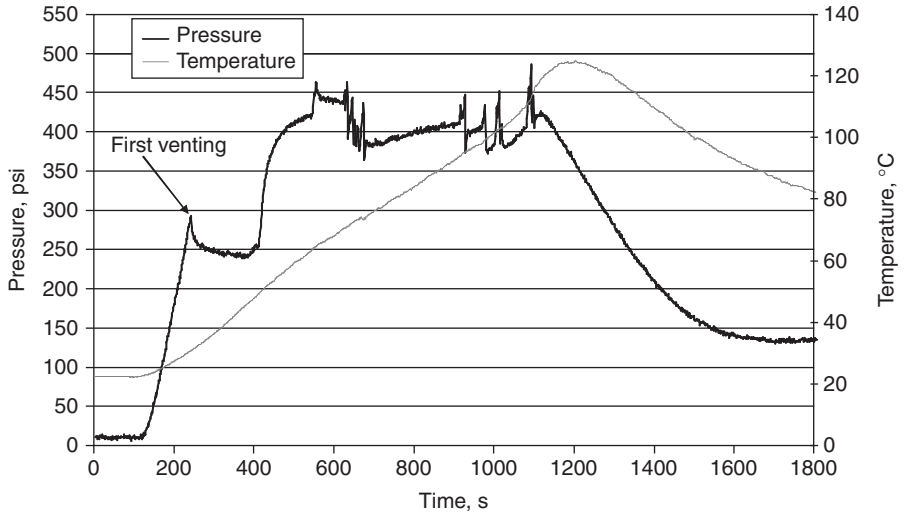

FIGURE 23.15 The 10 A overcharge test on sub *C* cells without internal fuse. (*Courtesy of PowerGenix, Inc.*)

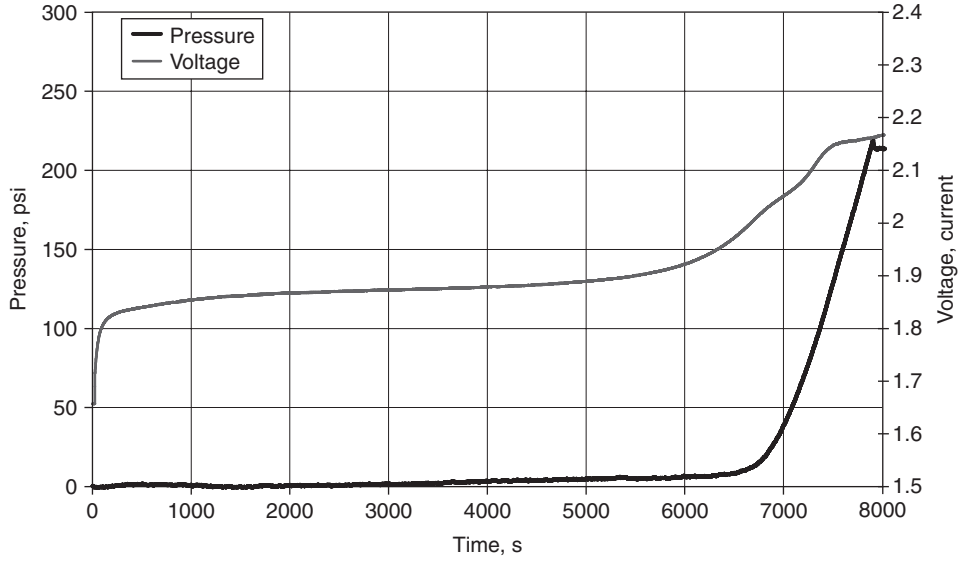

FIGURE 23.16 The gas pressure and voltage variation during charge a sub *C* of cell at 1 A. (*Courtesy of PowerGenix, Inc.*)

voltage of 1.875 V. The shape of the voltage–time charge curve resembles that of nickel-cadmium batteries and reflects the acceptance of charge by the positive nickel-hydroxide electrode. Significant oxygen gas pressure buildup occurs when the voltage of the cell increases above 1.95 V and the rate of generation of oxygen outstrips the rate of recombination. It is the relatively low oxygen recombination rate that prevents the use of constant current charging techniques at higher charge currents. An alternative is the constant current–constant voltage technique that resembles the taper current charge used in lead-acid and lithium-ion batteries. The cell is charged at a constant current until a predetermined voltage

is reached and held as the current tapers to a given value or a fixed time elapses. The constant-voltage value must be manufacturer determined since it is affected by many cell variables including the composition of the positive electrode, electrolyte concentration, cell impedance, gas recombination rate, as well as the charge current and cell temperature. For the example shown in Fig. 23.16, the optimal voltage is 1.9 V per cell at 22°C with a temperature variation of –3.5 mV per degree C.

