Kirk-Othmer Encyclopedia of Chemical Technology.
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BATTERIES, ALKALINE SECONDARY CELLS

Alkaline electrolyte storage battery systems are more suitable than others in applications where high currents are required, because of the high conductivity of the electrolyte. Additionally, in almost all of these battery systems, the electrolyte which is usually an aqueous solution containing 25–40% potassium hydroxide [1310-58-3], KOH, does not enter into the chemical reaction. Thus concentration and cell resistance are invariant with state of discharge and these battery systems give high performance and have long cycle life. The annual production value of alkaline storage batteries is growing: it was over $2 billion (worldwide) in 1990, representing approximately 20% of the value for all secondary batteries.

Positive electrode active materials have been made from the oxides or hydroxides of nickel, silver, manganese, copper, mercury, and from oxygen. Negative electrode active materials have been fabricated from various geometric forms of cadmium [7440-43-9], Cd, iron [7439-89-6], Fe, and zinc [7440-66-6], Zn, and from hydrogen [1333-74-0]. Two different types of hydrogen electrode designs are common: those used in space, which employ hydrogen as a gas, and those used in consumer batteries, where the hydrogen is used as a metallic hydride. As indicated in Table 1 and Figure 1, nine electrode combinations exist in some scale of commercial production. Five system combinations are in the research/development stage as of this writing, and two have been abandoned before or after commercial production for reasons such as short life, high cost, low voltage, low energy density, and excessive maintenance.

The annual production value of small, sealed nickel–cadmium cells is over $1.2 billion. However, environmental considerations relating to cadmium are necessitating changes in the fabrication techniques, as well as recovery of failed cells. Battery system designers are switching to nickel–metal hydride (MH) cells for some applications, typically in “AA”-size cells, to increase capacity in the same volume and avoid the use of cadmium.

There are many methods of fabricating the electrodes for these cell systems. The earliest commercially successful developments used nickel hydroxide [12054-48-7], $Ni(OH)_2$, positive electrodes. These electrodes are commonly called nickel electrodes, disregarding the actual chemical composition. Alkaline cells using the copper oxide–zinc couple preceeded nickel batteries but the CuO system never functioned well as a secondary battery. It was, however, commercially available for many years as a primary battery (see Batteries-primary cells).

The original alkaline battery, designed by Edison around 1900, contained nickel hydroxide mixed with graphite [7782-42-5] in perforated steel pockets as the positive active material and a high surface area iron powder as the negative. Both positive and negative electrodes were “pocket” plates, where the active material was contained in small, rectangular, boxlike pockets formed from finely perforated sheet steel. These plates very closely resembled the pocket plates in use in some 1990 designs of nickel–cadmium batteries.

Because the nickel–iron cell system has a low cell voltage and high cost compared to those of the lead–acid battery, lead–acid became the dominant automotive and industrial battery system except for heavy-duty applications. Renewed interest in the nickel–iron and nickel–cadmium systems, for electric vehicles started in the mid-1980s using other cell geometries.

In the early 1930s, production of nickel–cadmium batteries having thinner pocket-type plates and lower internal resistence became available. This grew to be an important design for truck, locomotive, and marine

Table 1. Rechargeable Alkaline Storage Battery Systems

System[a]	Historical name	Voltage, V	Production[b]
nickel–cadmium	Jungner	1.30	vl
nickel–iron	Edison	1.37	s
nickel–zinc	Drumm	1.70	vs
nickel–hydrogen		1.30	l
silver–cadmium		1.38 and 1.16[c]	vs
silver–iron	Jirsa	1.45 and 1.23[c]	s
silver–zinc	Andre	1.86 and 1.60[c]	s
silver–hydrogen		1.38 and 1.16[c]	vs
Manganese–zinc[d]		1.52	vs
mercury–cadmium		0.92	r
air(oxygen)–zinc		1.60	r
air(oxygen)–iron		1.40	r
air(oxygen)–aluminum			r
copper–lead		1.20	r
copper–cadmium	Darrieus	0.45	n
copper–zinc	Waddell-Entz, Edison-LeLande, Lelande-Chaperon	0.85	n

[a] The substance named first represents the positive electrode; the substance named second is the negative electrode. In all cases except for air(oxygen) systems, the active electrode material is the oxide or the hydroxide of the named species.

[b] vl = $>100 \times 10^6$ A·h/yr product; l = $>25 \times 10^6$ A·h/yr; s = $>5 \times 10^6$ A·h/yr; vs = $<5 \times 10^6$ A·h/yr; r = research and development phase; and n = no longer in production.

[c] Silver electrodes have two voltage plateaus.

[d] Secondary system.

engine starting applications. Very high rate cell designs of nickel–cadmium cells became possible with the development of the sintered nickel substrate in 1928 (1) and then in the late 1940s and early 1950s, the shortcomings of the sealed nickel–cadmium designs were overcome (2, 3). The use of sealed nickel–cadmium cells grew rapidly and beginning in the early 1990s, designs of nickel–hydrogen, the hydrogen as hydride, cells captured a strong commercial and technical interest. Table 2 details the advances in alkaline battery technology from 1948 to 1990.

The nickel–zinc combination has a high cell voltage (about 1.75 V), which results in a very favorable energy density compared to that of nickel–cadmium or lead–acid. Additionally, zinc is relatively inexpensive and, in the absence of mercury additive, is environmentally benign. The nickel–zinc system was discussed as early as 1899 (4). There has been a resurgence of interest in the system for electric vehicles, but the problems of limited cycle life have not been completely overcome.

Silver [7440-22-4], Ag, as an active material in electrodes was first used by Volta, but the first intensive study using silver as a storage battery electrode was reported in 1889 (5) using silver oxide–iron and silver oxide–copper combinations. Work on silver oxide–cadmium followed. In the 1940s, the use of a semipermeable membrane combined with limited electrolyte was introduced by André in the silver oxide–zinc storage battery.

Many of the most recent applications for alkaline storage batteries require higher energy density and lower cost designs than previously available. Materials such as foam and/or fiber nickel [7440-02-0], Ni, mats as substrates, and new processing techniques including plastic bounded, pasted, or electroplated electrodes, have enabled the alkaline storage battery to meet these new requirements, while reducing environmental problems in the manufacturing plants. In addition, substantial technical efforts have been devoted to the recovery of used batteries. The most recent innovations in materials relate to the development of metal–hydride alloys for the storage and electrochemical utilization of hydrogen. Modifications to the chemical structure and/or the cell design of manganese dioxide [1313-13-9], MnO_2, electrodes have resulted in sufficient improvement to allow the reintroduction of the rechargeable MnO_2–zinc cell to the market as a lower cost, albeit lower performance,

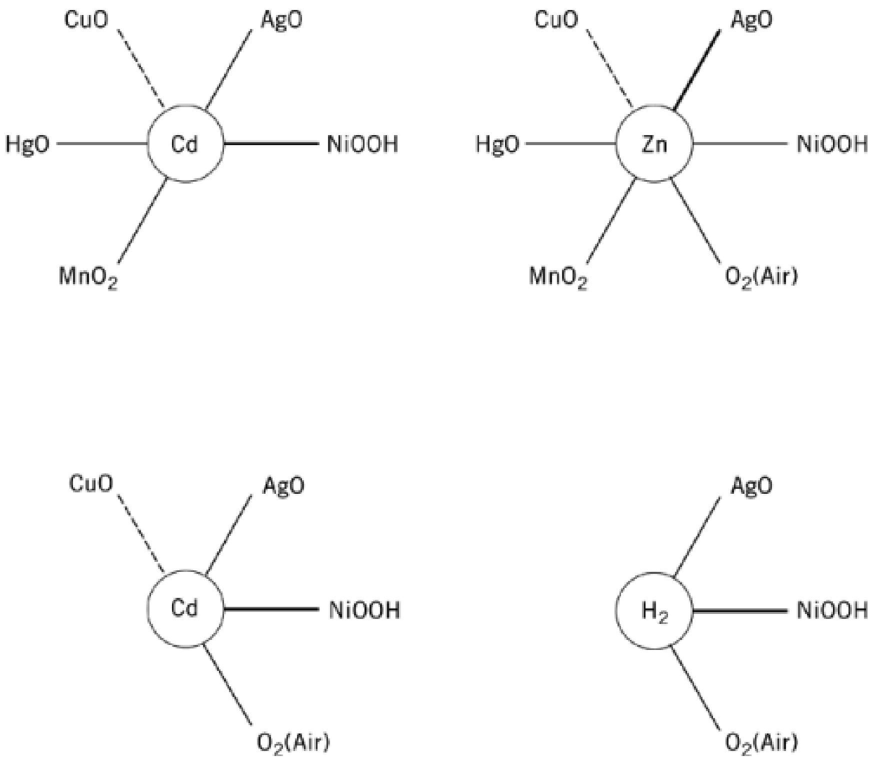


Fig. 1. Electrode combinations for alkaline storage batteries where the substance within the circle comprises the negative electrode and the combinations include (___) commercial products, (—) systems in research and development or limited production, and (---) historic system. The air (O_2)–H_2 system is commonly called a fuel cell.

alternative to nickel–cadmium consumer size cells. Improvements in materials science and electrical circuits have lead to better separators, seals, welding techniques, feedthroughs, and charging equipment.

1. Nickel–Cadmium Cells

1.1. Electrodes

A number of different types of nickel oxide electrodes have been used. The term nickel oxide is common usage for the active materials that are actually hydrated hydroxides at nickel oxidation state 2+, in the discharged condition, and nickel oxide hydroxide [12026-04-9], $NiO \cdot OH$, nickel oxidation state 3+, in the charged condition. Nickelous hydroxide [12054-48-7], $Ni(OH)_2$, can be precipitated from acidic solutions of bivalent nickel either by the addition of sodium hydroxide or by cathodic processes to cause an increase in the interfacial pH at the solution–electrode surface (see Nickel and nickel alloys; Nickel compounds).

Several investigators have used combined approaches, particularly in the *in situ* precipitation of active material in the pores of sintered substrates, using cathodic polarization and caustic precipitation in simultaneous or nearly simultaneous steps. A considerable amount of the reported information on the chemistry, electrochemistry, and crystal structure of the nickel electrode has been obtained on thin films (qv) made by the anodic corrosion of nickel surfaces. However, such films do not necessarily duplicate the chemical and/or crystallographic condition of active material in practical electrodes. In particular, the high surface area, space

Table 2. Technology and Processing Contributions to Alkaline Battery Development

Year	Procedure	Reference
1948	impregnation procedures for nickel and cadmium electrodes	6
1956	x-ray structure of nickel hydroxide electrode	7
1958	*in situ* x-rays of nickel and cadmium electrodes	8
	slurry-processed nickel-sintered electrode (SAFT)	9
1960	crystal structures of silver oxide	(10, 11)
	structure of nickel hydroxide electrode	12
	in situ study of the nickel electrode	13
1961	microporous plastic-reinforced zinc electrode	14
1962	microporous plastic-bound cadmium electrode	15
1965	solid-state chemistry of nickel hydroxide	16
	crystal structures of nickel hydroxide	17
1966–1970	impregnation procedures for nickel electrodes	(18–20)
1972	electrochemical impregnation method for nickel electrodes	21
1974	nickel foam substrates	22
1975	plastic-bonded nickel electrodes	23
1978	controlled microgeometry electrodeposited electrodes	24
1980	nickel composite electrode	25
1981	nickel fiber mat substrates	26
1984	nickel felt substrates	27
	production of nickel fiber electrodes	28
1987	rechargeable MnO_2–zinc cell	29
1989	modified manganese dioxide for deep-cycling	30
1990	metal–hydride-type hydrogen electrodes used in commercial nickel–MH cells	(31–35)

charge region, and lattice defect structure are different. Some of the higher $(3.5+)$ valence state electrochemical behavior seen in thin films has rarely been reproduced in practical electrodes.

The many varieties of practical nickel electrodes can be divided into two main categories. In the first, the active nickelous hydroxide is prepared in a separate chemical reactor and is subsequently blended, admixed, or layered with an electronically conductive material. This active material mixture is afterwards contained in a confining porous metallic structure or pasted onto a metallic mat or grid. Electrodes for pocket, tubular, pasted, and most button cells are made this way. The porous metallic structures such as the pocket or tube, ensure good particulate contact, prevent shedding, and confine expansion. Less expensive alternatives, those resulting from pasting on expanded metal, foam metal, punched corrugated sheet, or fiber metal nickel mat, do not confine expansion as well or provide the same amount of mechanical strength. Plastic reinforcement to minimize shedding and promote adherence to the substrate is often employed. The plastic mix can be achieved either by milling or extrusion of mixes at plastic flow temperatures or by using plastic–solvent combinations. The latter includes simple gels of water, KOH, and methylcellulose [9004-67-5].

The other type of nickel electrode involves constructions in which the active material is deposited *in situ*. This includes the sintered-type electrode in which nickel hydroxide is chemically or electrochemically deposited in the pores of a 80–90% porous sintered nickel substrate that may also contain a reinforcing grid.

Almost all the methods described for the nickel electrode have been used to fabricate cadmium electrodes. However, because cadmium, cadmium oxide [1306-19-0], CdO, and cadmium hydroxide [21041-95-2], $Cd(OH)_2$, are more electrically conductive than the nickel hydroxides, it is possible to make simple pressed cadmium electrodes using less substrate (see Cadmium and cadmium alloys; Cadmium compounds). These are commonly used in button cells.

1.2. Electrochemistry and Crystal Structure

The solid-state chemistry of the nickel electrode is complex. Nickel hydroxide in the discharged state has a hexagonal layered lattice, where planes of Ni^{2+} ions are sandwiched between planes of OH^-; as shown in Figure 2. This structure, similar to that of cadmium iodide [7790-80-9], CdI_2, is common to seven metal hydroxides including those of cadmium and cobalt. There are various hydrated and nonhydrated nickel hydroxides that have slightly different crystal habitats and electrochemical potentials. The most common form of charged material observed in batteries is NiOOH, density = 4.6 g/mL. In comparison, $Ni(OH)_2$ has a density of 4.15 g/mL. Thus the theoretical change in density on charge–discharge is only 9%, and the kinetics involve only a proton transfer. This reaction can be written in simplified form as:

$$2\ \beta\text{–NiOOH}^* + \mathrm{Cd} + 2\ \mathrm{H_2O} \rightleftarrows 2\ \mathrm{Ni\,(OH)}_2^* + \mathrm{Cd\,(OH)_2}$$

where the asterisks represent differing amounts of hydrated or absorbed water and/or electrolyte. It has also been established that species such as Li^+ and K^+ enter the nickel hydroxide structure to form a space–charge region and the actual reaction is believed to be more complicated than that shown. The interlayer separation of planes of nickel ions is increased by insertion of water or ions from the electrolyte. Different preparative and cycling conditions result in variations in defect crystal structures that affect electrochemical activity and the ability to retain charge (36). Additionally, electrode material oxidation states do not range precisely between $+2$ and $+3$, and because of hysteresis in the charge–discharge curves, direct measurement of an equilibrium potential is not possible.

The existence of $Ni(OH)_2$ and β-NiOOH as the usual discharged and charged materials was confirmed through x-ray diffraction powder patterns (7, 8, 37). The presence of other structural forms, in different electrolytes and under unusual cycling conditions, has also been observed. The crystalline-structural variability of $Ni(OH)_2$ has been described as being dependent on preparative procedure (16). Other phases form after prolonged overcharging of β-NiOOH in concentrated sodium hydroxide [1310-73-2], NaOH, or KOH. At elevated temperatures, in lithium hydroxide [1310-65-2], LiOH, electrolytes, $Ni(OH)_2$ is oxidized to a trivalent phase having the lithium nickelate [12031-65-1], $LiNiO_2$, crystalline structure and lithium additions to KOH electrolytes eliminate the formation of α-phase material. The sequence of these electrochemical processes has been summarized as: (*1*) an electrochemical exchange at the solid electrolyte interface involving a set of ionic-electronic lattice imperfections; (*2*) electron transport through the oxidized phase region to the metallic contact; (*3*) mass transport through the oxidized phase to the lower valence phase at the second interface; and (*4*) electrochemical exchange at the second solid-phase interface functioning as a source or sink for the ionic-electronic imperfections necessary to maintain the mass and charge balance.

A sequence of events taking place in the charge process has been described (16) demonstrating that during constant current charge, the surface double-layer region first produces a local interior space–charge field. As the semiconductor charge phase is extended into the interior, a distributed space–charge field is formed that is characterized by a combination of the semiconductor band structure and the mobility of dopant imperfections. When the state of charge increases, the magnitude of the space charge decreases. At the end of charge, there is only an ir (voltage) loss in the solid, and the applied field is mainly at the solid electrolyte interface. If charging is continued until a steady-state oxygen evolution is attained, the distributed space charge disappears. The semiconductor is characterized by a flat band potential and, if the nickel electrode is left on open circuit, the space charge-field gradually decays through atom movements in the solid phase, approximating a flat band potential condition.

The charge–discharge process cannot be satisfactorily represented by one equation (17). At least two reactions, based on different starting materials as well as different products, can be formulated. Both reactions are heterogeneous. In each of the reaction chains two distinct states exist in the oxidized phase. One of these can only be charged whereas the cathodic current are blocked. The other state, existing at a lower potential,

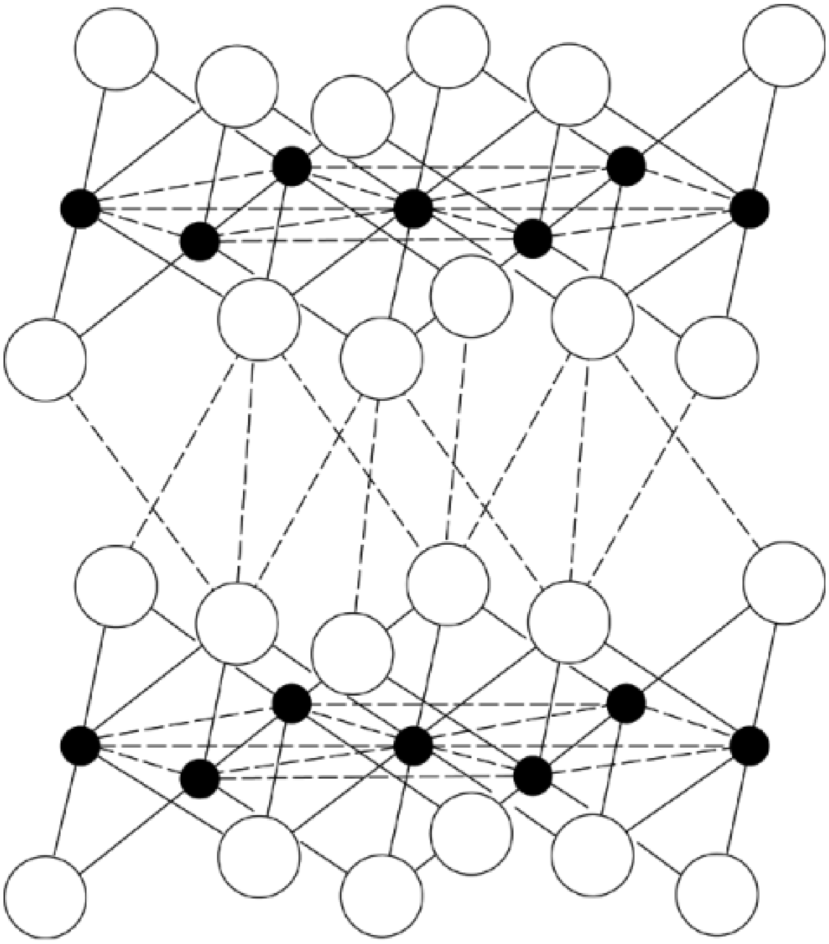
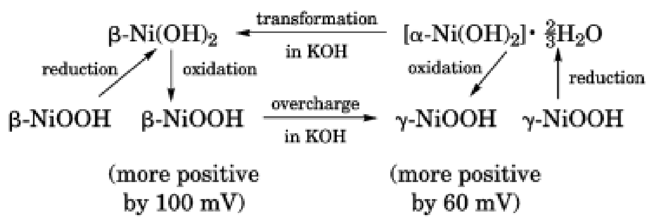


Fig. 2. Nickel hydroxide structure where (•) represents nickel and (○) represents oxygen or hydroxyl.

can only be discharged but was blocked in the anodic direction. When the observed potential differences are extrapolated into the region of very low current densities, the difference between the two states is ca 60 mV in one of the reaction chains and ca 100 mV in the other. Thermodynamically this means that neither reaction series can be described by a single, reversible potential as in the manner of the Cd–Cd$(OH)_2$ or PbO_2–$PbSO_4$ electrodes. Rather, the semiconductor properties of oxidized nickel hydroxides play some part.

