SECONDARY BATTERIES

Secondary or rechargeable batteries are widely used in many applications. The most familiar are starting, lighting, and ignition (SLI) automotive applications; industrial truck materials handling equipment; and emergency and standby power. Small, secondary batteries are also being used in increasing numbers to power portable devices such as tools, toys, lighting, and photographic, radio, and more significantly, consumer electronic devices (computers, camcorders, cellular phones). More recently, secondary batteries have received renewed interest as a power source for electric and hybrid electric vehicles. Major development programs have been initiated toward improving the performance of existing battery systems and developing new systems to meet the stringent specifications of these new applications.

The applications of secondary batteries fall into two major categories:

1. Those applications in which the secondary battery is used as an energy storage device, being charged by a prime energy source and delivering its energy to the load on demand, when the prime energy source is not available or is inadequate to handle the load requirement. Examples are automotive and aircraft systems, uninterruptible power supplies and standby power sources, and hybrid applications.

2. Those applications in which the secondary battery is discharged (similar in use to a primary battery) and recharged after use, either in the equipment in which it was discharged or separately. Secondary batteries are used in this manner for convenience, for cost savings (as they can be recharged rather than replaced), or for power drains beyond the capability of primary batteries. Most consumer electronics, electric-vehicle, traction, industrial truck, and some stationary battery applications fall in this category.

Conventional aqueous secondary batteries are characterized, in addition to their ability to be recharged, by high power density, flat discharge profiles, and good low-temperature performance. Their energy densities and specific energies, however, are usually lower, and their charge retention is poorer than those of primary battery systems. Rechargeable batteries, such as lithium ion technologies, however, have higher energy densities, better charge retention, and other performance enhancements characterized by the use of higher energy materials. Power density may be adversely affected because of the use of aprotic has been compensated for by using high surface area electrodes. Secondary batteries have been in existence for over 100 years. The lead-acid battery was developed in 1859 by Plante´. It is still the most widely used battery, albeit with many design changes and improvements, with the automotive SLI battery by far the dominant one. The nickel-iron alkaline battery was introduced by Edison in 1908 as a power source for the early electric automobile. It eventually saw service in industrial trucks, underground work vehicles, railway cars, and stationary applications. Its advantages were durability and long life, but it gradually lost its market share because of its high cost, maintenance requirements, and lower specific energy. The pocket-plate nickel-cadmium battery has been manufactured since 1909 and was used primarily for heavy-duty industrial applications. The sintered-plate designs, which led to increased power capability and energy density, opened the market for aircraft engine starting and communications applications during the 1950s. Later the development of the sealed nickel-cadmium battery led to its widespread use in portable and other applications. The dominance of this technology in the portable rechargeable market has been surplanted initially by nickel-metal hydride and more recently by lithium-ion batteries which provide higher specific energy and energy density.

As with the primary battery systems, significant performance improvements have been made with the older secondary battery systems, and a number of newer types, such as the silver-zinc, the nickel-zinc, nickel-hydrogen, and lithium ion batteries, and the high temperature system, have been introduced into commercial use or are under advanced development. Much of the development work on new systems has been supported by the need for high-performance batteries for portable consumer electronic applications and electric vehicles. Figure 1 illustrates the advances achieved in and the projections of the performance of rechargeable batteries for portable applications. The specific energy and energy density of portable rechargeable nickel-cadmium batteries have not improved significantly in the past decade, and now stand at 35 Wh/kg and 100 Wh/L, respectively. Through the use of new hydrogen-storage alloys, improved performance in nickel-metal hydride batteries has been achieved and that system now provides 75 Wh/ kg and 240 Wh/L. A major increase in performance of lithium ion systems was seen in the late 1990s due to the use of carbon materials in the negative electrode with much higher specific capacity. These batteries now provide a specific energy of 150 Wh/kg and an energy density of 400 Wh/L in the small cylindrical sizes employed for consumer electronics applications.