23.4.4 Failure Mechanisms of Nickel-Zinc Cells and Batteries

The failure modes of nickel-zinc batteries and cells are intimately linked to the application, the rate of charge and discharge, and the mechanical and thermal characteristics of the battery pack. Many of the historical early failure modes associated with nickel-zinc cells have been eliminated, to be replaced in later life by the more generic modes experienced by other systems. The predominant failure mode of multicell batteries is the dry-out associated with continuous overcharge and overdischarge of specific cells that have deviated from the average capacity. This can occur naturally over hundreds of cycles despite efforts to match their initial capacities, or it may be gradually precipitated by variations in the thermal environment as a result of suboptimal pack design. The service life benefits of good thermal management in the design of high-rate nickel-zinc battery packs can be substantial, particularly in higher voltage packs. Dry-out can also eventually be a problem for prismatic single cells with relatively low pressure vents where gas recombination may not be high enough to prevent gradual water loss over hundreds of cycles. This does not appear to be an issue for the sealed cylindrical cells even when subjected to high-rate discharges. The major failure mode at high charge and discharge rates is the gradual pore blockage of the separator as zinc deposits build up, a result of the rapid changes in the hydroxide concentration. However, this is rarely seen below 600 cycles. At low discharge rates ($< C/2$), cells may fail more often by the formation of soft shorts after several hundred cycles. These failure mechanisms are not unique to nickel-zinc batteries, and may be exacerbated by manufacturing defects that can promote shorts due to misalignment of components or damage to key elements such as the microporous separator. The elimination of cell manufacturing defects follows industry standards with focus on active process monitoring and the implementation of preshipment cycling and storage conditioning with close inspection of delivered capacities, open-circuit voltages, and impedance measurements.

23.5 APPLICATIONS

Nickel-zinc batteries are the low-cost, small, lightweight alternative to nickel-metal hydride, nickel-cadmium, and lithium-ion technologies. Unlike lithium-ion, they are abuse-tolerant, do not require extensive battery management electronics, and have the ability to deliver high currents that exceeds all three competitive technologies. They are an ideal candidate to replace nickel-cadmium in all applications because of their performance and environmental advantages.

23.5.1 Power Tools

Excellent abuse tolerance and high-power delivery are prerequisites for this application. The most common cells used in the power tool application are the 4/5 sub *C* and the sub *C* sizes. The direct replacement of nickel-cadmium or nickel-metal hydride by nickel-zinc technology results in an almost 30% reduction in the number of cells required and a corresponding reduction in the size and weight of the battery. The result is that an unwieldy 18 V nickel-cadmium pack can be replaced with an equivalent nickel-zinc pack in a lighter, smaller, 14.4 V form factor. A significant benefit of the reduction in cell count is the lowering of the pack impedance, which improves the power delivery

TABLE 23.3 A Comparison of Battery Performance for Professional Drills Using a 1 Inch Auger Bit in 2 Inch by 4 Inch Douglas Fir

Professional drill model	Technology	Cell count	Capacity (Ah)	Energy content (Wh)	No. of 1 in auger bit holes	Holes per watthour
Brand A 19.2 V	Ni-Zn	12	1.7	33	25	0.8
Brand B 18 V	Ni-Cd (sintered)	15	2.4	43	18	0.4
Brand D 36 V	Li-ion	10	3.0	102	49	0.5

and torque of the motor. Table 23.3 compares the number of 1 in auger bit holes that can be drilled using professional-grade cordless drills powered by three different battery technologies. Despite having less watthour energy content than the sintered nickel-cadmium powered drill, the nickel-zinc unit was capable of drilling 40% more holes. The nickel-zinc powered drill was also able to drill half as many holes with one third of the energy content as a 36 V lithium-ion powered drill. Significantly, the lithium-ion pack was approximately twice the size of the nickel-zinc unit. The advantage of the nickel-zinc pack over competitive packs is maintained for all high-power operations such as drilling holes with larger diameter spade bits and cutting wood with circular and reciprocating saws. In this respect, the nickel-zinc technology demonstrates a clear advantage in performing the more demanding tasks that might normally favor the use of a corded AC tool. Lower-power applications such as dry wall screw insertion are more likely to deliver performance levels that accurately reflect the energy content of the battery.