The description of the process is best illustrated as (17):



The nickel oxide modification obtained electrochemically in KOH electrolyte contained potassium ion and its nickel oxidation level are higher than that of $NiO_{1.5}$. Conclusions regarding the transitions between the reduced and oxidized products within the two series are that the redox process was not reversible and although the oxidized phases of the β- and the γ-nickel hydroxides differ in energy contents, differences in analyses and x-ray patterns are not significant.

Some γ-NiOOH has been shown to be formed in sintered nickel electrodes (38), and changes in water and KOH concentration during the cycling of nickel electrodes has been studied (12, 39–41). Although there is some disagreement on the movement of water, KOH is adsorbed on the nickel electrode when the cell is charged and desorbed from the electrode when the cell is discharged.

The chemistry, electrochemistry, and crystal structure of the cadmium electrode is much simpler than that of the nickel electrode. The overall reaction is generally recognized as:

$$\mathrm{Cd} + 2\,\mathrm{OH}^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \mathrm{Cd(OH)_2} + 2\,e^-$$

However, there is a strong likelihood of a soluble intermediate in the formation of $Cd(OH)_2$. Cadmium has an appreciable solubility in alkaline solutions: $\sim 2 \times 10^{-4}$ mol/L in 8 M potassium hydroxide at room temperature. In general it is believed that the solution process consists of anodic dissolution of cadmium ions in the form of complex hydroxides (see Cadmium compounds).

In more recent studies involving cyclic line scan voltammetry of the nickel electrode, it was suggested that nickel can exist in the positive 2, 3, and 4 oxidation states (42). The structural parameters (43) using transmission extended x-ray absorption fine structure (exafs) and *in situ* electrodes confirmed earlier x-ray data (7, 8), showing that the presence of cobalt [7440-48-4], Co, does not change crystal lattice parameters. The density and compressibility of nickel electrodes have been found to be highly variable (44). Cobalt additions appear to reduce the compressibility of nickel hydroxide, resulting in a firmer attachment of the active material to the substrate. However, a felt metal grid has been shown (45) to reduce shear failures of the electrode structure and minimize the need for stabilizing additives, such as cobalt.

In addition to the normal charge–discharge reaction, properly fabricated sealed nickel–cadmium cells have a mechanism for absorbing infinite amounts of overcharge. The cell must be fabricated with an excess amount of uncharged active material [$Cd(OH)_2$] in the cadmium electrode. When the nickel electrode nears full charge oxygen is evolved. This oxygen diffuses through open areas of the separator and reacts with the charged cadmium species forming cadmium oxide that hydrates to cadmium hydroxide.

$$\mathrm{Cd\,(OH)_2} + 2\,e^- \longrightarrow \mathrm{Cd} + 2\,\mathrm{OH}^-$$

Therefore, the cadmium electrode is being electrically charged and chemically discharged at the same rate.

$$2\,\mathrm{Cd\,(OH)_2} \longleftarrow 2\,\mathrm{Cd} + \mathrm{O_2} + 2\,\mathrm{H_2O}$$

1.3. Sealed Cells

Most sealed cells are based on the principles appearing in patents of the early 1950s (2, 3) where the virtues of limiting electrolyte, a separator that would absorb and retain electrolyte, and leaving free passage for the oxygen from the positive to the negative plate were described. First, the negative electrode has a surplus of uncharged active material so that the positive plate starts to produce oxygen before the negative plate is fully charged. The oxygen reacts with the negative active material, so that the negative electrode never becomes fully charged and consequently never evolves hydrogen. Second, the amount of electrolyte used is generally lower than can normally be absorbed in the electrodes and separators, facilitating the transfer of oxygen from the positive to the negative plate. Oxygen transport, at least to a certain extent is carried out in the gaseous stage. Third, the separators generally used can pass oxygen to the gaseous state for rapid transfer to the negative plate. Although both pocket and sintered electrodes of the nickel–cadmium type have been used in sealed-cell construction, the preponderant majority of cells in commercial production use sintered positive (nickel) electrodes, and either sintered or pasted negative (cadmium) electrodes.

Although the charged form of the anode is metallic cadmium, some traces of the discharged form always remain in the electrode even at prolonged overcharge. Indeed, as the anode is oxidized (discharged), x-ray diffraction peaks show lines from both Cd and $Cd(OH)_2$. These lines have sharper peaks than those obtained using the cathodic nickel hydroxides, confirming the more crystalline nature of cadmium.

Cadmium electrodes maintain a flat E° potential throughout discharge, as is true of most electrodes in which the materials of the charged and discharged state form distinct independent crystalline forms. Because the conductivities of cadmium electrodes are high, and no ir drops or films are generated during discharge, they also display a flat working voltage curve.

The nickel–cadmium cell, unlike the lead–acid system, has a negative temperature voltage coefficient that is in the range of $-(0.2 - 0.4))$ mV/$^\circ$C, depending on design factors and the nature and doping of the nickel active materials. Thus at higher temperatures the cell has a slightly lower open circuit voltage and this, combined with a reduction of internal resistance at higher temperatures, can result in a reduced back emf in charging. Therefore, special precautions must be taken in charging under constant voltage conditions to avoid the so-called runaway condition; ie, an increase in charge current that comes from a reduction in back emf resulting in an increase in temperature and then a new increase in charge current. Cells can be destroyed in this runaway condition unless current limiters are provided in the charge circuit. The runaway condition problem is not limited to the nickel–cadmium battery. However, it is more likely in those systems where the voltage change with temperature is negative and in those designs where there is very low internal resistance.

The capacity utilization of active material depends on cell design, discharge rate, temperature, and charging conditions. High rate ability depends on the degree of conducting support provided for the active material surface that is in contact with electrolyte, separator resistance, and state-of-charge. The maximum capacity that can normally be achieved from nickel active materials is $0.30\ \mathrm{A{\cdot}h/g}$ calculated on the basis of $Ni(OH)_2$. The capacity of negative active material is ca $0.37\ \mathrm{A{\cdot}h/g}$ based on $Cd(OH)_2$. In actual cell use, working capacities range from 60 to 80% of these values, depending on discharge rate and temperature.

1.4. Cell Fabrication Methods

1.4.1. Pocket Cells

A view of a pocket electrode nickel–cadmium cell is shown in Figure 3. The essential steps of positive (nickel) electrode construction are (*1*) cold-rolled steel ribbon is cut to proper width and is perforated using either needles or rolls; (*2*) the perforated steel ribbon is nickel-plated and usually annealed in hydrogen. The ribbon is formed into a trough shape, is filled with active material by either a briquetting or a powder-filling technique; (*3*) a second strip is formed into a lid that covers and locks with the filled trough; (*4*) the filled strips are cut to length and are arranged to form an electrode sheet by interleaving. This operation, carried out by means of rollers in a forming roll, is often combined with the pressing of a pattern into the electrode sheet in order to ensure good contact between ribbon and active material and to add mechanical strength to the construction; and (*5*) the electrode sheet is then cut to pieces of appropriate size and side bedding and lugs attached to form a metallic frame. The frame material is usually also cold-rolled steel ribbon.

The pockets are usually arranged horizontally in the electrodes as shown in Figure 3, but in a few cases vertical pockets are used. No significant difference has been observed between the two arrangements.

Pocket-type cadmium electrodes are made by a procedure similar to that described for the positive electrode. Because cadmium active material is more dense than nickel active material, and because cadmium has a $_{2+}$ valence, cadmium electrodes, when fabricated to equal thicknesses, have almost twice the working

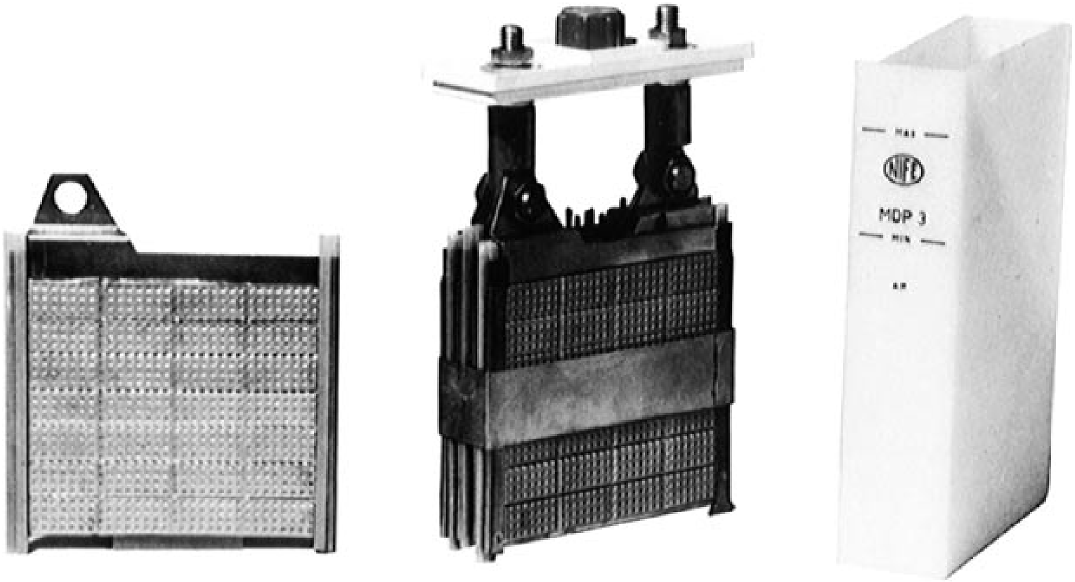


Fig. 3. View of pocket electrode nickel–cadmium cell.

capacity of the nickel electrode. A cell having considerably greater negative capacity provides for loss of negative capacity during life and avoids generation of hydrogen during charging. Thus in actual practice plates of equal thickness are used. Some manufacturers prefer to make the electrolyte transfer area larger for the negative electrode by increasing the area of perforation, usually by increasing the hole size. Pocket electrode plates usually have thicknesses of 0.7–6.3 mm.

After the individual pocket electrodes are fabricated, they are assembled into electrode groups. Electrodes of the same polarity are electrically and mechanically connected to each other and to a pole bolt as illustrated in Figure 3. Plates of opposite polarity are interleaved with separators. Ordinarily single-plates are used for each leaf in a plate group, but some manufacturers prefer to use two thin plates back to back to form one leaf in the positive group. Both bolting and welding methods are used in the assembly of electrodes into groups.

To complete the assembly of a cell, the interleaved electrode groups are bolted to a cover and the cover is sealed to a container. Originally, nickel-plated steel was the predominant material for cell containers but, more recently plastic containers have been used for a considerable proportion of pocket nickel-cadmium cells. Polyethylene, high impact polystyrene, and a copolymer of propylene and ethylene have been the most widely used plastics.

Steel containers are mechanically stronger than plastic and easier to fabricate in large sizes. Also they dissipate heat better and tend to keep the electrodes cooler during high temperature or high rate operations. However, cells assembled in steel containers must not have contact with each other during assembly to prevent intercell shorts. Plastic containers are the better option for most small and medium-sized cells because they require no protection against corrosion, they permit visual observation of the electrolyte level, they are lighter than steel containers, they can be closely packed into a battery, and small cells can be cemented or taped into batteries, eliminating a tray.

The cells are usually filled with an electrolyte solution of potassium hydroxide of density 1.18–1.23 g/mL, which may also contain lithium hydroxide. A potassium hydroxide solution of 1.20 g/mL freezes at $\sim-27^{\circ}\mathrm{C}$. Thus cells intended for climates colder than $-27^{\circ}\mathrm{C}$ have an electrolyte density of 1.25 g/mL or greater. In some designs there is a large volume of excess electrolyte above the electrodes in order to reduce the need for rewatering to once every few years. In these cells, the initial electrolyte density is lower than normal because the solution concentrates during operation. Concentrations might be as high as 1.26 g/mL at the time of rewatering (topping up). Lithium hydroxide has been shown to increase the life of positive pocket electrodes in cycling operation. However, the addition also increases the electrolyte resistivity, and is not ordinarily used in high rate starter batteries.

Individual cells are usually precycled before assembling into batteries. These early charge–discharge cycles, often called formation cycles, improve the capacity of the cell by increasing the surface area of the active material and effecting crystal structure changes.

The individual cells are assembled into batteries after a leakage test to check for faulty welding joints in steel containers or cracks and improper seals in the plastic encased cells. Cells that are to be delivered without electrolyte are emptied after the formation cycles. The steel-cased cells have to be separated by mechanical means to prevent intercell shorts and are often assembled into wooden crates. The cells in plastic cases can be cemented together or strapped with tape.

1.4.2. Tubular Cells

Although the tubular nickel electrode invented by Edison is almost always combined with an iron negative electrode, a small quantity of cells is produced in which nickel in the tubular form is used with a pocket cadmium electrode. This type of cell construction is used for low operating temperature environments, where iron electrodes do not perform well or where charging current must be limited.

1.4.3. Sintered Cells

The fabrication of sintered electrode batteries can be divided into five principal operations: preparation of sintering-grade nickel powder; preparation of the sintered nickel plaque; impregnation of the plaque with active material; assembly of the impregnated plaques (often called plates) into electrode groups and into cells; and assembly of cells into batteries.

A good powder for sintering purpose should be very pure (Fe, Cu, and S should be especially avoided) and should have a very low apparent density, in the range of 0.5–0.89 g/mL. An excellent powder for this purpose is made by the decomposition of nickel carbonyl [13463-39-3], $Ni(CO)_4$, (see Carbonyls). Nickel carbonyl is a poisonous vapor obtained by passing carbon monoxide [630-08-0] over finely divided metallic nickel at about 200°C in rotary kilns using special gas-tight seals. The gas is condensed and the liquid carbonyl distilled to eliminate impurities. The purified liquid nickel carbonyl is injected into large decomposers that have heated walls. The nickel carbonyl decomposes into carbon monoxide, which can then be recirculated, and a finely divided nickel powder. The structure of such powders is shown in Figure 4.

Sintering is a thermal process through which a loose mass of particles is transformed to a coherent body. It usually takes place at a temperature equal to two-thirds the melting point, or ca 800–1000°C for nickel. The sintered nickel structure without active material is called a plaque and it can be prepared by either dry or wet processes (see Metallurgy, powder).

In the dry process, nickel powders are sifted into ceramic or carbon molds with a reinforcing layer of wire mesh cloth or electroformed nickel. In most production processes part of the powder is sifted into the mold, a grid is inserted, and a second layer of sifted powder is added. The reinforcing grid is provided to reduce shrinkage during the sintering, reduce electrical resistivity, and provide extra mechanical strength. The molds are transferred to a sintering furnace that contains a reducing or inert atmosphere. Usually a reducing atmosphere is maintained by cracking ammonia ($2\ NH_3 \longrightarrow N_2 + 3\ H_2$) or partially dissociating natural gas. After 5–10 min in a hot zone, the molds are transferred to a cold zone in the furnace. Most furnaces for the dry processes are horizontal and of the moving-belt type.

To reduce labor and other expenses, most sintered nickel plaques are produced by a wet-slurry method. A nickel slurry is prepared by mixing a low density nickel powder with a viscous aqueous solution such

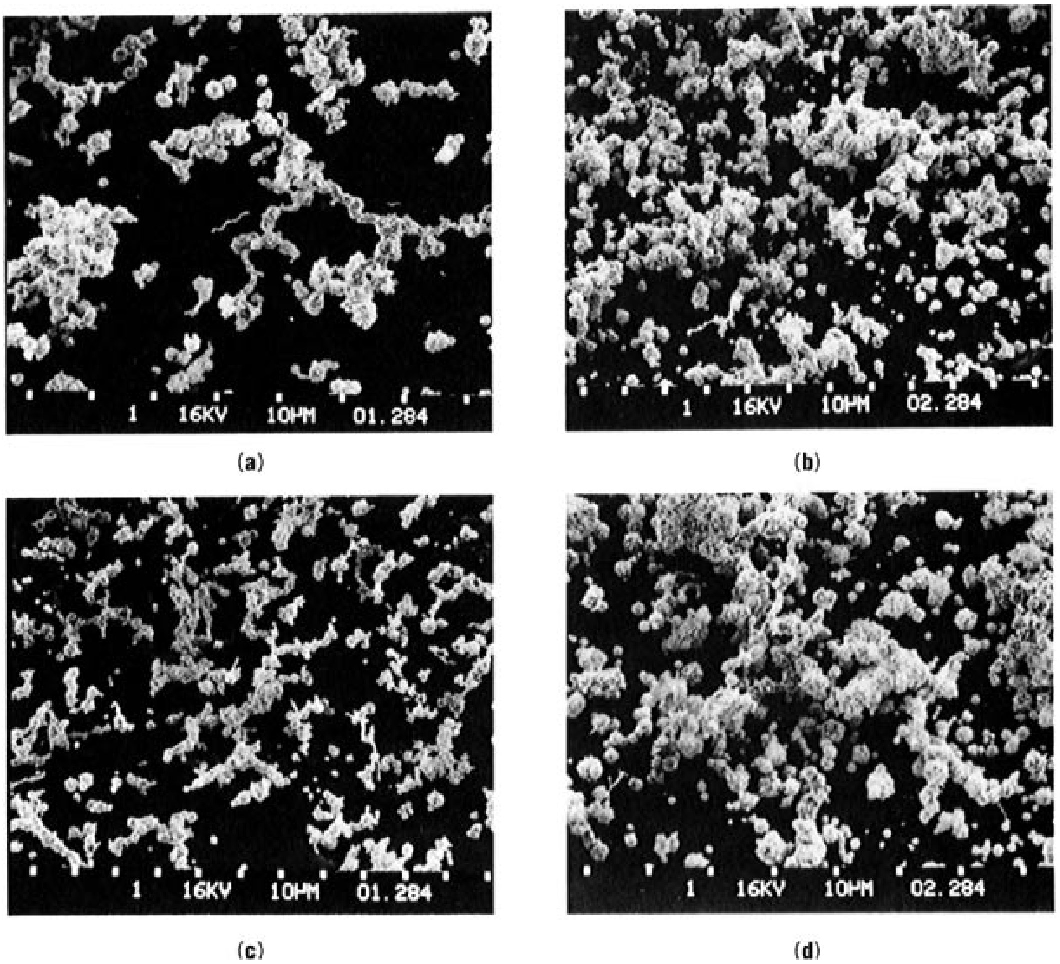


Fig. 4. Microstructure of carbonyl nickel powder at various magnifications (**a**) and (**c**) 1000x, (**b**) and (**d**) 1500x.(Courtesy of Inco.)

as carboxymethylcellulose [9004-42-6] (CMC). Pure nickel gauze, a nickel-plated gauze, or a nickel-plated perforated steel strip is continuously carried through a container filled with the nickel paste and sintering is done in a horizontal furnace. The time of the sinter in the furnace is ca 10–20 min.

Usually the plaques produced by either method are coined (compressed) in those areas where subsequent welded tabs are connected or where no active material is desired, eg, at the edges. The uncoined areas usually have a Brunauer-Emmet-Teller (BET) area in the range of 0.25–0.5 m^2/g and a pore volume $>80\%$. The pores of the sintered plaque must be of suitable size and interconnected. The mean pore diameter for good electrochemical efficiency is 6–12 μm, determined by the mercury-intrusion method.

The process by which porous sintered plaques are filled with active material is called impregnation. The plaques are submerged in an aqueous solution, which is sometimes a hot melt in a compound's own water of hydration, consisting of a suitable nickel or cadmium salt and subjected to a chemical, electrochemical, or thermal process to precipitate nickel hydroxide or cadmium hydroxide. The electrochemical (46) and general (47) methods of impregnating nickel plaques have been reviewed.

In the original process for the positive electrode, the plaques were placed in a metal vessel, which was evacuated to <5.3 kPa (40 mm Hg), and a nearly saturated solution of nickel nitrate (density 1.6 g/mL) admitted. After a 5–15 min soaking period, the plaques were transferred at 101 kPa (1 atm) to a polarizing unit where they were cathodically polarized in hot caustic solution. After polarization the plates were washed and dried. These four steps were repeated four or five times until the desired weight gain of active material was achieved.