The lithium / lithiated manganese dioxide rechargeable AA cell was withdrawn from the market in the late 1990s and, although significant research and development with lithium metal continue in this field, no products are commercially available at the present time. The worldwide secondary battery market is now approximately $20 billion annually. A world perspective of the use of secondary batteries by application is presented in Table 1. The lead-acid battery is by far the most popular, with the SLI battery accounting for a major share of the market. This share is declining gradually, due to increasing applications for other types of batteries. The market share of the alkaline battery systems is about 25%. A major growth area has been the non-automotive consumer applications for small secondary batteries. Lithium ion batteries have emerged in the last decade to capture a 50% share of the market for small sealed consumer batteries, as indicated in Table 1. The typical characteristics and applications of secondary batteries are summarized in Table 2.

TYPES AND CHARACTERISTICS OF SECONDARY BATTERIES

The important characteristics of secondary or rechargeable batteries are that the charge and discharge the transformation of electric energy to chemical energy and back again to electric energy should proceed nearly reversibly, should be energy efficient, and should have minimal physical changes that can limit cycle life. Chemical action, which may cause deterioration of the cell's components, loss of life, or loss of energy, should be absent, and the cell should possess the usual characteristics desired of a battery such as high specific energy, low resistance, and good performance over a wide temperature range. These requirements limit the number of materials that can be employed successfully in a rechargeable battery system.