23.5.2 Lawn and Garden Tools

Power tools in this market segment tend to be larger and higher voltage than electric drills and circular saws. Typical tools include hedge trimmers, string trimmers, and electric lawn mowers that tend to be more seasonal in their use. Many of these tools use a lead-acid battery to maintain competitive pricing with AC-driven or gasoline versions, but this can lead to early problems with sulfation if the tool is not used for prolonged periods or the battery is not fully charged prior to storage. Overall, nickel-zinc technology provides a significant gain in the total cost of ownership combined with a 50% reduction in the size and weight of the power source. A high-rate nickel-zinc cell can offer as much as double the service life of a standard lead battery with less catastrophic long-term storage failures.

23.5.3 Light Electric Vehicles (LEVs)

Nickel-zinc batteries can offer electric scooters or electric bicycles a 50% smaller, lighter alternative to the lead-acid packs available now without sacrificing any range or hill-climbing capability. The relatively low cost per watthour of energy compared to other alkaline systems can provide the option of increasing battery capacity to more than double the range of the lead-acid pack with a similar size and weight. The battery-pack voltage of these vehicles is normally 24 or 48 V with a capacity requirement exceeding 15 Ah. This requirement may be met with a series-string 12 V nickel-zinc prismatic monoblocks or single cells. Alternatively, larger form factor cylindrical cells such as F or double D-size can provide battery capacities of 15 Ah without the need for parallel strings. These larger and more expensive packs can justify the inclusion of BMS modules that extend pack cycle life by limiting the overdischarge and by monitoring smaller series strings during the charge operation to prevent individual cell overcharge.

23.5.4 Hybrid Electric Vehicles (HEVs)

Hybrid electric vehicle battery packs operate in a power-assist mode where the most important characteristic of the battery is the ability to absorb high-rate regenerative braking charge and provide the high-rate discharge necessary for acceleration. The superior power density of the nickel-zinc alkaline system allows for a smaller and lighter battery pack compared to the nickel-metal hydride system without any sacrifice in performance. Since nickel-zinc is approximately 25% less costly than nickel-metal hydride, there is considerable opportunity for the development of lower-cost hybrid electric vehicle.

Figure 23.17 shows a size comparison of the nickel-zinc pack (top) against the standard nickel-metal hydride pack for a Toyota Prius. Table 23.4 outlines in more detail the differences between the two packs. While the pack energies were equivalent, the nickel-zinc pack was 30% smaller and lighter and delivered 30% more peak power.

FIGURE 23.17 A nickel-zinc D cell Prius battery pack compared to the existing prismatic nickel-metal hydride pack. (*Courtesy of PowerGenix, Inc.*)

TABLE 23.4 Comparison of Nickel-Metal Hydride and Nickel-Zinc Prius Packs

Parameter	PEVE NiMH	PGX Ni-Zn
Form factor	Prismatic	Cylindrical
Number of cells	168	128
Nominal voltage	201.6 V	204.8 V
Nominal capacity	6.5 Ah	6.5 Ah
Pack energy	1338 Wh	1357 Wh
Pack peak power	20 kW	26 kW
Gravimetric energy density	46 Wh/kg	69.3 Wh/kg
Bare pack weight	29.1 kg	19.2 kg

Evaluation criteria for hybrid electric vehicle batteries are given in the Partnership for a New Generation of Vehicles Battery Test Manual (see Chap. 29). Nickel-zinc batteries appear capable of meeting all key criteria of the power assist specification, including the 300,000 cycles required to be carried out over a specified state-of-charge range.