For the negative electrolyte, cadmium nitrate solution (density 1.8 g/mL) is used in the procedure described above. Because a small (3–4 g/L) amount of free nitric acid is desirable in the impregnation solution, the addition of a corrosion inhibitor prevents excessive contamination of the solution with nickel from the sintered mass (see Corrosion and corrosion inhibitors Corrosion and corrosion control). In most applications for sintered nickel electrodes the optimum positive electrode performance is achieved when one-third to one-half of the pore volume is filled with active material. The negative electrode optimum has one-half of its pore volume filled with active material.

Other processes have been developed in which the impregnation is accomplished in one or two steps; the most promising is electrodeposition directly from nitrate solutions having pH controlled at 4–5. After electrodeposition, the plaques are either cathodically polarized in sodium hydroxide solution or electrochemically formed in sodium hydroxide to eliminate all traces of nitrate. The latter steps must proceed at low current densities to avoid blistering and shedding of the loaded plaques.

Some manufacturers add a small (10–20% of the positive loading) amount of cadmium to positive plates as an antipolar mass to prevent some of the problems of reversal in sealed cells. This practice may, however, create as many problems as it solves in that positive capacity is reduced proportionally to the quantity of antipolar mass added.

In most cases, the impregnation process is followed by an electrochemical formation where the plaques are assembled into large temporary cells filled with 20–30% sodium hydroxide solution, subjected to 1–3 charge–discharge cycles, and subsequently washed and dried. This eliminates nitrates and poorly adherent particles. It also increases the effective surface area of the active materials.

Formation also offers a convenient means of regulating the state of charge of the plates prior to cell assembly. This is important in sealed cell manufacture, where cell performance is optimized when 10–15% of the negative active mass is in the charged condition prior to initial cell charging. Some manufacturers have found that elimination of formation is feasible by extensive conversion of the nitrates in the impregnation process, followed by meticulous washing. However, charge retention can suffer to some degree because of traces of nitrate in the finished cells.

1.4.4. Cell Assembly

The methods for cell assembly, starting with the processed plaques depend on whether the cells are to be vented or sealed. For vented cells, processed plaques are usually compressed to 85–90% of their processed thickness allowing sufficient porosity for electrolyte retention and strengthening the plate structure. For sealed cells, sizing of the negative plaques is usually avoided because maximum surface area is important to oxygen recombination.

The next operation is the cutting of plaques into individual plates, usually through the coined areas (Fig. 5). Plate edges are sometimes coated with an adherent plastic film to smooth any rough edges that could otherwise penetrate the thin separators used in sintered-plate cells. A tab of nickel or nickel-plated steel is welded to each plate. In some cases, this is accomplished by spot or projection welding at the coined area. For plates provided with perforated sheet grids the tabs are spot welded directly to the sheet at the proper point at the edge of the sheet. For both types of cells most of the requirements of the separators are high electronic resistance and low electrolytic resistance in the usual electrolyte (30% KOH solution). Separators should be

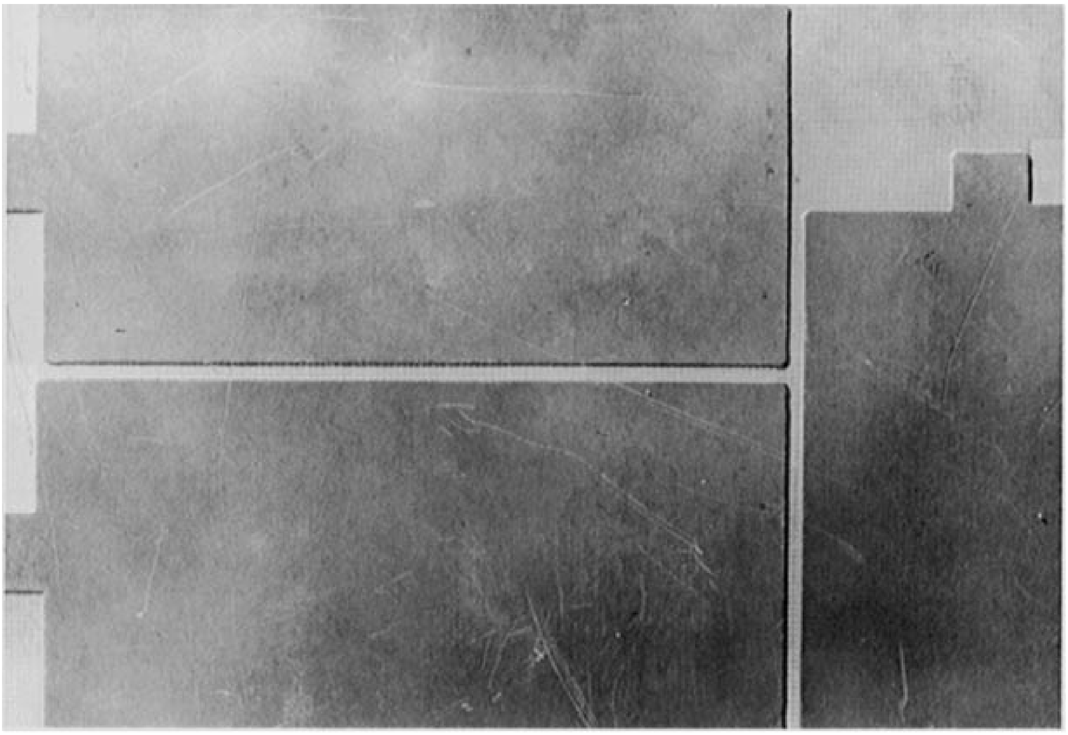


Fig. 5. Coined master plaque.

as thin as possible and have small and evenly distributed pores. Additionally, they should be resistant to heat, KOH, gases formed on charge, and other components of the system.

The most important separator material, property difference for vented and sealed cells is permeability to oxygen. In the charging of the vented cells, it is important to minimize oxygen transport from the positive to the negative plates. In float-charge applications, oxygen recombination at the negative plates results in generation of heat and ultimately to thermal runaway if excessive charge current is drawn with rising temperature. The opposite is required in sealed cells, where oxygen recombination is necessary to prevent an increase of internal pressure. Glycerol-free cellophane is used as part of the separator in the vented cells. Other components in typical vented cell separators are woven nylon, felted nylon, felted nylon–cellulose, felted (vinyl chloride–acrylonitrile) copolymer, microporous polypropylene, and irradiated polyethylene. Most sealed-cell separators are single-layer felted materials, usually nylon or polypropylene, chosen for the ability to retain electrolyte and prepared in such a manner as to allow oxygen permeability, eg, calendering of such materials should be avoided.

Another difference between vented and sealed cell manufacture is found in the ratio of negative to positive active material. Although both types of cells require an excess of negative material, in the vented type a ratio of 1.5 is sufficient for the high rates of discharge and low temperature conditions encountered. In the sealed type a typical ratio is 2, to provide for sufficient sites for the oxygen recombination, to provide for the residual negative capacity mentioned earlier, and to preclude the possibility of the negative plate reaching the fully charged state exemplified by H_2 evolution.

Both vented and sealed cells use the same basic electrolyte (30% KOH), but different amounts are required. The vented cell contains a considerable amount of free electrolyte to allow for decomposition and loss of water on charge and to allow for maximum performance on discharge. The sealed cell contains only enough electrolyte to fill the plate pores and to completely saturate the separator; excess electrolyte inhibits oxygen recombination by reducing the number of sites, ie, oxygen–cadmium–electrolyte interfaces, for oxygen recombination. In certain applications, 15–30 g/L lithium hydroxide is added to the electrolyte. Where elevated temperature operation is encountered, this addition improves charge acceptance, especially in sealed cells. Larger (50 g/L) amounts of lithium hydroxide are used in repeated cycling with constant voltage charging and in float-charge applications (vented cells). This larger amount of lithium hydroxide maintains capacity better than KOH alone but increases electrolyte resistance and adversely affects low temperature performance.

The presence of certain forms of cellulose (qv) in the electrolyte is beneficial for negative electrodes, probably by preventing the formation of large grain sizes of cadmium on charge. Cellophane in vented cell separators usually provides sufficient cellulose for this effect. Early sealed cells using a single layer of cellulosic filter paper as separator gave excellent performance but had reduced cycle life as a result of the degradation of the cellulose. In later sealed cells, where felted nylon or felted polypropylene was used as separator, the addition of small amounts of cellulose to the electrolyte, improved negative plate performance, but led to early separator degradation.

Assembly of vented cells begins by interleaving the electrodes and separators. The most widely used separator is a sandwich of woven nylon (0.08–0.10 mm), cellophane (0.05 mm), and woven nylon (0.08–0.10 mm) of the proper width, usually 0.6 cm wider than the plate height, and of a length to form a continuous barrier around the edges of all the plates. The electrode tabs of each polarity are brought together and connected to the cell terminals by spot welding or, in a few cases, by bolting. The stack is attached to the cell cover by inserting terminals through holes that are marked for polarity. When threaded terminal posts are used, sealing is accomplished by compressing a neoprene gasket or O-ring between a flat or groove on the horizontal surface of the terminal and the inside surface of the cover, with the proper torque being applied by means of a nut on the outside of the cover. In the case of a smooth terminal post, compression is effected by means of a snap ring and belleville washer arrangement.

The most common cell case and cover materials are nylon and styrenic (ABS). After inserting the cell element, with cover attached, into the cell case, cover and case are cemented. For nylon, a most satisfactory adhesive is phenol. For styrene copolymers, either a solvent seal or an ultrasonic seal is effective (see Adhesives).

The cell filler caps in the covers are designed to prevent spillage and usually contain a venting mechanism to allow for escape of gas during charge and to prevent the carbon dioxide of the air from contacting the electrolyte. Most filler caps are a type of rubber-ring screw vent assembly provided with holes or slits that are sealed by the rubber ring. These are usually made of nylon or polystyrene, but in certain applications they are made of nickel-plated steel.

In filling cells with electrolyte, vacuum techniques are employed for uniformity and for hastening the complete wetting of plates and separator. A properly manufactured cell is ready for use immediately after the first charge following electrolyte fill. The first charge is ideally at the 10-h rate for 20 h. Higher rates can be used but should not exceed the 5-h rate.

Plastic-cased cells are assembled into batteries by placing them a small distance apart or in contact with heat-conducting fins in a specially treated steel container. The cell spacing depends on the battery application. For example, in aircraft starting batteries provision is required for circulating cooling air between cells. The steel boxes (battery cases) are previously prepared by coating all surfaces with a tough, insulating plastic (usually epoxy). Excellent results are obtained using a fluidized bed technique of application, which results in a uniformly thick coating. Intercell connectors are normally of nickel-plated copper, but in small sizes connectors are often of nickel or nickel-plated steel.

The prismatic sealed cells are made in a manner similar to the above. Most prismatic sealed cells use a metal case and cover. The most desirable case material is stainless steel, although nickel-plated steel can be used. Terminal feed-through is effected by ceramic-to-metal or glass-to-metal sealing techniques; and

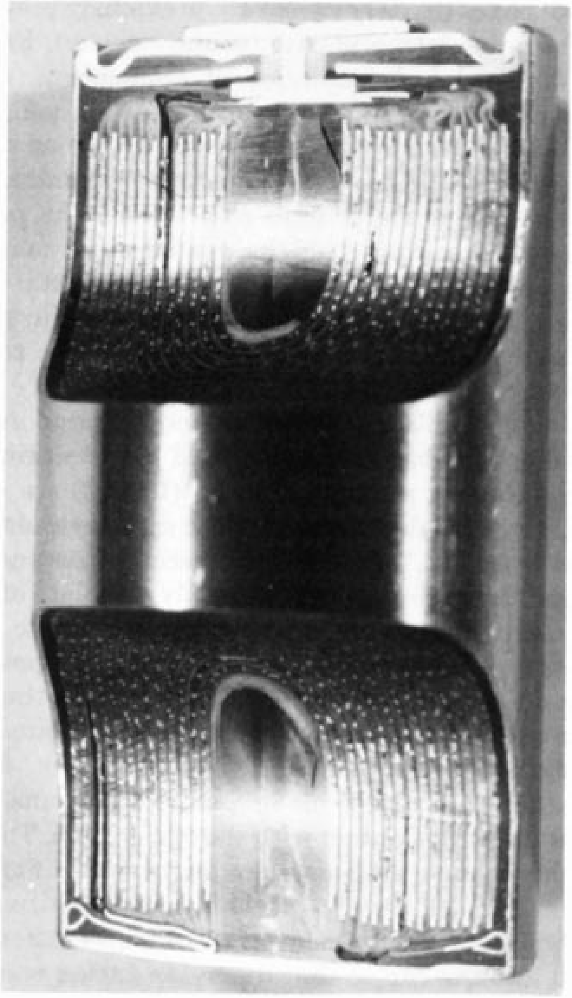


Fig. 6. Partial cutaway of a coiled, sintered-plate, nickel–cadmium cell ("D"-size).

case-to-cover seal, by inert gas welding. Most prismatic sealed cells incorporate a high release, resealable vent in the cover that usually consists of a metallic spring working on an elastomer sealing disk or ring.

The prismatic sealed cells are not self-supporting and are normally used in battery operation where the battery case is used to constrain cell cases because internal cell pressures in the range of 690 kPa (100 psi) are common.

By far the majority of sealed cells are of the small cylindrical self-supporting type in the familiar "AA," "C," and "D" commercial sizes such as that shown in Figure 6. The element for these cells contains only one plate of each polarity; thus the electrodes are relatively long. The plates and the single-layer separator are rolled into a tight spiral, the plates arranged so that the positive tabs protrude from the element in one direction and the negative tabs in the opposite direction. The top and bottom of the element are protected and insulated by circular plastic disks having slits for the protruding tabs.

Elements are then inserted in nickel-plated steel cans, normally with the negative tab bent 90° to make contact with the can bottom. The tab is spot welded to the can bottom employing a long slender electrode that

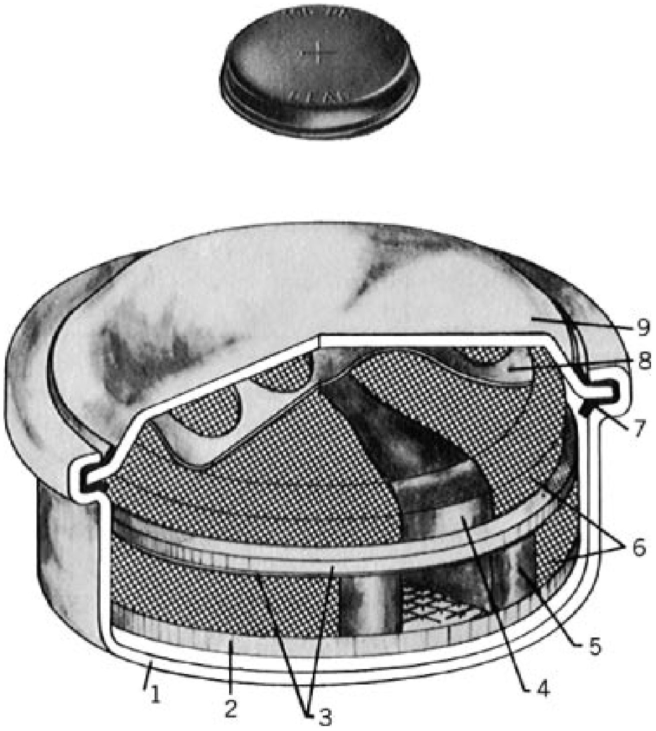


Fig. 7. Section of disk-type cell where: 1, is the cell cup; 2, is the bottom insert; 3, is the separator; 4, is the negative electrode; 5, is the positive electrode; 6, is the nickel wire gauze; 7, is the sealing washer; 8, is the contact spring; and 9, is the cell cover.

fits through the center hole of the element. The cell cover is welded to the positive tab. The cover is nickel-plated steel with a nylon gasket around the edges. After adding electrolyte, the cover is pressed into the can so that the nylon gasket rests on a shelf formed into the can well by scoring (after insertion of element). The rim of the can and sometimes the upper part of the gasket is folded over either in a press or by a rolling, rotating tool.

The cover assembly usually contains a safety vent. The most common type consists of a steel or nickel diaphragm built into the cover and a bent point cut from the cover. At a certain internal cell pressure, the diaphragm moves to the bent point and is pierced. Some cylindrical sealed cells use one or more terminal feed-throughs employing glass-to-metal or ceramic-to-metal techniques.

Battery assembly using cylindrical cells varies, and cell-to-cell connections are spot welded after using either flat tabs or cup tabs. Cell-to-cell insulation is effected either by using plastic cell jackets (shrink-on) or by inserting cells in plastic modules with each cell occupying its own cavity.

1.5. Other Cells

Other methods to fabricate nickel–cadmium cell electrodes include those for the button cell, used for calculators and other electronic devices. This cell, the construction of which is illustrated in Figure 7, is commonly made using a pressed powder nickel electrode mixed with graphite that is similar to a pocket electrode. The cadmium electrode is made in a similar manner. The active material, graphite blends for the nickel electrode, are almost the same as that used for pocket electrodes, ie, 18% graphite.

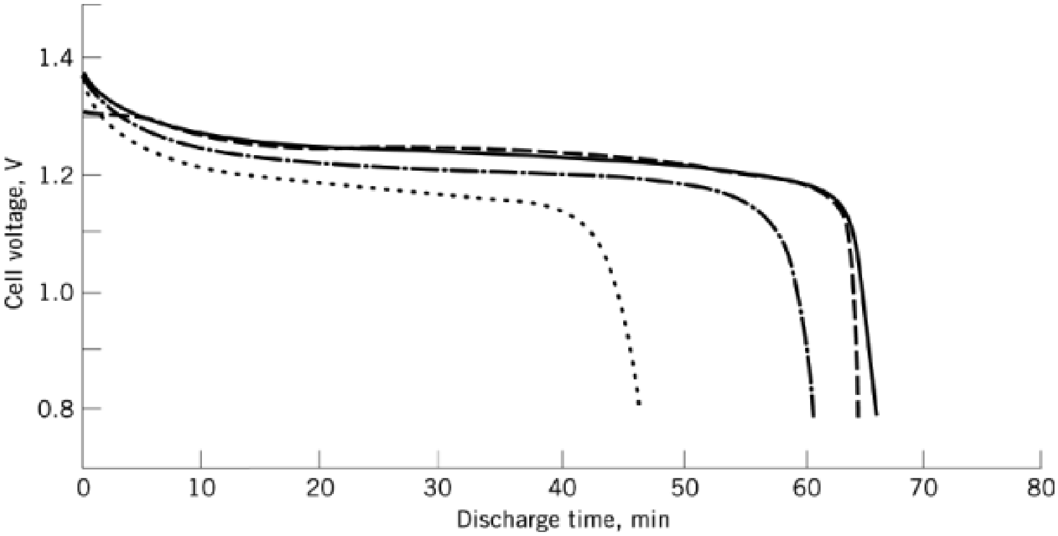


Fig. 8. Discharge capacity of small sealed nickel–cadmium cells where the initial charge is $0.1\ \mathrm{C}\times 16\ \mathrm{h}$ at 20°C and the discharge is 1 C at temperatures of (•••) −20°C, (–•–) 0°C, (——) 20°C, and (— — —) 60°C. C is the current required to discharge the cell in one hour.

Table 3. Nominal Capacities of Consumer Nickel–Cadmium Cells

	Capacity, A·h	
Size	Normal cells	High capacity cells
“AA”	0.5	0.7–0.8
“Sub-C”	1.2	1.7
“C”	2.0	2.3
“D”	4.0	5.0
“F”	7.0	

Lower cost and lower weight cylindrical cells have been made using plastic bound or pasted active material pressed into a metal screen. These cells suffer slightly in utilization at high rates compared to a sintered-plate cylindrical cell, but they may be adequate for most applications. The effect of temperature and discharge rate on the capacity of sealed nickel-cadmium cells is illustrated in Figure 8 and Table 3.

1.6. Applications

Nickel–cadmium cells represent almost 20% of the market for all storage batteries, including lead–acid, manufactured in the world. Uses are divided into three categories: pocket cells are used in emergency lighting, diesel starting, and stationary and traction applications where the reliability, long life, medium-high rate capability, and low temperature performance characteristics warrant the extra cost over lead–acid storage batteries; sintered, vented cells are used in extremely high rate applications, such as jet engine and large diesel engine starting; and sealed cells, both the sintered and button types, are used in computors, phones, cameras, portable tools, electronic devices, calculators, cordless razors, toothbrushes, carving knives, flashguns, and in space applications, where nickel–cadmium is optimum because it can be recharged a great number of cycles and given prolonged trickle overcharge. Cells of this category are generally made in sizes comparable to conventional dry cells, such as “D”, “C”, “AA”, etc. In sizes larger than the “D” cell, sealed lead–acid cells offer a useful economic alternative for applications where the extra weight and space of the lead–acid is not critical.

In order to reduce costs, achieve higher energy density, and minimize environmental problems, a growing percentage of prismatic and cylindrical cells are now made by pasting on substrate. The newer substrates include nickel fiber mat, nickel foam, and nickel-plated graphite fiber. One manufacturer uses a nickel-plated plastic fiber substrate for the fabrication of large nickel–cadmium cells in prismatic configurations (28). These cells are reported to require less maintenance than the older design pocket cells (48). In small industrial sizes, pasted cells are offered as sealed batteries.

1.7. Charger Technology

Alkaline storage batteries are commonly charged from rectified d-c equipment, solar panels, or other d-c sources and have fairly good tolerance to ripple and transient pulses. Because the voltage of the nickel electrode is variable, the cutoff voltage is not a good control parameter for nickel–cadmium cells. It is, however, often used in vented cell chargers. For sealed nickel–cadmium cells, and other systems where a combination mechanism exists, a negative voltage slope detector is often incorporated into the charger control circuit. As the charge of a cell or battery progresses there is a slow rise in the unit voltage. When the nickel electrode approaches full charge, the oxygen evolved combines with the cadmium electrode reducing the overpotential on the cadmium electrode. This slight change in cell voltage can be detected by electronic voltage slope detectors and used to reduce the charge current or shut off the charge.

1.8. Nickel–Iron Cells

The original tubular design nickel–iron battery developed by Edison has little commercial application. However, there has been renewed interest in the system for electric vehicles (EV). The EV design is based on a high rate, usually sintered, iron electrode as well as high rate nickel electrodes. Design and performance characteristics have been reported (49–54) as has data on pulse characteristics (55). The battery for electric vehicles is usually used in a 100–220 V array with approximately a 200 A·h capacity. The system is capable of high discharge pulses even at low states of charge. Testing data on EV regimes has been given (56–58).

1.9. Electrochemistry and Kinetics

The electrochemistry of the nickel–iron battery and the crystal structures of the active materials depends on the method of preparation of the material, degree of discharge, the age (life cycle), concentration of electrolyte, and type and degree of additives, particularly the presence of lithium and cobalt. A simplified equation representing the charge–discharge cycle can be given as:

$$2\ \mathrm{NiOOH}^* + \alpha\text{–}\mathrm{Fe} + 2\ \mathrm{H_2O} \rightleftarrows 2\ \mathrm{Ni\,(OH)_2^*} + \mathrm{Fe\,(OH)_2}$$

where the asterisks indicate adsorbed water and KOH. However, the discharge can be carried to a lower plateau for the iron electrode, although this is usually undesirable for life cycle, represented by:

$$8\ \mathrm{NiOOH}^* + 3\ \mathrm{Fe} + 4\ \mathrm{H_2O} \rightleftarrows 8\ \mathrm{Ni\,(OH)_2^*} + \mathrm{Fe_3O_4}$$

When discharges are carried out beyond the voltage range of the ferrous hydroxide [18624-44-7], $\mathrm{Fe(OH)_2}$, plateau which is ca -0.90 to -0.85 V vs HgO, a second reaction in the voltage range of -0.65 to -0.5 V takes place (59, 60).

$$3\,\mathrm{Fe(OH)_2} + 2\,\mathrm{OH^-} \rightleftharpoons \mathrm{Fe_3O_4} + 4\,\mathrm{H_2O}$$

Discharging to this lower cell voltage usually results in shorter cycle life. Enough excess iron should be provided in the cell design to avoid this problem.

Active iron in the metallic state is slowly attacked by the alkaline electrolyte according to

$$\mathrm{Fe} + 2\,\mathrm{H_2O} \longrightarrow \mathrm{Fe(OH)_2} + \mathrm{H_2}$$

This reaction is accelerated by increased temperature, increased electrolyte concentration, and by the use of sodium hydroxide rather than potassium hydroxide in the electrolyte. It is believed that the presence of lithium and sulfur in the electrode suppress this problem. Generally, if the cell temperature is held below 50°C, the oxidation and/or solubility of iron is not a problem under normal cell operating conditions.

1.10. Electrode Structures

The classical iron active material for pocket and pasted iron electrodes was formed by roasting recrystallized ferrous sulfate [7720-78-7], $FeSO_4$, in an oxidizing atmosphere to ferric oxide [1309-37-1], Fe_2O_3, and then reducing the latter in hydrogen. The α-iron formed was then heated to a mixture of Fe_3O_4 and Fe. As such it was pure enough to be used for pharmaceutical purposes. For battery use, a small amount of sulfur, as FeS, was added as were other additives which were believed to increase the cycle life by acting as depassivating agents, ie, helping to reduce the tendency of iron to evolve hydrogen upon standing in alkaline electrolyte. Extensive studies on the stability of iron active material have been reported (61–63). Addition of cadmium and antimony salts have been claimed to decrease hydrogen evolution on stand by 50% (62). However, some blends also reduce electrode capacity. A blend of materials such as mucic acid [526-99-8], $C_6H_{10}O_8$, with indium [7440-74-6], In, increases the iron stability on stand without changing electrode capacity (63). The effects of electrolyte makeup and concentration on iron corrosion have also been studied (64).

A study of sintered iron electrodes claimed advantages of high rate capability, long life, and low hydrogen evolution (52). Fine carbonyl generated iron powder was coated on a nickel screen and sintered in a hydrogen–nitrogen atmosphere. Sintered raw plaques were believed suitable if the porosity was between 50 and 80%. The sinter had to be strong enough to leave a conductive skeleton after part of the iron was corroded to active material. This process is unlike sintered-type nickel electrodes in which active material is deposited directly into the pores of a very porous plaque. Sintered iron electrodes (49) are now in pilot production in Sweden and the United States.

Sintered nickel electrodes used in nickel iron cells are usually thicker than those used in Ni/Cd cells. These result in high energy density cells, because very high discharge rates are usually not required.

1.11. Performance Characteristics

The sintered nickel-sintered iron design battery has outstanding power characteristics at all states of discharge making them attractive to the design of electric vehicles (EV) which must accelerate with traffic even when almost completely discharged. Although the evolution of hydrogen is a problem preventing sealed cell design, introduction of automatic watering systems have ameliorated the maintenance time requirements. Typical performance curves are given in Figures 9 and 10 and the design characteristics of an advanced nickel–iron battery are given in Table 4 (49).

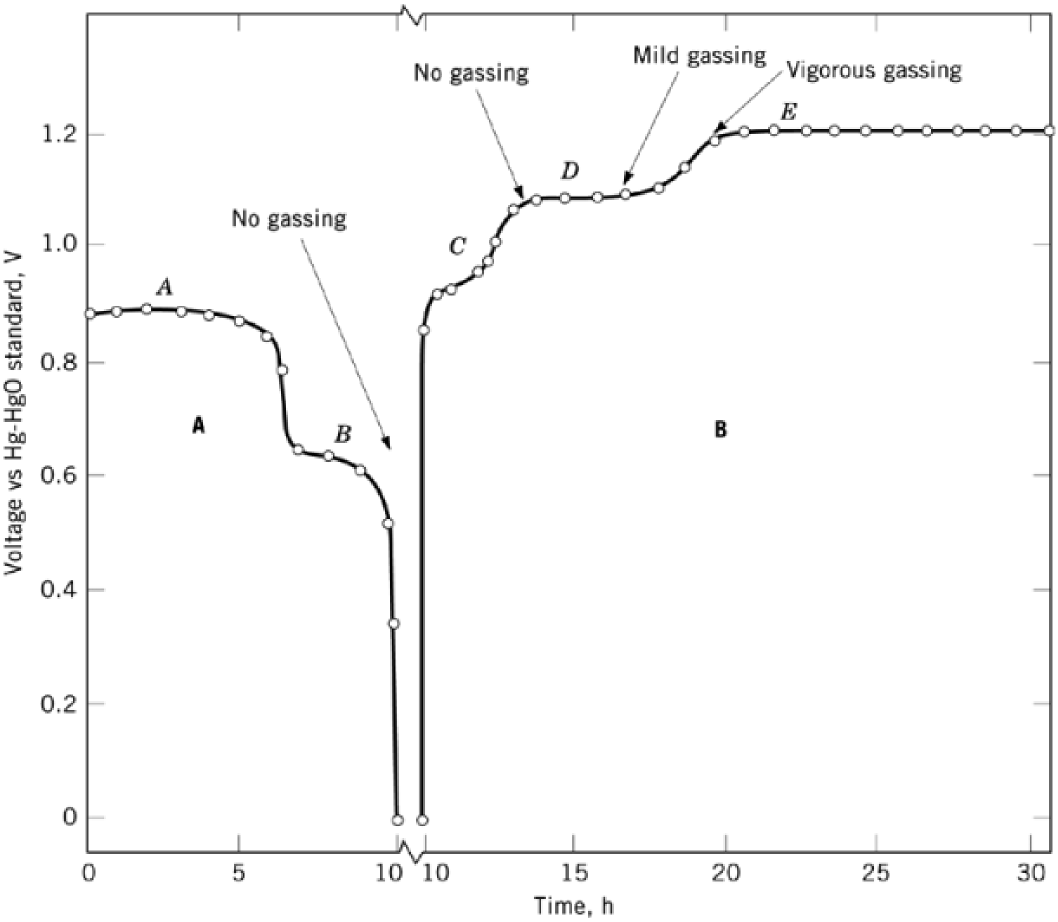


Fig. 9. Discharge and charging curves for a sintered iron electrode at a constant current of 0.2 A where the apparent geometrical surface area is 36 cm^2 and porosity is 65%. **A** and **B** represent the discharging and charging regions, respectively. Overall electrode reactions, midpoint potentials, and, in parentheses, theoretical potentials at pH 15 are *A*, $\alpha\text{-Fe}+2\ OH^- \longrightarrow Fe(OH)_2 + 2\ e^-$, 0.88 V (1.03 V); *B*, $Fe(OH)_2 \longrightarrow FeOOH + H^+ + e^-$, 0.63 V (0.72 V); *C*, $FeOOH + H^+ + e^- \longrightarrow Fe(OH)_2$, 0.93 V (0.72 V); *D*, $Fe(OH)_2 + 2\ e^- \longrightarrow \alpha\text{-Fe}$, 1.08 V (1.03 V); and *E*, $2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$, 1.20 V (0.99 V).

2. Silver–Zinc Cells

The silver–zinc battery has the highest attainable energy density of any rechargeable system in use as of this writing. In addition, it has an extremely high rate capability coupled with a very flat voltage discharge characteristic. Its use, in the early 1990s, is limited almost exclusively to the military for various aerospace applications such as satellites and missiles, submarine and torpedo propulsion applications, and some limited portable communications applications. The main drawback of these cells is the rather limited lifetime of the silver–zinc system. Life is normally limited to less than 200 cycles with a total wet-life of no more than about two years. The silver–zinc system also carries a very high cost and applications are justified only where cost is a minor factor. The high cost of silver battery systems is attributable to the cost of the active silver material used in the positive electrodes. In 1991 silver prices were in the range of $128/kg ($4/troy oz).

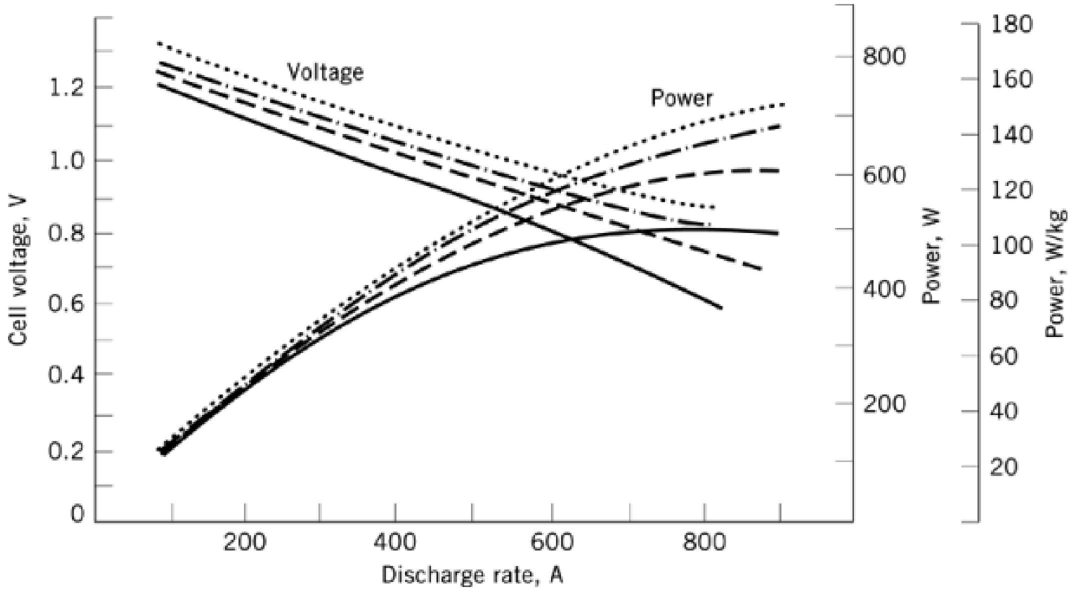


Fig. 10. Power and voltage characteristics of the nickel–iron cell where the internal resistance of the cell, R_i, is 0.70 mΩ, at various states of discharge: (•••) 8%; (–•–) 32%; (— — —) 52%; and (——) 72%.(Courtesy of Westinghouse Electric Corp.)

Cellophane or its derivatives have been used as the basic separator for the silver–zinc cell since the 1940s (65, 66). Cellophane is hydrated by the caustic electrolyte and expands to approximately three times its dry thickness inside the cell exerting a small internal pressure in the cell. This pressure restrains the zinc anode active material within the plate itself and renders the zinc less available for dissolution during discharge. The cellophane, however, is also the principal limitation to cell life. Oxidation of the cellophane in the cell environment degrades the separator and within a relatively short time short circuits may occur in the cell. In addition, chemical combination of dissolved silver species in the electrolyte may form a conductive path through the cellophane.

A second lifetime limitation is the zinc anode. In spite of the separator and cell designs, some zinc material is solubilized during the charge–discharge reaction. Over a period of cycling there is a shift of active material, originally distributed evenly over the face of the electrode, to the center and bottom areas of the electrode (50). This shape change limits the life of the cell as exemplified by a fading of the capacity and a build-up of internal pressure that may eventually lead to a short circuit.

2.1. Reaction Mechanisms

There is considerable difference of opinion concerning the specific cell reactions that occur in the silver–zinc battery. Equations that are readily acceptable are

$$2\,\mathrm{AgO} + \mathrm{Zn} + \mathrm{H_2O} \rightleftarrows \mathrm{Ag_2O} + \genfrac{}{}{0pt}{}{\mathrm{Zn(OH)_2}}{(\mathrm{ZnO} + \mathrm{H_2O})} \qquad E^\circ = 1.85\ \mathrm{V}$$

and

$$\mathrm{Ag_2O} + \mathrm{Zn} + \mathrm{H_2O} \rightleftarrows 2\,\mathrm{Ag} + \genfrac{}{}{0pt}{}{\mathrm{Zn(OH)_2}}{(\mathrm{ZnO} + \mathrm{H_2O})} \qquad E^\circ = 1.59\ \mathrm{V}$$

Table 4. Component Data and Energy Density for 300 A·h Nickel Oxide–Iron Cells

	Cell types			
Parameter	Prototype	Near-term	Advanced	
nickel–oxide electrodes				
thickness, mm	3.2	3.1	4.8	3.2
capacity, A·h	20	25	36	24
number cell^{-1}	15	12	7	2
iron electrodes				
thickness, mm	1.2	1.4	1.9	
capacity, A·h	22	28	38	
number cell^{-1}	14	11	8	
separation				
distance, mm	0.8	0.8	0.5	
weight, g				
nickel oxide electrodes	3000	2500	2500	
iron electrodes	1330	1180	1090	
electrolyte	1280	1100	920	
separators	150	120	60	
connections	320	320	320	
cell case	300	280	250	
Total	*6380*	*5500*	*5140*	
volume, L	2.85	2.48	2.14	
cell voltage, V[a]	1.18	1.21	1.21	
energy density				
per weight, W·h/kg	55.5	66.0	70.6	
per volume, W·h/L	124	146	170	

[a] Mean value (C/4); where C is the current required to discharge the cell in one hour.

The charge and discharge of silver–zinc cells occurs on two voltage levels, generating silver peroxide and silver monoxide [20667-12-3]. Silver peroxide [25455-73-6] is often represented as Ag_2O_2, and the zinc hydroxide [20427-58-1] or zinc oxide [1314-13-2], ZnO, is represented as potassium zincate [59271-74-8], $K_2Zn(OH)_4$, or various other forms of hydrated zinc oxide. The two-level voltage of the silver–zinc system plays an important part in both charging and discharging of cells and batteries.

2.2. Electrochemistry

Silver–zinc cells have some unusual thermodynamic properties. The equations indicate that the higher valence silver oxide is AgO, silver(II) oxide [1301-96-8]. However, in the crystallographic unit cell, which is monolithic, there are four silver atoms and four oxygen atoms, and none of the Ag–O bonds conforms to a silver(II) bond length. Instead there are two Ag–O bonds of 0.218 nm corresponding to silver(I) and two Ag–O bonds of 0.203 nm corresponding to silver(III) (67). This structure has also been proposed on the basis of magnetic and semiconductor properties (67) and confirmed using neutron diffraction (68, 69).

For the Ag–O material a reversible voltage of 1.856 V is obtained and the $(\partial E/\partial T)_P$ is positive, $+5.7 \times 10^{-5}$ V/°C. For the Ag_2O material a reversible voltage of 1.602 V is obtained in 11.6 N KOH but the $\partial E/\partial T$ is negative, -16.9×10^{-5} V/°C. This is about one-third the value of nickel–cadmium cells. However, because the negative coefficient compound is not present in the fully charged state, the high risk of thermal runaway described for nickel–cadmium cells does not exist. The high conductivity of the silver active material and the low internal resistance of the remaining components do, however, make thermal runaway a possibility to be considered in charger and system design.

2.3. Electrodes

All of the finished silver electrodes have certain common characteristics: the grids or substrates used in the electrodes are exclusively made of silver, although in some particular cases silver-plated copper is used. Material can be in the form of expanded silver sheet, silver wire mesh, or perforated silver sheet. In any case, the intent is to provide electronic contact of the external circuit of the battery or cell and the active material of the positive plate. Silver is necessary to avoid any possible oxidation at this junction and the increased resistance that would result.

Finished electrodes need fairly good physical strength so that they can be handled easily during separator wrapping and cell assembly. This is usually accomplished by a sintering process. Finished electrodes should also have a relatively high surface area per unit weight of active material coupled with an apparent porosity of about 50–60% based on the active material. The high surface area of the active material is attained by high surface area starting materials. These can be finely divided powders of metallic silver or either the monovalent or divalent oxides of silver. Silver electrodes can attain coulombic efficiencies of up to 85% of theoretical when manufactured from high surface area active material.

There are three methods of silver electrode fabrication: (*1*) the slurry pasting of monovalent or divalent silver oxide to the grid, drying, reducing by exposure to heat, and then sintering to agglomerate the fine particles into an integral, strong structure; (*2*) the dry processing of fine silver powders by pressing in a mold or by a continuous rolling operation onto a silver grid followed by sintering; and, (*3*) the use of plastic-bonded active material formed by imbedding the active material (fine silver powder) in a plastic vehicle such as polyethylene, which can then be milled into flexible sheets. These sheets are cut to size, pressed in a mold on both sides of a conductive grid, and the pressed electrode subjected to sintering where the plastic material is fired off, leaving the metallic silver. Silver electrodes produced by these processes range from 0.18 to 1.52 mm in thickness. Electrodes prepared by method (*1*) usually cannot be below 0.76 mm in thickness whereas the thinner electrodes can be prepared by methods (*2*) and (*3*).