23.5.5 AA Consumer Cells

More than 90% of AA consumer cells are primary cells that ultimately end up in landfills. Both nickel-metal hydride and nickel-zinc cells provide a rechargeable option with overall cost benefits to the consumer. Unfortunately, the substitution of nickel-metal hydride for the primary 1.5 V zinc–manganese dioxide cell results in reduced performance and premature device shutdown as a result of having a 1.3 V operating voltage. Nickel-zinc technology provides a number of advantages that promote its adoption as a rechargeable alternative to the alkaline primary battery. Its operating voltage is compatible with the existing primary cells coupled with a low enough impedance to meet the demands of high-current draw devices such as digital cameras with built-in photoflash. The performance of the commercially available cells (Fig. 23.18) compares extremely favorably to other primary and rechargeable AA cells as shown in Fig. 23.19. The 1500 mAh nickel-zinc cell is capable of taking more than 5 times the number of pictures as the primary alkaline cell and has equivalent performance to the nickel-metal hydride cell with a much larger 2500 mAh capacity. In addition, the nickel-zinc cell is environmentally friendly and fully compliant with the European Union regulation for the Reduction of Hazardous Substances (RoHS).

FIGURE 23.18 Commercially available AA-size nickel-zinc cells. (*Courtesy of PowerGenix Inc.*)

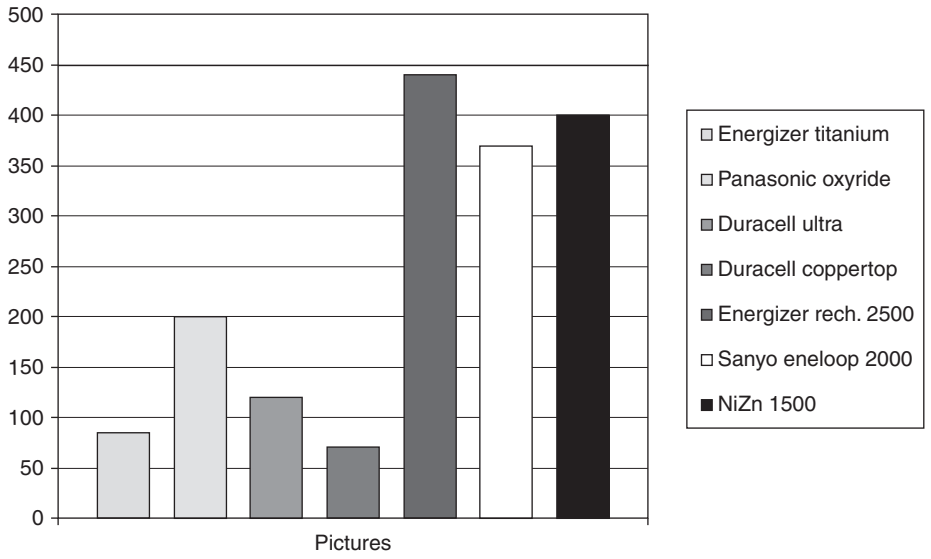

FIGURE 23.19 The number of pictures per cycle of various AA cells. (*Courtesy of PowerGenix, Inc.*)

23.6 ENVIRONMENTAL ASPECTS OF THE NICKEL-ZINC BATTERY

The nickel-zinc battery offers compelling environmental reasons for its adoption in a progressively "green" world. Nickel-zinc batteries are recognized and listed in the Rechargeable Battery Recycling Corporation (RBRC) recycle program, and may be recycled at more than 50,000 collection sites in North America.

The European Union RoHS regulation of 2006 required manufacturers to meet concentration limits on specific heavy metals and organic compounds. An equivalent directive was adopted in California, and similar requirements are likely to be imposed in China and Korea. Although batteries are exempt from the general RoHS provisions, a 2003 battery directive exists in Europe that tightens the limits for lead, mercury, and cadmium. Furthermore, unlike the general RoHS provisions, the concentration limits apply to the entire cell rather than specific components.

The 2003 battery directive requires the following maximum levels by weight:

- Cadmium –0.002%
- Mercury –0.0005%
- Lead –0.004%

Most nickel-zinc batteries meet these requirements. In general, nickel-zinc batteries are much less hazardous than both nickel-cadmium and nickel-metal hydride batteries and represent a greater opportunity for more complete recycling of the component chemicals.

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