Silver electrodes prepared by any of the three methods are almost always subjected to a sintering operation prior to cell or battery assembly. Sintering is basically a heating operation at temperatures well below the melting point of pure silver, 960.5°C, during which an agglomeration of the particles occurs, greatly strengthening the electrodes produced. Sintering is normally carried out in electric muffle furnaces, either on an individual batch process or a continuous conveyor belt-type operation. Reducing atmospheres are not necessary for silver electrode sintering because the process is carried out well above the decomposition temperatures of the various silver oxides. Sintering process parameters vary, however, examples are: 537°C for 30 min and 732°C for 3 min. The longer exposure at a somewhat lower temperature is said to produce electrodes that are less susceptible to shedding. Such a procedure, however, requires a furnace with a long heating zone, is more expensive, and is not practical to most manufacturers.

Zinc electrodes for secondary silver–zinc batteries are made by one of three general methods: the dry-powder process, the slurry-pasted process, or the electroformed process. Current-carrying grids for zinc electrodes can be the same regardless of the process of plate manufacture chosen. Expanded metal, screen, or perforated metal is the generally accepted form for these grids. Silver is the material of preference. However, cost considerations often dictate that copper be used. In these cases silver-plated copper forms are usually employed to avoid the possibility of copper dissolving in the caustic solution during over-discharge of a cell.

The active material used in any of the processes for the manufacture of electrodes is a finely divided zinc oxide powder, USP grade 12. The zinc oxide active material is usually blended with from 1–4% mercuric oxide in the dry state for any of the dry processing procedures. Mercuric oxide is converted to mercury during charge which then amalgamates the zinc formed at the same time. This tends to suppress the evolution of hydrogen on the zinc electrode during charged stand, and is required in most military applications to avoid a hydrogen hazard.

In the dry powder process the active material mix is spread evenly in a mold, the grid and lead assembly inserted, and the entire electrode then pressed in a hydraulic press. Often binder additives such as poly(vinyl alcohol) (PVA) or fine Teflon powder are added to the active material mix to increase the cohesiveness of the finished electrodes. Cellulosic paper liners are also used, and they are inserted into the mold prior to introduction of the active mix and grid. After the active mix and grid are introduced, the paper liner is then folded over the top of the electrode and the electrode pressed as before. Porosities obtained by pressing electrodes in this manner are usually in the range of 50%, although in actual production these figures can range from about 35–60% depending on the rate of discharge required. In the slurry or paste method a paste is prepared by mixing water with the active material mix (zinc oxide plus mercuric oxide). Sometimes a binder such as CMC, or a flock such as short rayon or Dynel fibers is added to the paste to increase the cohesiveness of the pasted electrode. Pasting is usually done on large strips of grid material.

After pasting, the strips are air dried at relatively low heats, individual electrodes are cut from the strip, and the electrodes are pressed to desired thicknesses. The porosities and densities of the active material made by the pasting processes are approximately the same as those indicated for the dry pressed powder processes. One danger in pasting electrodes is the occurrence of sharp grid edges on the electrodes after cutting to size. Often a secondary operation of smoothing or trimming is required to avoid this problem.

The electroforming or deposition of zinc from solution uses a slurry of zinc oxide in strong caustic solution or actual metallic zinc anodes in caustic solution. In the slurry method, the zinc oxide is deposited on silver or copper grids that comprise the grids of the finished electrodes. In the metallic zinc anode method, the solutions are not depleted but rather the anodes are depleted. Both methods utilize large sheets onto which the active zinc material is deposited. Often individual plate leads are welded in position prior to deposition. In other cases active zinc must be scraped from the grid in a secondary operation and the plate leads then welded into position. Zinc plates prepared by these deposition methods usually have the active material in a voluminous, mossy state. After plating, the sheets of deposited material must be washed to completely free them of any traces of caustic solution to avoid fire hazards during production and the subsequent drying operation.

After the plates have been washed and dried thoroughly, they are pressed in a preliminary operation to the desired thickness. Individual electrodes are then cut from the sheets and a secondary pressing operation to final thickness is done. Often a secondary operation is required to remove sharp edges of electrodeposited zinc electrodes.

2.4. Silver–Zinc Separators

The basic separator material is a regenerated cellulose (unplasticized cellophane) which acts as a semipermeable membrane allowing ionic conduction through the separator and preventing the migration of active materials from one electrode to the other.

A stronger separator is one made of sausage casing material (FSC), a regenerated cellulose similar to cellophane but including some fibrous material. FSC is usually extruded in tubes and electrodes are inserted into each end of the tube. The tube is folded to form the so-called U wrap.

Another method of extending the life of the cellulosic separators has been to incorporate a silver organic compound, eg, silver xanthate [6333-67-1], into the cellulosic separator. This is done by passing the separator material through a hot caustic solution containing a silver salt. The result is a deposition of a silver organic compound within the structure of the cellophane or FSC separator. This type of material resists the degradative effects of oxidation more than the untreated material. In general the positive electrodes are wrapped in the layers of separator. Normally, an absorber is used around each positive electrode to maintain an adequate supply of electrolyte. Absorbers are usually of nonwoven materials, such as polyamide or Dynel felts. In some cases, nonwoven cellulosic felts are also used, but these tend to degrade more rapidly. The absorber wrapped positive electrodes are usually wrapped in several layers of cellophane or FSC and then folded to form Us. Negative electrodes are alternately stacked forming the cell assembly. Normally ca three or four layers of

PUDO (battery-grade) cellophane 0.025 mm thick are used in so-called high rate designs. For lower rate cells where longer life is required the number of layers of cellophane may be as many as ten. Occasionally cells are constructed with the negative electrodes wrapped in the separator material. This is said to reduce the shape change effect on the negative electrodes and increase life of the cell. These so-called reverse-wrap cells are usually reserved for low rate applications only.

2.5. Electrolyte

The electrolyte in silver–zinc cells is 30–45% KOH. The lower concentrations in this range have higher conductivities and are preferred for high rate cells. Higher concentrations have a less deleterious effect on cellulosic separators and are preferable for extended life characteristics. The higher concentrations also have a greater capacity for dissolving zinc oxide and accelerate change in shape of the zinc electrode. In most cases, a concentration of about 40% KOH is considered as the optimum. Occasionally, some manufacturers use as electrolyte a saturated zincate solution at the particular concentration desired. This supposedly slows the effect of zinc dissolution. However, in actual use such additives have not been shown to have much beneficial effect. Other additives, such as LiOH, which are used in other alkaline systems, have no beneficial effect on silver–zinc batteries. In practice the electrolyte is added to the cell in the discharged condition, and a period of soaking is allowed for the separators to absorb electrolyte and the electrodes to become thoroughly impregnated with electrolyte.

2.6. Cell Hardware

Cell jars are constructed almost exclusively of injection-molded plastics, which are resistant to the strong alkali electrolyte. The most generally used materials are modified styrenes or copolymers of styrene and acrylonitrile (SAN). Another material that has been found to increase shock resistance of cells is ABS plastic (acrylonitrile–butadiene–styrene). All of these plastics can be injection-molded, are solvent-sealable and, in general, meet operating temperature ranges up to about 70°C. For applications that require greater resistance to temperature, some of the more recent plastics such as polysulfone and poly(phenylene oxide) (PPO) injection-moldable materials able to withstand operating temperatures up to 150°C are used.

Cell terminal connections are usually brought out by two-threaded terminals that protrude through the cell jar cover. They are usually steel, brass, or copper with a hollow construction. The plate leads are soldered in place in the center hollow portion of the terminal to effect an electrical contact and cell seal. The terminal itself is potted into the jar cover using epoxy-type potting compounds. Normally, terminal hardware is silver-plated. However, for corrosion resistance nickel-plating has been used.

2.7. Performance

2.7.1. Charging

Charging of silver–zinc cells can be done by one of several methods. The constant-current method which is most common consists of a single rate of current usually equivalent to a full input within the 12–16-h period. A typical two-level constant-current charge curve results as shown in Figure 11. The first 20–30% of the $A \cdot h$ input is attained at slightly above the monovalent silver level of ca 1.65 V. After this input a sharp rise to the divalent level takes place, and the remainder of the charge is completed at a voltage somewhat above the divalent silver level of 1.90–1.95 V. When the silver electrodes have reached full charge, there is a sharp rise to about 2.0–2.05 V; at this point oxygen is liberated at the positive electrode. Normally the charge is terminated to avoid excessive overcharge of the zinc electrodes and further oxygen evolution. If the charge is continued beyond this point, charging voltage remains at approximately a 2.05–2.1 V level until all of the zinc material is

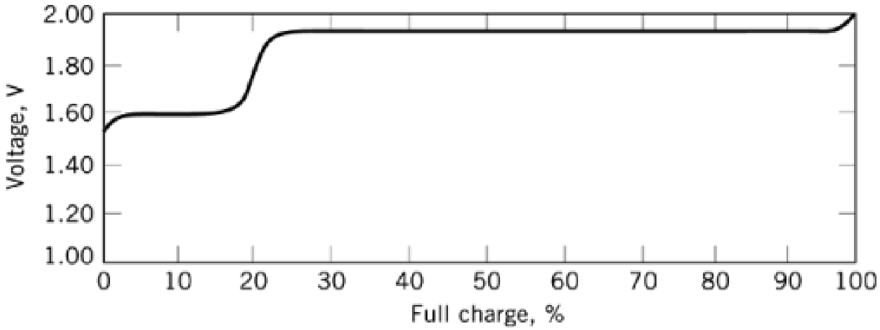


Fig. 11. Constant-current charge curve for a high rate Ag–Zn cell at room temperature. Charging carried out at the 10-h rate.

fully charged. Then another rise in voltage occurs to ca 2.2–2.3 V, and both hydrogen and oxygen are liberated. Further charging results in electrolysis of the water in the electrolyte.

Other acceptable charging methods that have been used are the two-level charging, modified constant potential, and constant potential methods. The two-level method is one in which a relatively high rate of charge is used until a specified input is obtained, at which time the charging rate is lowered to a second level until a voltage cut-off is reached. In the modified constant potential method an initial charging rate is set, somewhat higher than would be used for a single-level constant, current charge; and then the charging current is allowed to drift downward as the battery voltage rises during charge. The constant potential systems are usually current-limited to avoid excessive inrush currents, and are essentially similar to modified constant potential methods in that the initial current is a very high value which rapidly decreases and approaches zero during final stages of charge.

Charge acceptance of the silver–zinc system is normally on the order of 95–100% efficient based on coulombic (ampere-hour output over input) values. This is true of any of the charging methods when carried out in the proper manner. Thus overcharge is rarely necessary in charging silver–zinc cells and batteries.

2.7.2. Discharge

Silver–zinc cells have one of the flattest voltage curves of any practical battery system known. However, there are two voltage plateaus. Even at rates as high as 10 minutes a fairly flat characteristic is obtained. The actual level of voltage is, of course, rate dependent. However, because of the high conductivity of the silver electrode, derating of voltage with higher rates is less than other systems. Figure 12 gives typical discharge curves for a high rate silver–zinc cell. At the low rates the initial part of the voltage discharge curve exhibits the higher level or peroxide voltage. After about 20–25% of the A·h capacity has been discharged, this drops to the monovalent level. As the rate increases, the proportion of the discharge capacity at the higher voltage level becomes less, and at very high rates a dip often occurs at the beginning of discharge as in the 10-min curve. The capacity of the silver–zinc cells is also rate dependent, but less derating occurs here than in most other batteries. For example, from Figure 12 it can be seen that even at the 10-min rate a high rate silver–zinc cell provides over 60% of its rated capacity.

Performance of silver–zinc cells is normally considered to be adequate in the temperature range of 10–38°C. If a wider temperature range is desired silver–zinc cells and batteries may be used in the range 0–71°C without any appreciable derating. Lower temperatures result in some reduction of cell voltage capacities at medium to high rates, and higher temperatures curtail life because of deterioration of the separator materials. Operation at temperatures below 0°C results in more serious derating and normally external heat is provided for operation in this range. Long use at temperatures above 71°C seriously curtails life.

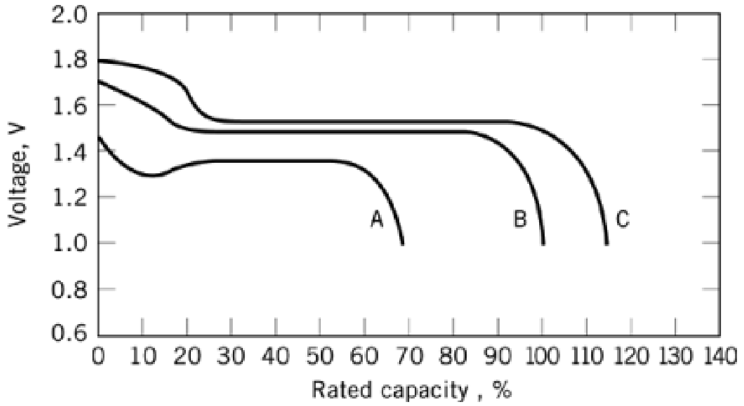


Fig. 12. Silver–zinc cell discharge curves at rates of A, 10 min; B, 1 h; and C, 10 h.

2.7.3. Cell Life

Silver–zinc cells are usually manufactured as either low or high rate cells. Low rate cells contain fewer and thicker electrodes and have many layers of separator (up to the equivalent of 10 layers of cellophane). High rate cells, on the other hand, contain many thinner electrodes and have separator systems of the equivalent of three to four layers of cellophane. Approximately 10–30 cycles can be expected for high rate cells depending on the temperature of use, the rate of discharge, and methods of charging. Low rate cells have been satisfactorily used for 100–300 cycles under the proper conditions. In general, the overall life of the silver–zinc cell with the separator systems normally in use is approximately 1–2 yr.

3. Other Silver Positive Electrode Systems

3.1. Silver–Cadmium Cells

The first silver–cadmium batteries were manufactured in 1900 for motor cars. Use of this electrochemical system was quite limited. Then in the late 1950s, there was interest for applications such as appliances, power tools, and scientific satellites when it was hoped that silver–cadmium batteries could offer an energy density close to silver–zinc batteries and a life characteristic approaching that of the nickel–cadmium system. In satellite applications the nonmagnetic property of the silver–cadmium battery was of utmost importance because magnetometers were used on satellites to measure radiation and the effects of magnetic fields of energetic particles. Satellites had to be constructed of nonmagnetic components in sealed batteries.

The overall reactions are

$$2\,\text{AgO} + \text{Cd} + \text{H}_2\text{O} \rightleftharpoons \text{Ag}_2\text{O} + \text{Cd}\,(\text{OH})_2 \qquad E^\circ = 1.38\ \text{V}$$

$$\text{Ag}_2\text{O} + \text{Cd} + \text{H}_2\text{O} \rightleftharpoons 2\,\text{Ag} + \text{Cd}\,(\text{OH})_2 \qquad E^\circ = 1.16\ \text{V}$$

The silver–cadmium cell exhibits a two-plateau voltage characteristic on charge and discharge. At moderate discharge rates at 25°C, approximately 20% of the A·h capacity is delivered at a nominal 1.2 V; and the remaining capacity is delivered at 1.08–0.9 V. The discharge voltage characteristics are very sensitive to current rates, amount of cycling, charged stand time, float-charging, and temperature. For example, cells that are continuously float-charged exhibit a flat discharge voltage and no loss of capacity. At moderate charge rates, the voltage characteristic consists of two levels, 1.3 V and 1.5 V, nominal. Either constant current or constant potential charging is used. During cycling, $\mathrm{A{\cdot}h}$ efficiencies are $>95\%$ and $\mathrm{W{\cdot}h}$ efficiencies are $<75\%$.

The positive plates are sintered silver on a silver grid and the negative plates are fabricated from a mixture of cadmium oxide powder, silver powder, and a binder pressed onto a silver grid. The main separator is four or five layers of cellophane with one or two layers of woven nylon on the positive plate. The electrolyte is aqeous KOH, 50 wt %. In the aerospace applications, the plastic cases were encapsulated in epoxy resins. Most useful cell sizes have ranged from 3 to $15\ \mathrm{A{\cdot}h}$, but small $(0.1\ \mathrm{A{\cdot}h})$ and large $(300\ \mathrm{A{\cdot}h})$ sizes have been evaluated. Energy densities of sealed batteries are $26 - 31\ \mathrm{W{\cdot}h/kg}$.

Silver–cadmium satellite batteries have been used in cyclic periods of five hours or more with discharge times of 30–60 min. Based on nominal capacities, depths of discharge have been 8–30%. The electrical performance of silver–cadmium batteries degrades below 0°C and above 40°C. At low temperatures the main problems are capacity maintenance during cycling and a dip in voltage on initiation of discharge. Operational and test programs have shown cycle life periods of 3 yr at low temperatures. At temperatures of 40°C and 50°C, the cycle life is 1 yr and 0.2 yr, respectively. The cycle life at intermediate temperatures is 1.4–2.0 yr.

Another application for silver–cadmium batteries is propulsion power for submarine simulator-target drones. High current drains are required (average C, pulses up to 6C), and greater recyclability than the silver–zinc counterparts used in torpedo propulsion. Batteries designed for this use utilize vented cells, high temperature plastic cell jars, and cell designs having a large number of thin electrodes to maximize electrode surface area.

3.2. Silver–Iron Cells

The silver–iron battery system combines the advantages of the high rate capability of the silver electrode and the cycling characteristics of the iron electrode. Commercial development has been undertaken (70) to solve problems associated with deep cycling of high power batteries for ocean systems operations.

Cells consist of porous sintered silver electrodes and high rate iron electrodes. The latter are enclosed with a seven-layered, controlled-porosity polypropylene bag which serves as the separator. The electrolyte contains 30% KOH and 1.5% LiOH.

Initial experiments were conducted with $350{-}\mathrm{A{\cdot}h}$ cells that maintained capacity over 200 cycles. Conventional silver-zinc cells lose capacity in similar deep-cycle operations. Cell tests conducted under a variety of temperature and pressure conditions revealed no discernable effects up to pressures of 69 MPa (10,000 psi) using a flooded electrolyte system. Tests at 0–25°C showed less than 5% capacity loss resulting from temperature when tested at the 8-h discharge rate. The cells as produced have a discharge voltage of ca 1.1 V. Voltage capacity characteristics of a nominal $140{-}\mathrm{A{\cdot}h}$ silver–iron cell are shown in Figure 13. The discharge capacity of a typical cell is $145 - 155\ \mathrm{A{\cdot}h}$ at discharge rates of 80–10 A. A battery of 24 series-connected cells (containing excess electrolyte) weighs 40 kg and provides an energy density of $3.5\ \mathrm{kW{\cdot}h}$. At the 3-h rate the energy density is $100\ \mathrm{W{\cdot}h/kg}$, or about three and a half times the energy density of comparable lead–acid batteries.

Applications have been found for these batteries in emergency power applications for telecommunications systems in tethered balloons. Unfortunately, the system is expensive because of the high cost of the silver electrode. Applications are, therefore, generally sought where recovery and reclamation of the raw materials can be made.

Small silver–iron sealed button cells have been produced in Sweden (70) for long-life operation of hearing aids, calculators, and electric razors. These units have energy densities similar to silver–zinc button cells but are reported to be capable of being fully charged and discharged up to five hundred times without leakage or change in performance. Comparable performance silver–zinc cells have limited cycle life of the order of 75–100 cycles.

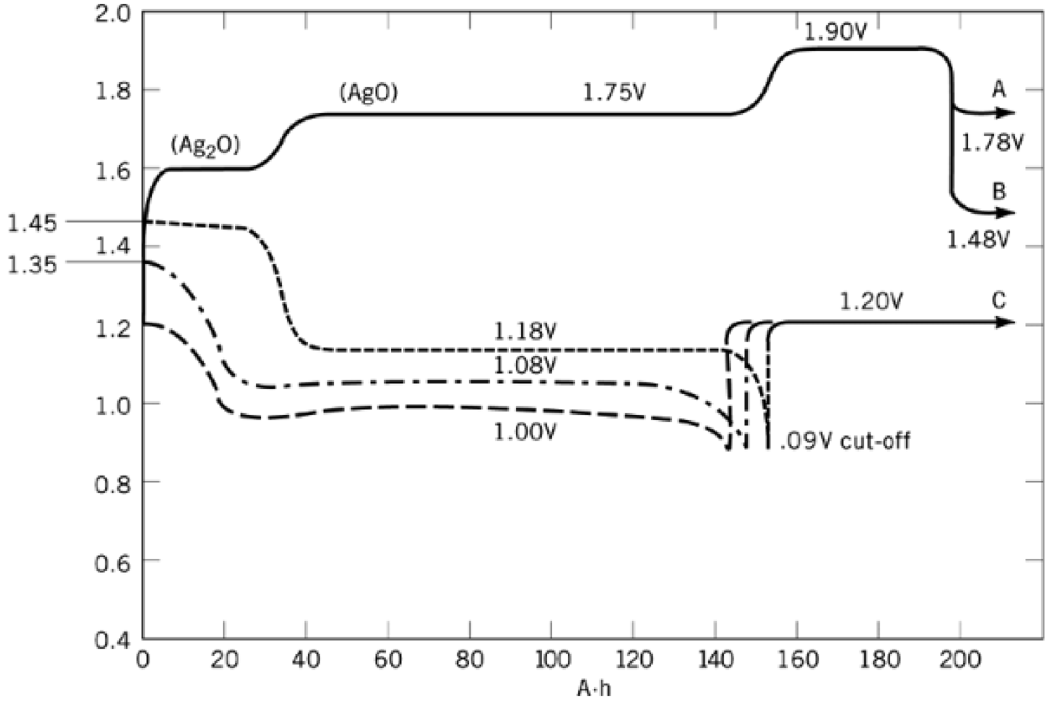


Fig. 13. Charge–discharge characteristics of a nominal 140–A·h silver–iron cell where the charge (——) is at 25 A for 8 h, A represents a 0.25 A float charge; B an open circuit; and the discharge at open circuit after 1 h is shown for (---) 10 A, (–––) 45 A, and (— — —) 80 A; and C represents the open circuit discharge.

4. Nickel–Zinc Cells

Nickel–zinc cells offer potential advantages over other rechargeable alkaline systems. The single-level discharge voltage, 1.60–1.65 V/cell is approximately 0.35–0.45 V/cell higher than nickel–cadmium or nickel–iron and approximately equal to that of silver–zinc. In addition, the use of zinc as the negative electrode should result in a higher energy density battery than either nickel–cadmium or nickel–iron and a lower cost than silver–zinc. In fact, nickel–zinc cells having energy densities in the range of 40 – 60 W·h/kg have been successfully demonstrated.

Work in the 1930s resulted in a rechargeable nickel–zinc railroad battery utilizing standard Edison tubular or Jungner pocket nickel positives and electro-deposited zinc negatives. Cells were constructed utilizing physical separations between the plates and containing a large excess of KOH electrolyte. This Drumm battery exhibited a limited life caused by negative shape change and premature short circuits. Shape change is a phenomenon caused by zinc replating in a nonuniform manner during charge and resulting in a loss of negative capacity. Short circuits resulted from zinc dendrites formed during discharge that grew perpendicular to the face of the negative electrode until electrical contact was made with the positive. In the late 1950s and 1960s interest in the nickel–zinc system was again aroused as a possible substitute for silver–zinc batteries (71–75). By then the technology of nickel and zinc electrodes was well developed and led to a higher energy density nickel–zinc battery having tightly packed electrodes, barrier separators, and limited electrolyte. Most of this work related to vented batteries for low to medium rate applications, such as portable military communication applications.

Some efforts toward sealed battery development (76) were made. However, a third electrode, an oxygen recombination electrode was required to reduce the cost of the system. High rate applications such as torpedo propulsion were investigated (77) and moderate success achieved using experimental nickel–zinc cells yielding energy densities of 35 W·h/kg at discharge rates of 8 C. A commercial nickel–zinc battery is considered to be the most likely candidate for electric vehicle development (78, 79). If the problems of limited life and high installation cost ($100 – 150/kW·h) are solved, a nickel–zinc EV battery could provide twice the driving range for an equal weight lead–acid battery. Work is developmental; there is no commercial production of nickel–zinc batteries.

5. Reaction Mechanism

The overall reactions in the nickel–zinc cell can be represented by

$$2\,\mathrm{NiOOH} + \mathrm{Zn} + 2\,\mathrm{H_2O} \rightleftharpoons 2\,\mathrm{Ni(OH)_2} + \mathrm{Zn(OH)_2} \qquad E^\circ = +1.73\ \mathrm{V}$$

Alternatively the discharged state of the zinc electrode is represented as ZnO.

5.1. Cell Construction

Nickel–zinc batteries are housed in molded plastic cell jars of styrene, SAN, or ABS material for maximum weight savings. Nickel electrodes can be of the sintered or pocket type, however, these types are not cost effective and several different types of plastic-bonded nickel electrodes (78–80) have been developed.

Nickel hydrate, usually 5–10% cobalt added, serves as the active material and is mixed with a conductive carbon, eg, graphite. The active mass is mixed with an inert organic binder such as polyethylene or poly(tetrafluoroethylene) (TFE). The resultant mass is rolled into sheets on a compounding mill or pressed into electrodes as a dry powder on a nickel grid. The resultant electrodes offer a high energy density and low cost of fabrication. In performance, the plastic-bonded electrodes can support rates up to C/2, discharge capacity in 2 h, at voltages equivalent to those of sintered electrodes, but at higher rates some derating occurs. Life of plastic-bonded electrodes has not been fully evaluated, but a life of 500 cycles appears attainable.

Negative electrodes are fabricated of zinc oxide by any of the methods (pasting, pressing, etc) described. Binders, usually TFE, are used to reduce the solubility of the electrode in KOH. In addition, other techniques such as extended edges, inert extenders, contouring, and variable density have been tried in an effort to reduce shape change of the negative electrode upon cycling. The electrolyte is KOH, usually a 30–35% aqueous solution with the addition of LiOH at a level of 10–25 g/L to enhance nickel capacity throughout life.

Separators are both of the organic and inorganic type. During the 1960s most cells were built using cellophane or FSC (fibrous sausage casing) separators. Developments by NASA (81) and others in the area of inorganic films, consisting of a layered or film structure of a heavy metallic oxide such as zirconia, ZrO_2, or magnesia, MgO, bonded by an inert organic film and often layered with an organic resin-impregnated asbestos mat led to use of these materials as separators. In Ni–Zn electric vehicle batteries (82), over 800 cycles at 50% depth are claimed for these inorganic separators. Drawbacks are the relatively high cost of manufacture and the increased resistance per layer, which in effect limits discharge rate.

5.2. Performance

The limited life of nickel–zinc batteries is the principal drawback to widespread use. Normally the nickel cathode is not a factor. Even plastic-bonded nickel electrodes perform for a greater number of cycles than either the zinc counter electrodes or the separator used and to a great extent it is the zinc electrode that limits the

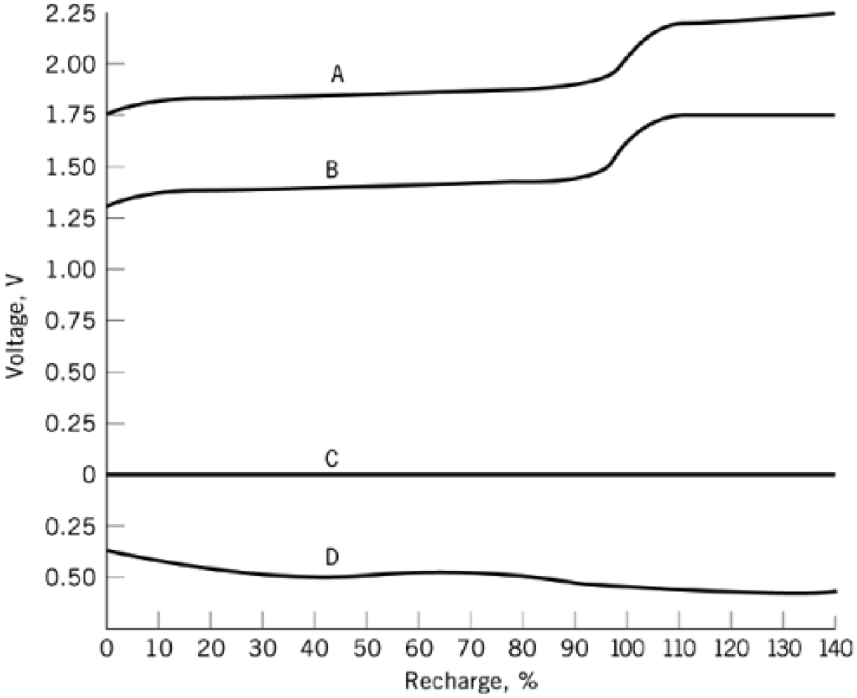


Fig. 14. Nickel–zinc electrode potential on charge A, the Ni–Zn cell; B, the Zn vs Hg ref.; C, the Hg–HgO ref.; and D, the Ni vs Hg ref.

life of a nickel–zinc cell. In order to charge nickel electrodes sufficiently, a discreet amount of overcharge is necessary. Unfortunately, overcharge is not desirable for the zinc electrodes, as it promotes dendritic growth which will eventually penetrate the separator and cause short circuits. This can be alleviated somewhat by an overdesign in zinc capacity, but that reduces energy density. Typical cell and electrode voltage curves are shown in Figure 14 and cycle life data as a function of depth of discharge in Figure 15.

Nickel–zinc batteries containing a vibrating zinc anode has been reported (83). In this system zinc oxide active material is added to the electrolyte as a slurry. During charge the anode substrates are vibrated and the zinc is electroplated onto the surface in a uniform manner. The stationary positive electrodes (nickel) are encased in a thin, open plastic netting which constitutes the entire separator system.

The vibration serves a dual purpose. First, a macroturbulence is created which keeps the ZnO uniformly dispersed in the electrolyte. Second, the microturbulence created at the surface of the negative electrode minimizes the zincate concentration gradients, discouraging the formation of zinc dendrites and causing a uniform deposit of zinc. Any zinc dendrites that may form are brushed off against the plastic netting by the vibratory motion. Thus the problems of shape change, dendritic shorting, and separator failure are in theory solved by this system; the zinc electrode dissolves during discharge, replates during charge, and no separator is required. A disadvantage is reduced energy density, especially on a volume basis, as a result of the increased electrode spacing and the quantity of electrolyte required. The vibration hardware imposes an additional 5% weight penalty as well as increased cost. Alternatively, similar benefits have been reported from experiments in which the electrolyte is pulsed.

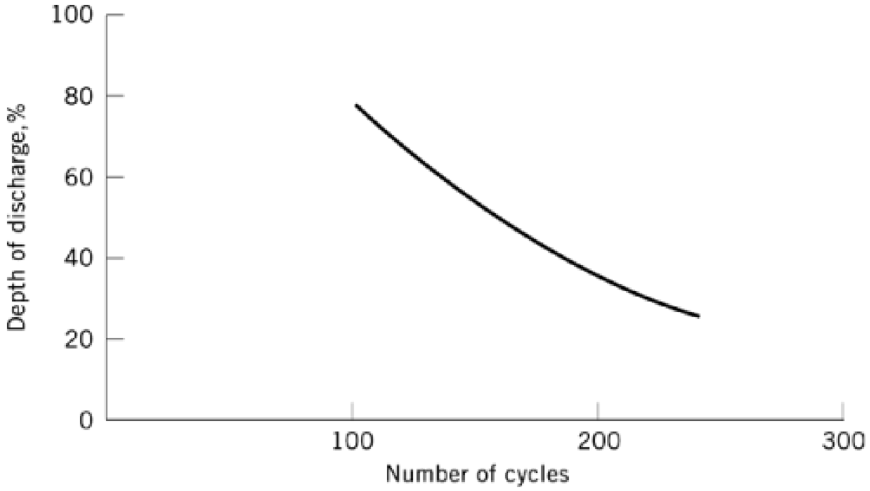


Fig. 15. Cell performance as a function of the number of cell recharge cycles.

6. Nickel–Hydrogen Cells

There are two types of nickel–hydrogen cells; those that employ a gaseous H_2 electrode and those that utilize a metal hydride, MH.

6.1. Gaseous Hydrogen Systems

The nickel–hydrogen cell incorporating a gaseous hydrogen electrode is a hybrid consisting of one gaseous and one solid electrode. The nickel electrode is of the type used in a nickel–cadmium battery and the hydrogen electrode is a gas diffusion electrode of the type used in alkaline fuel cells (qv). These two electrodes are capable of extremely long, stable life. This system was developed to serve as a long life, lightweight battery for satellite applications that would be superior to the aerospace nickel–cadmium batteries (84–86).

The couple has a theoretical energy density of 172 W·h/kg and complete cells are capable of delivering $55 - 66$ W·h/kg. The cell reaction is

$$\mathrm{NiOOH} + \frac{1}{2}\,\mathrm{H_2} \rightleftharpoons \mathrm{Ni\,(OH)_2}$$

However, the generation and migration of water in the half-cell reactions must be considered in the cell design. At the nickel electrode:

$$\mathrm{NiOOH} + \mathrm{H_2O} + e^- \rightleftharpoons \mathrm{Ni\,(OH)_2} + \mathrm{OH^-}$$

and at the hydrogen electrode:

$$\frac{1}{2}\,\mathrm{H_2} + \mathrm{OH^-} \rightleftharpoons \mathrm{H_2O} + e^-$$

During charge the nickel hydroxide is converted to NiOOH, the charged state of nickel, and on the surface of the hydrogen electrode, hydrogen gas is evolved. By placing the electrode stack in a sealed container, the

Fig. 16. Cutaway view of a typical construction of a nickel–hydrogen cell.

hydrogen is captured for subsequent reuse. During discharge the same hydrogen is reconsumed on the same electrode surface and the nickel electrode is reduced to provide electric energy.

Another desirable feature of this battery system is its capability of high rate of overcharge. During overcharge oxygen gas is generated on the surface of the nickel electrode. Simultaneously hydrogen continues to be evolved on the surface of the hydrogen electrode. Because there is a large area of catalyzed hydrogen electrode and ready access of the oxygen to diffuse to that surface, the oxygen readily recombines within the cell to form water and the cell pressure remains constant.

The primary packaging arrangements for this chemistry has been single cylindrical cells as shown in Figure 16, where a stack of disk electrodes are placed within a cylindrical outer housing having domed end caps. The housing also serves as a lightweight pressure vessel for hydrogen containment with all the free volume inside the housing used for hydrogen storage. Two insulated feed throughs are provided in the cell housing for electric contact to the positive and negative electrodes. The electrode stack is a repeating sequence of sintered nickel, absorber separator, typically asbestos, or other inorganic stable materials, teflon bonded platinum black fuel cell-type electrodes, and gas spacers. The electrolyte is typically 30–35% KOH with a LiOH additive for the nickel electrode.

Figure 17 shows a typical charge–discharge voltage and pressure profile for a 50 A·h cell. In this design the cell is precharged at 517 kPa (75 psi) hydrogen and the operating pressure range is from 517 to 4100 kPa (75–600 psi). Monitoring cell pressure, which is typically done with pressure transducers, enables the user to

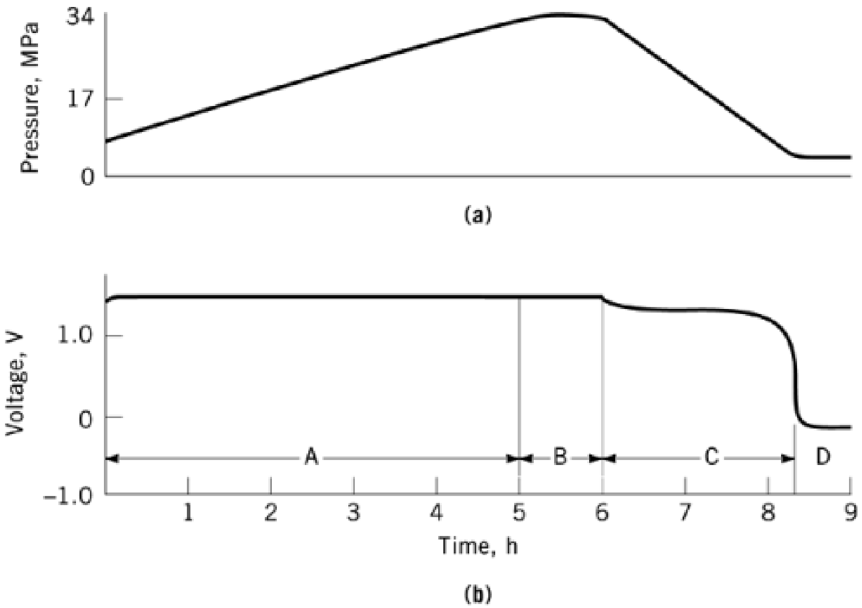


Fig. 17. 50 A·h nickel–hydrogen performance showing (**a**) pressure and (**b**) voltage curves where region A represents charging at 10 A, region B represents overcharge at 10 A, region C represents discharge at 25 A, and region D represents reversal at 25 A. To convert MPa to psi, multiply by 145.

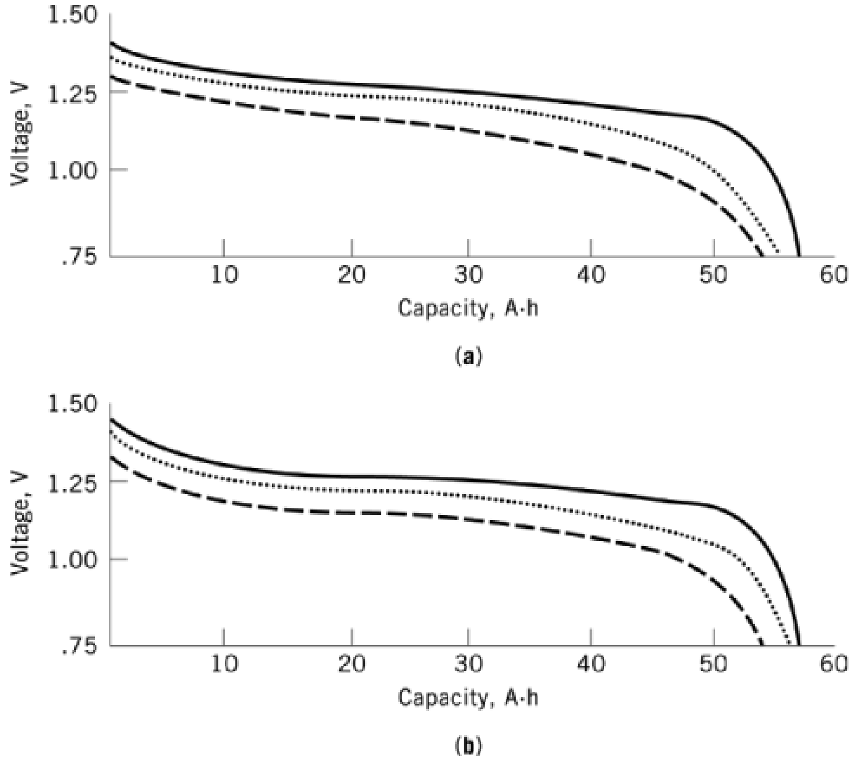
follow the cells state of charge. This is an additional desirable feature of this system. Figure 18 shows cell discharge characteristics as a function of rate, demonstrating the high rate capability of this battery. Figure 19 gives open circuit stand characteristics. This cell exhibits a greater self-discharge than the nickel–cadmium chemistry because of the reaction of pressurized hydrogen with the active nickel material.

Because this battery is only produced for special satellite applications, production quantities are limited. Rigorous quality inspections, expensive light-weight housing and seals, and the use of high loading platinum hydrogen electrodes all make this type of battery very expensive. For typical satellite applications multiple single-cells are connected in series and are packaged in an egg crate mounting. In this arrangement the waste heat generated during discharge and overcharge is conducted from the stack out the cylinder wall through conduction rings to a radiator plate of the satellite.

Limited development efforts have been undertaken to develop a lower cost battery for terrestrial use utilizing reduced catalyst quantities and multicell packaging. Multicell common pressure vessel arrangements have also been considered for aerospace applications, but these configurations have not found market acceptance.

6.1.1. Metal Hydride Systems

The success of the gaseous nickel–hydrogen system led to the investigation of replacing the gaseous hydrogen with metal hydrides in order to reduce the cell pressure and the volume required for hydrogen storage. A number of metal hydrides were developed for reversible hydrogen storage. Of particular interest were $LaNi_5$ and $MnNi_5$ (Misch metal [8049-20-5]) the isotherms of which are shown in Figures 20 and 21, and FeTi. In the initial efforts these materials were packed into the free volume of standard nickel hydrogen cells using standard catalyzed gas diffusion hydrogen electrodes. The metal hydrides absorb up to one hydrogen atom per metal atom and cells incorporating hydrides could be fabricated that were more compact than gas pressure cells. However these hydrides deactivated upon repeated deep-cycling and gradually lost their hydrogen absorption



(a)

(b)

Fig. 18. Discharge characteristics for 50 A·h nickel–hydrogen batteries at (——) 10 A, (●●●) 25 A, and (— — —) 50 A at (**a**) 20°C and (**b**) 0°C.

ability presumably because of attack on the hydrides by water vapor or oxygen gas within the cell environment.

An alternative approach utilizes the hydride material as the hydrogen electrode. In this case, as the hydrogen is generated on the hydrogen electrode, it enters the hydride lattice for storage. On discharge the hydrogen leaves the hydride for reaction. The cell reactions are essentially the same as gaseous nickel hydrogen cells.

$$\mathrm{Ni\,(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O} + e^-$$

$$\mathrm{M + H_2O} + e^- \rightleftharpoons \mathrm{MH + OH^-}$$

and overall

$$\mathrm{Ni\,(OH)_2 + M \rightleftharpoons NiOOH + MH}$$

The overcharge reactions for the cell are the same as for nickel–cadmium and nickel–hydrogen cells. The oxygen generated on the nickel electrode at the end of charge and overcharge finds its way to the anode and reacts to form water in the Ni–H_2 case and $Cd(OH)_2$ in the Ni–Cd case.

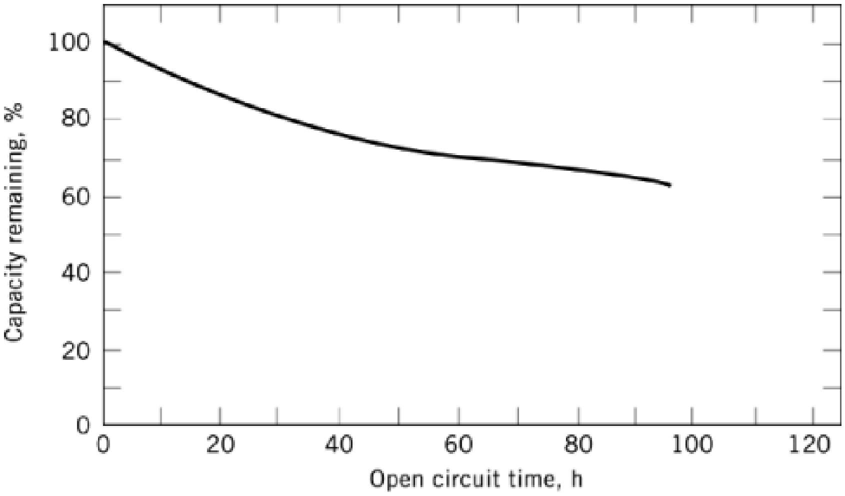


Fig. 19. Self-discharge at ambient temperatures for a 35 A·h cell, NTS-2 prototype Sanyo Electric Co. cell.

Table 5. International MH Alloys

Designation[a]	Composition[b]
IBA MH no. 1	$MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$
IBA MH no. 2	$MmNi_{3.5}Co_{0.7}Al_{0.8}$
IBA MH no. 3	LmNi alloy
IBA MH no. 4	$Ti_{1.6}V_{2.2}Zr_{1.6}Ni_{4.2}Cr_{0.7}$
IBA MH no. 5	$MmNi_{3.5}Co_{0.7}Al_{0.8}$
IBA MH no. 6	$MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$

[a] Standard battery materials are maintained by The Inter-national Battery Materials Association (IBA) (87).

[b] Mm is Misch metal; Lm is lanthanum.

A critical issue is the stability of the hydride electrode in the cell environment. A number of hydride formulations have been developed. Table 5 shows hydride materials that are now the focus of attention. Most of these are Misch metal hydrides containing additions of cobalt, aluminum, or manganese. The hydrides are prepared by making melts of the formulations and then grinding to fine powers. The electrodes are prepared by pasting and or pressing the powders into metal screens or felt. The additives are reported to retard the formation of passive oxide films on the hydrides.

A number of manufacturers started commercial production of nickel–MH cells in 1991 (31–35). The initial products are “AA”-size, “Sub-C”, and “C”-size cells constructed in a fashion similar to small sealed nickel–cadmium cells. Table 6 compares the Ovonics experimental cell and a similar sized nickel–cadmium cell. Ovonics also delivered experimental electric vehicle cells, 22 A·h size, for testing. The charge–discharge of “AA” cells produced in Japan (Matsushita) are compared in Figure 22.

From these data, the hydride cells contain approximately 30–50% more capacity than the Ni–Cd cells. The hydride cells exhibit somewhat lower high rate capability and higher rates of self-discharge than nickel–cadmium cells. Life is reported to be 200–500 cycles. Though not yet in full production it has been estimated that these cells should be at a cost parity to nickel–cadmium cells on an energy basis.

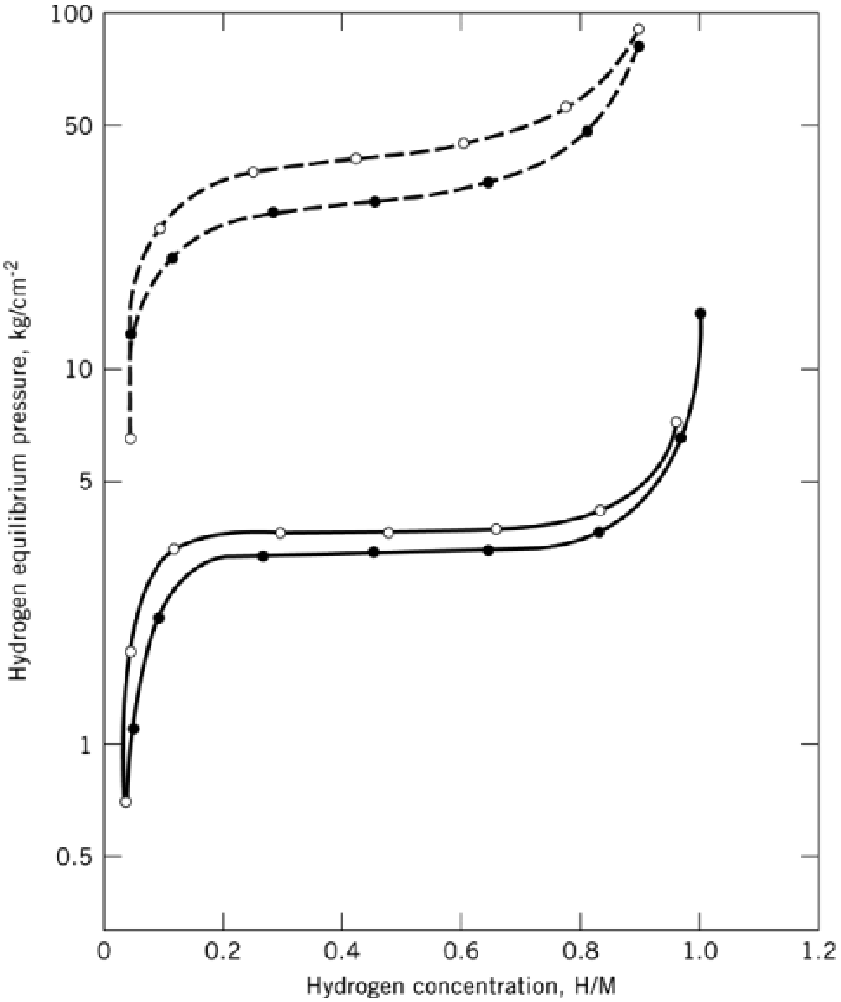


Fig. 20. Pressure concentration curves of $MmNi_5$ (---) and $LaNi_5$ (—) at 45°C where open circles denote absorption and closed circles desorption of hydrogen. H/M represents the ratio in the hydride of the mole fraction of hydrogen to the mole fraction of the metal.

7. Other Cell Systems

7.1. Silver–Hydrogen Cells

With the development of the nickel–hydrogen system limited attention was directed to the development of a silver–hydrogen cell (89, 90). The main characteristics of interest were the potential for a higher gravametric energy density based on the ligher weight of the silver electrode vs that of the nickel. The cell reactions for this couple are

Hydrogen electrode

$$2\,H_2O + 2\,e^- \rightleftharpoons H_2 + 2\,OH^-$$

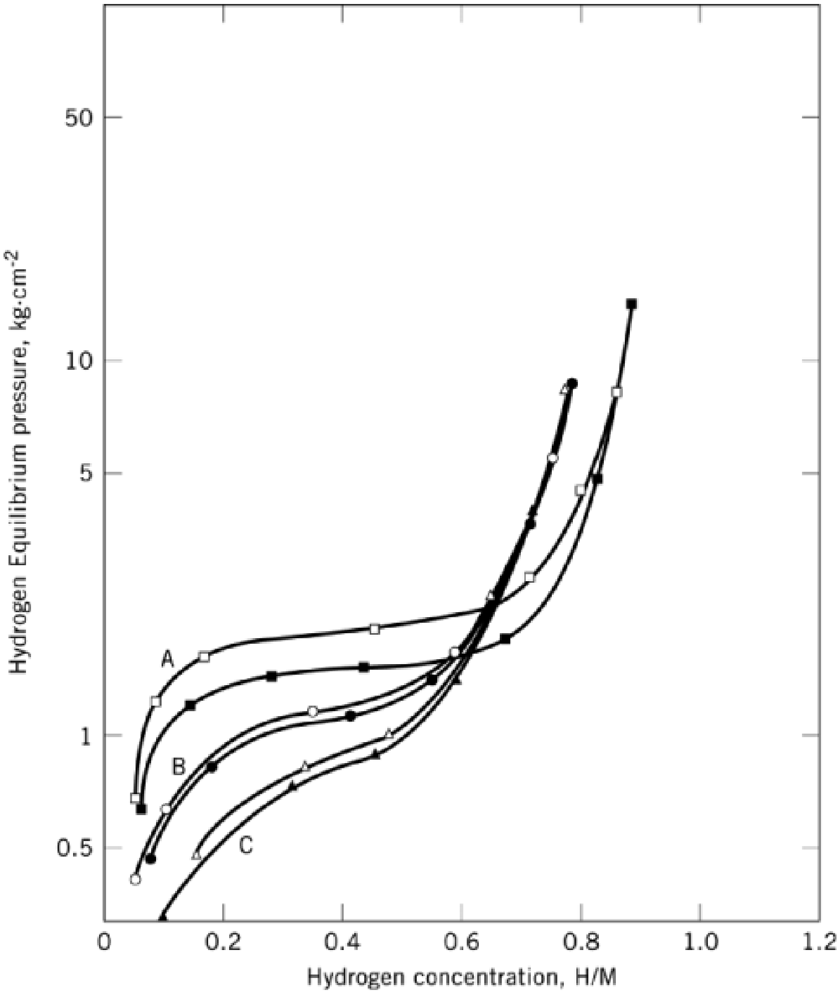


Fig. 21. Pressure constant temperature (PCT) curves of $MmNi_5$ alloy system where open symbols represent absorption and closed symbols represent desorption for A, $MmNi_{4.3}Mn_{0.4}Al_{0.3}$; B, $MmNi_{3.8}Mn_{0.4}Al_{0.3}Co_{0.5}$; and C, $MmNi_{3.5}Mn_{0.4}Al_{0.3}Co_{0.75}$. H/M represents the ratio in the hydride of the mole fraction of hydrogen to the mole fraction of the metal.

Silver electrode

$$Ag + OH^- \rightleftharpoons \frac{1}{2} Ag_2O + \frac{1}{2} H_2O + e^-$$

$$\frac{1}{2} Ag_2O + OH^- \rightleftharpoons AgO + \frac{1}{2} H_2O + e^-$$

Overall reaction

$$H_2 + AgO \rightleftharpoons Ag + H_2O$$

Table 6. Specification of "C" Cells

Parameter	Ni–MH cell[a]	Ni–Cd cell
capacity A·h (nominal)	3.5	2.0
voltage, V	1.2	1.2
cycles[b]	>450	>450
memory effect limitation	none	severe
toxicity of material	No, Cd, Pb, Hg, Li	Cd
operating temperature, °C	−20 to +50	−40 to +60[c]
discharge rate, A	up to 12–15	up to 15
internal resistance, Ω (ANSI method)	25	13–20
charge retention, %[d]	50	60–70
overcharge capability[e]	continuous up to C/5 rate (700 mA)	continuous up to C/5 rate (400 mA)
over–discharge capability	20%	3%

[a] From Ovonics.

[b] One hour charge/one hour discharge at 100% depth of discharge.

[c] Special design required at +60.

[d] Capacity retained in 30 d at 25°C.

[e] Ni–MH cell 1-h charge (3.5 A) to thermal cutout followed by trickle charge of 0.350 A is acceptable. The Ni–Cd charger can be used with these cells. Ni–Cd: 1-h charge (2.0 A) to thermal cutout followed by trickle charge of 0.200 A is acceptable.

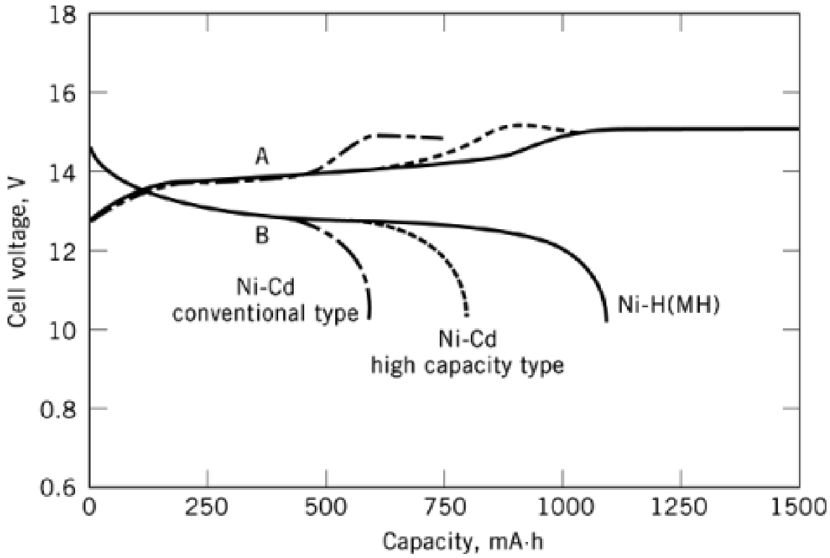


Fig. 22. Charge A and discharge B curves of (——) a Ni–H(MH) cell employing $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ alloy compared with those of (—·—) conventional and (---) high capacity types of Ni–Cd cells (88).

The packaging approach utilized for this battery is similar to that for nickel–hydrogen single cylindrical cells as shown in Figure 23. The silver electrode is typically the sintered type used in rechargeable silver–zinc cells. The hydrogen electrode is a Teflon-bonded platinum black gas diffusion electrode.

Because the silver oxide electrode is slightly soluble in the potassium hydroxide electrolyte the separator is of a barrier type to minimize silver diffusion to the opposite electrode. Figure 24 shows a charge–discharge profile of a 25 A·h cell that exhibits the two voltage plateaus seen for silver electrodes in the silver–zinc battery system. The silver–hydrogen cell exhibits a lower self-discharge than nickel–hydrogen cells as a result of the slower rate of reaction of hydrogen with silver oxide. The actual cells do not exhibit substantial differences

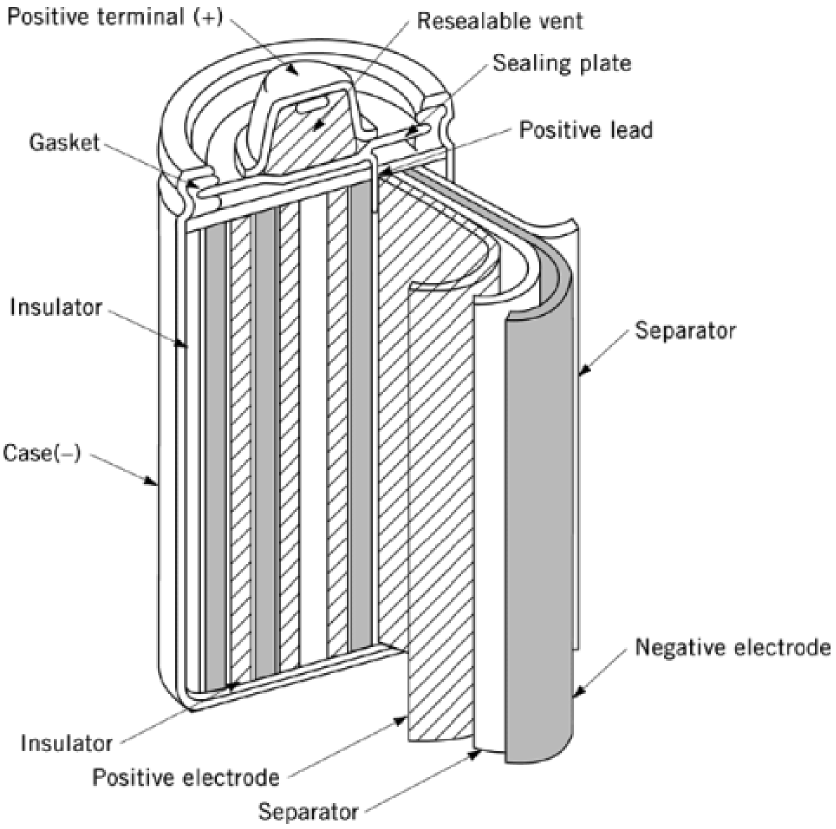


Fig. 23. Schematic diagram of Ni–H(MH) cell (88).

in energy density when compared to those of nickel–hydrogen. Therefore this system is not being actively pursued.

7.2. Zinc–Oxygen Cells

On the basis of reactants the zinc–oxygen or air system is the highest energy density system of all the alkaline rechargeable systems with the exception of the $H_2 \cdot O_2$ one. The reactants are cheap and abundant and therefore a number of attempts have been made to develop a practical rechargeable system. The reactions of this system are as follows:

Zinc electrode

$$\mathrm{Zn} + 2\,\mathrm{OH}^- \rightleftharpoons \mathrm{Zn\,(OH)_2} + 2\,e^-$$

Oxygen electrode

$$\frac{1}{2}\,\mathrm{O_2} + \mathrm{H_2O} + 2\,e^- \rightleftharpoons 2\,\mathrm{OH}^-$$

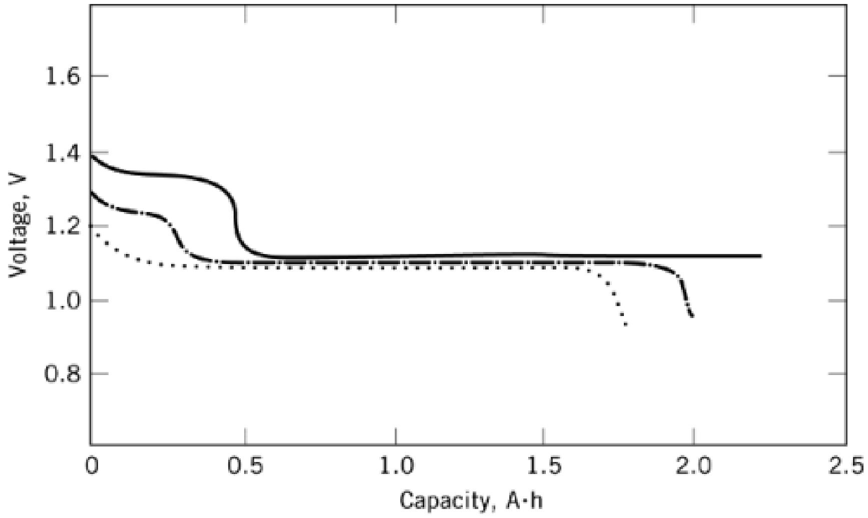


Fig. 24. Silver–hydrogen cell discharge characteristics where (•••) represents a 0.5 h rate at 4 A or 80 mA/cm^2; (—•—) represents a 1 h rate at 2 A; and (——) represents a 4 h rate at 0.5 A or 10 mA/cm^2.

Overall reaction

$$\mathrm{Zn} + \mathrm{H_2O} + \frac{1}{2}\,\mathrm{O_2} \rightleftharpoons \mathrm{Zn\,(OH)_2}$$

In open cycle systems the oxygen reactant is released into the surrounding air during charge, and during the subsequent discharge oxygen from the surrounding air is consumed on a fuel cell-type electrode. The oxygen is delivered by forced or free confection depending on the system design. Whereas the zinc–oxygen cell has significant potential, it also has a number of inherent problems. First is the poor rechargeability of the normal zinc electrode; then there is the poor stability of the oxygen electrode when used in a bifunctional, ie, charge and discharge mode, contamination of the electrolyte by carbon dioxide from the air when used as an open cycle system, and poor retention of energy efficiency because of the irreversibility of the oxygen electrode reaction.

The system shown in Figure 25, in which the electrolyte was circulated through a multicell stack to improve the rechargeability of the zinc electrode has been studied by Sanyo Electric. However, such circulating systems are prone to electrolyte leakage and have common manifolds that cause internal self-discharge. Systems in which zinc particles or zinc-coated beads are circulated through the electrode stack and are utilized as a fluidized electrode have also been investigated by many organizations. In these systems the zinc particles contact the anode current collector to undergo reaction. In order to dissolve all the reaction product during discharge, it is necessary to use relatively large quantities of electrolyte so that a zincate solubility of approximately 200 g/L is not exceeded. The CGE (91) (Fig. 26) system utilized a tubular cell and a separate regeneration stack to deposit new zinc particles from the discharged electrolyte, which is saturated with dissolved zincate. By utilizing a separate regeneration stack the stability problem of the bifunctional oxygen electrode is avoided and regeneration can be carried out at any location so that the battery can be refueled rapidly. A sealed system in a configuration similar to single cylindrical gaseous nickel–hydrogen cells has also been studied (92).

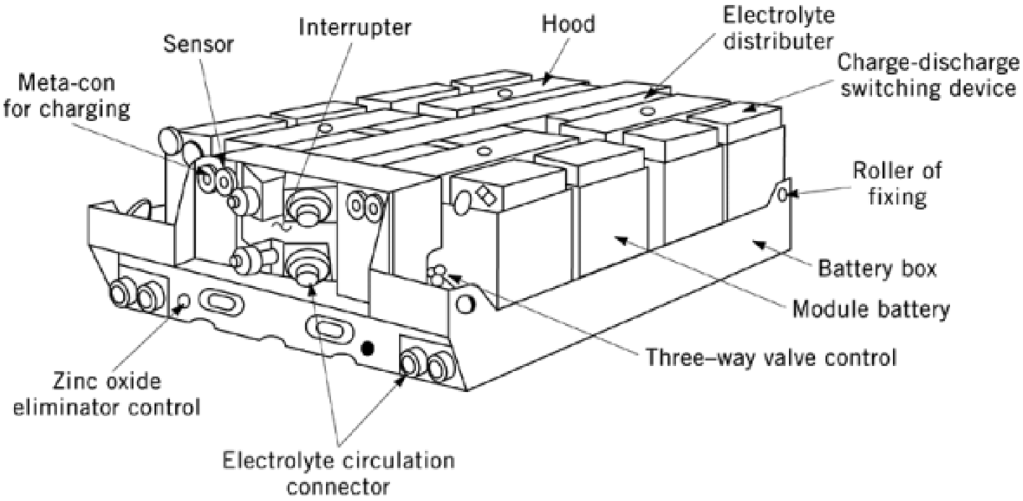


Fig. 25. Zinc–air 124-V battery system. Meta-con is a connector.(Courtesy of Sanyo Electric Co.)

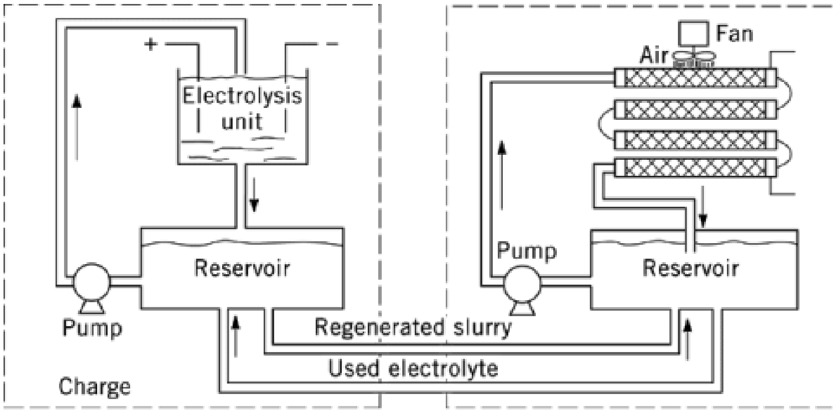


Fig. 26. Schematic diagram of the separate charge and discharge modules of the Génerale d'Electricité circulating zinc–air battery (91).

7.3. Iron–Air Cells

The iron–air system is a potentially low cost, high energy system being considered mainly for mobile applications. The iron electrode, similar to that employed in the nickel–iron cell, exhibits long life and therefore this system could be more cost effective than the zinc–air cell. Reactions include:

Iron electrode

$$\mathrm{Fe} + 2\,\mathrm{OH}^- \rightleftharpoons \mathrm{Fe(OH)}_2 + 2\,e^-$$

Oxygen electrode

$$\frac{1}{2}\,\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} + e^- \rightleftharpoons 2\,\mathrm{OH}^-$$

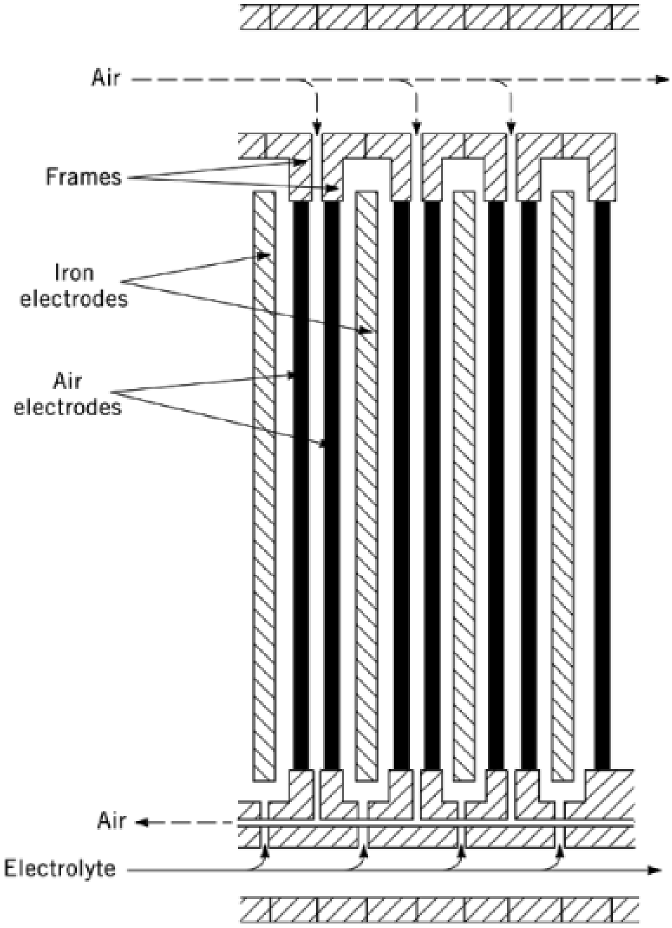


Fig. 27. Cross-section of SNDC iron–air battery pile (93).

Overall reaction

$$\mathrm{Fe} + \frac{1}{2}\,\mathrm{O_2} + \mathrm{H_2O} \rightleftarrows \mathrm{Fe\,(OH)_2}$$

In the experimental systems studied the iron electrode has been of the sintered type and the oxygen–air electrodes have been of the bifunctional type.

A system as shown in Figure 27, which incorporates circulating electrolyte for thermal management and removal of gases generated during charge, has been developed (93). The iron electrode has a low hydrogen overvoltage and therefore the electrode evolves hydrogen during charge and to some extent during open circuit stand. A similar system, where the primary emphasis is on the development of a stable bifunctional air electrode is under investigation (94). A Teflon-bonded formulation consisting of a carbon-base, catalyzed with silver and other additives, is reported to be stable for up to 500 cycles. Because of the inefficiency of the iron electrode, and the irreversibility of the oxygen electrode, this system exhibits recharge energy efficiencies of less than 50%.

7.4. Hydrogen–Oxygen Cells

The hydrogen–oxygen cell can be adapted to function as a rechargeable battery, although this system is best known as a primary one (see Fuel cells). The electrochemical reactions involve:

Electrodes

$$H_2 + 2\,OH^- \rightleftharpoons 2\,H_2O + 2\,e^-$$

$$\frac{1}{2}\,O_2 + H_2O + 2\,e^- \rightleftharpoons 2\,OH^-$$

Overall

$$H_2 + \frac{1}{2}\,O_2 \rightleftharpoons H_2O$$

During charge, water is electrolyzed to produce hydrogen and oxygen which are stored as pressurized gas. During discharge those gases electrochemically react to produce water. The reactants have a theoretical energy content of 770 W·h/kg and the interest that has been directed at this system has been primarily for light batteries for military and/or aerospace applications. In the 1960s a multicell bipolar stack contained inside a cylindrical pressure vessel was studied (95). The stack was internally manifolded to feed hydrogen and oxygen to separate compartments within the pressure vessel at operating pressures that ranged between 0.7 and 2.4 MPa (100–350 psi). Figure 28 shows a charge–discharge profile of the system.

Because of cross-gas leakage and other complexities, a single-cell was developed. In this configuration the electrodes were constructed in the form of a cylinder; the hydrogen gas was stored in the central compartment, and the oxygen gas in the space between the electrode core and the outer pressure vessel. These two compartments were sized in a two to one volume ratio to maintain the two gases at the same pressure as they are generated during charge. A flexible bellows was placed between the two compartments to compensate for slight differences in the compartments' volume and temperature effects. This system was not pursued however; it was dropped in favor of the simpler single-gas nickel–hydrogen system.

As primary alkaline fuel cells were developed for space applications, consideration was given to separate stack rechargeable designs. In these approaches, the product water formed during the discharge of a primary fuel cell is stored, then fed to a separate electrolizer stack during charge. The hydrogen and oxygen gas generated during charge is stored in separate pressure vessels. This approach overcomes the stability problem of the bifunctional oxygen electrode and the respective stacks can be optimized for their function. This system is still rather complex and bulky and has not yet been applied.

7.5. Mechanically Rechargeable Batteries

To avoid the time required for electric recharge, the problems of *in situ* electric recharge, or to utilize anodes that are not electrically rechargeable in aqueous electrolytes, mechanically rechargeable batteries have been studied. These systems are metal–air couples. batteries were developed for military portable electronic equipment in the 1970s. These batteries were never deployed because of difficulties of leakage, problems of repeatedly replacing the anodes, and the development of lithium primary batteries having superior performance.

Lithium as an anode in alkaline electrolyte has been considered in the battery system shown in Figure 29. Even though lithium reacts directly with water, it was possible to operate the battery because of a protective

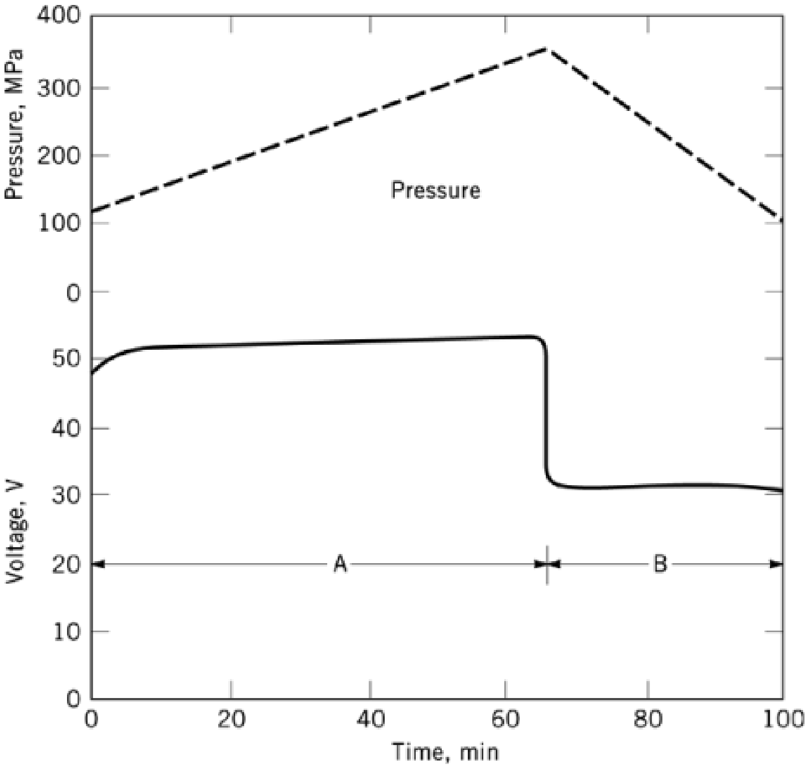


Fig. 28. Cycle of 34-cell regenerative hydrogen–oxygen fuel cell where A represents the charging region at 10 A, B represents discharging at 18.2 A. Both (—) voltage and (---) pressure changes are shown. To convert MPa to psig, multiply by 145.

lithium hydroxide film that forms on the anode. However, the film was not totally protective and units exhibited poor efficiency and were very complex.

The most significant results with these battery types focus on aluminum as the anode. Figure 30 shows an aluminum–air cell being developed for electric vehicle applications. The aluminum hydroxide reaction product would be returned to the factory to be reprocessed into fresh aluminum anodes. One set of anodes could yield up to 500 miles range before replacement. However, the corrosion reaction of the aluminum with the electrolyte is still a problem. Additionally, the system is complex and it is anticipated that replacing the anodes repeatedly will be as problematic as the zinc systems. The system has poor energy efficiency when consideration is given to the full cycle of electric generation, aluminum production, battery efficiency, and reprocessing of the battery reaction product back to aluminum.

8. Electrolyte

Potassium hydroxide is the principal electrolyte of choice for the above batteries because of its compatibility with the various electrodes, good conductivity, and low freezing point temperature. Potassium hydroxide is a white crystalline substance having a mol wt = 56.10; density = 2.044 g/mL, and mp = 360°C (see Potassium compounds). It is hygroscopic and very soluble in water. The most conductive aqueous solution at 25°C is at 27% KOH, but the conductivity characteristics are relatively flat over a broad range of concentrations.

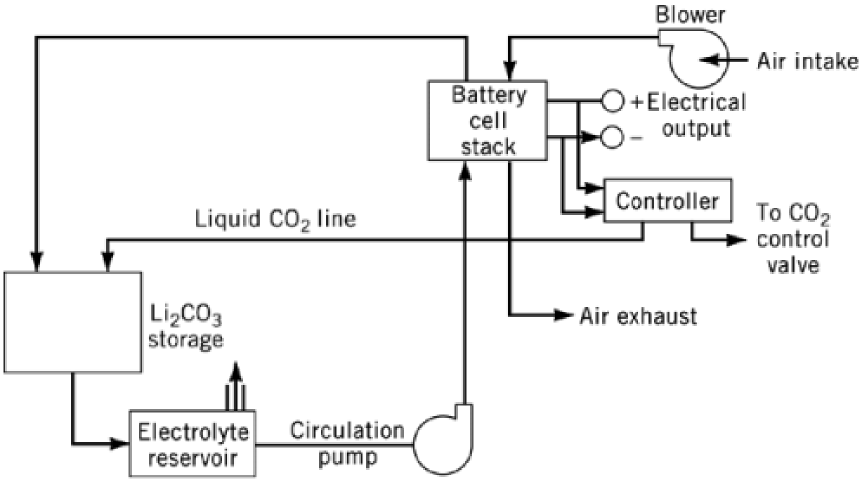


Fig. 29. Schematic of lithium–air automotive propulsion system.

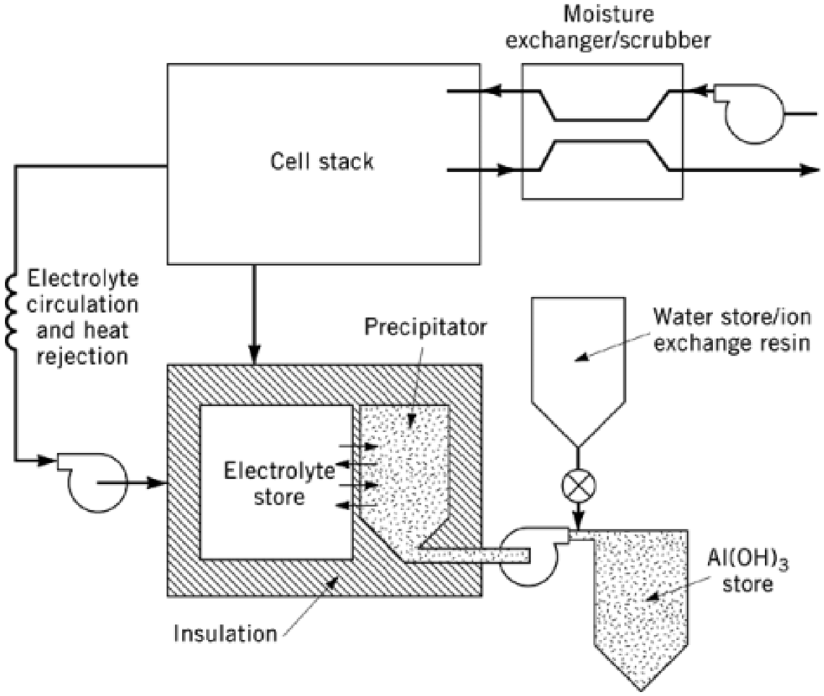


Fig. 30. Aluminum–air power cell system. The design provides for forced convection of air and electrolyte, heat rejection, electrolyte concentration control via $Al(OH)_3$ precipitation, and storage for reactants and products.

The characteristics for aqueous KOH (97–99) solutions vary somewhat for battery electrolytes when additives are used. Furthermore, potassium hydroxide reacts with many organics and with the carbon dioxide in air to form carbonates. The build-up of carbonates in the electrolyte is to be avoided because carbonates reduce electrolyte conductivity and electrode activity in some cases.

9. Safety and Disposal

The potassium hydroxide electrolyte used in alkaline batteries is a corrosive hazardous chemical. It is a poison and if ingested attacks the throat and stomach linings. Immediate medical attention is required. It slowly attacks skin if not rapidly washed away. Extreme care should be taken to avoid eye contact that can result in severe burns and blindness. Protective clothing and face shields or goggles should be worn when filling cells with water or electrolyte and performing other maintenance on vented batteries.

Alkaline batteries generate hydrogen and oxygen gases under various operating conditions. This can occur during charge, overcharge, open circuit stand, and reversal. In vented batteries free ventilation should be provided to avoid hydrogen accumulations surrounding the battery. A vented battery must never be placed in a sealed container for which it was not designed. As a result of operation, hydrogen–oxygen mixtures that are flammable or explosive can exist in the cells' head space. Ignition of this mixture, which is rare, can result in blowing off cell lids. This can occur from internal short circuits or external sparks that propagate back into the cell housing.

Alkaline batteries are capable of high current discharges and accidental short circuits should be avoided. Short circuiting can result in significant heat generation, electrolyte boiling, and cell rupture. High voltage cell strings also present an electric shock hazard; therefore tools should be insulated and operators should not wear rings.

Spontaneous low resistance internal short circuits can develop in silver–zinc and nickel–cadmium batteries. In high capacity cells heat generated by such short circuits can result in electrolyte boiling, cell case melting, and cell fires. Therefore cells that exhibit high resistance internal short circuits should not continue to be used. Excessive overcharge that can lead to dry out and short circuits should be avoided.

Because of increasing environmental concerns, the disposal of all batteries is being reviewed (70–76). Traditionally silver batteries were reclaimed for the silver metal and all other alkaline batteries were disposed of in landfills or incinerators. Some aircraft and industrial nickel–cadmium batteries are rebuilt to utilize the valuable components.

To reduce or eliminate the scattering of cadmium in the environment, the disposal of nickel–cadmium batteries is under study. Already a large share of industrial batteries are being reclaimed for the value of their materials. Voluntary battery collection and reclaiming efforts are under way in both Europe and Japan. However the collection of small batteries is not without difficulties. Consideration is being given to deposit approaches to motivate battery returns for collection and reclamation.

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