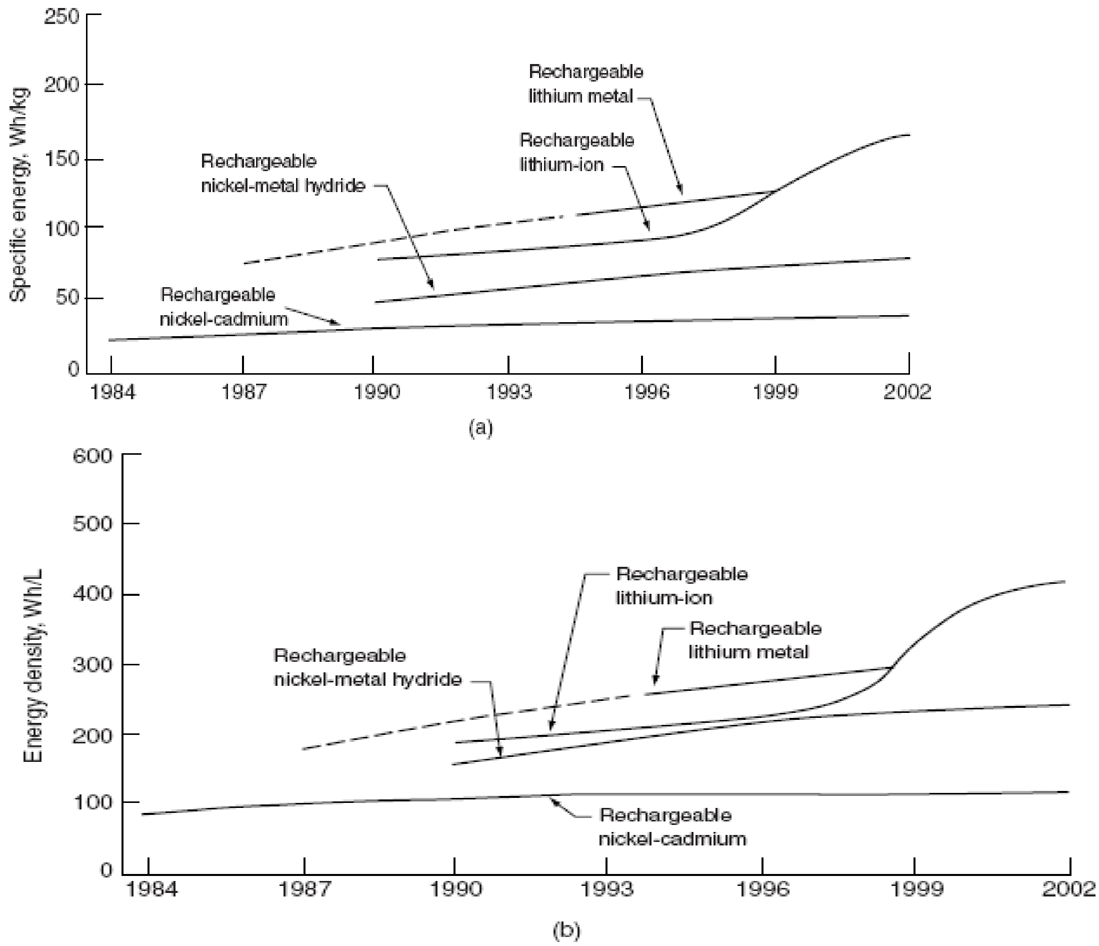


Figure 1: Advances in performance of portable rechargeable batteries. (*a*) Specific energy (Wh/ kg). (*b*) Energy density (Wh/ L).

Table 1: Worldwide Secondary Battery Market at Manufacturers' Prices 1999 (in millions of dollars)*†

Market segment	Battery system		
	Lead-acid	Alkaline	Lithium ion
Vehicle SLI	9600	—	—
Industrial:			
Standby and UPS	1500	400	—
Tractions incl. forklift trucks	1200	200	—
Consumer and instruments, small sealed cells	200	2430	2500
Energy storage			
Solar and load levelling	130	30	—
Military, aircraft, and space, incl. submarines	70	400	—
Vehicular propulsion			
Golf carts	200	—	—
Electric vehicles and hybrid electric vehicles	40	200	—
Total	12,940	3460	2500

* Values do not include complete data from former Soviet Union and China.
† Retail values can be as much as three times manufacturers' prices.

Table 2: Major Characteristics and Applications of Secondary Batteries

System	Characteristics	Applications
Lead-acid:		
Automotive	Popular, low-cost secondary battery, moderate specific-energy, high-rate, and low-temperature performance; maintenance-free designs	Automotive SLI, golf carts, lawn mowers, tractors, aircraft, marine
Traction (motive power)	Designed for deep 6–9 h discharge, cycling service	Industrial trucks, materials handling, electric and hybrid electric vehicles, special types for submarine power
Stationary	Designed for standby float service, long life, VRLA designs	Emergency power, utilities, telephone, UPS, load leveling, energy storage, emergency lighting
Portable	Sealed, maintenance-free, low cost, good float capability, moderate cycle life	Portable tools, small appliances and devices, TV and portable electronic equipment
Nickel-cadmium:		
Industrial and FNC	Good high-rate, low-temperature capability, flat voltage, excellent cycle life	Aircraft batteries, industrial and emergency power applications, communication equipment
Portable	Sealed, maintenance-free, good high-rate low-temperature performance, excellent cycle life	Railroad equipment, consumer electronics, portable tools, pagers, appliances, and photographic equipment, standby power, memory backup
Nickel-metal hydride	Sealed, maintenance-free, higher capacity than nickel-cadmium batteries	Consumer electronics and other portable applications; electric and hybrid electric vehicles
Nickel-iron	Durable, rugged construction, long life, low specific energy	Materials handling, stationary applications, railroad cars
Nickel-zinc	High specific energy, extended cycle life and rate capability	Bicycles, scooters, trolling motors
Silver-zinc	Highest specific energy, very good high-rate capability, low cycle life, high cost	Lightweight portable electronic and other equipment; training targets, drones, submarines, other military equipment, launch vehicles and space probes
Silver-cadmium	High specific energy, good charge retention, moderate cycle life, high cost	Portable equipment requiring a lightweight, high-capacity battery; space satellites
Nickel-hydrogen	Long cycle life under shallow discharge, long life	Primarily for aerospace applications such as LEO and GEO satellites
Ambient-temperature rechargeable ‘‘primary’’ types [Zn/MnO_2]	Low cost, good capacity retention, sealed and maintenance-free, limited cycle life and rate capability	Cylindrical cell applications, rechargeable replacement for zinc-carbon and alkaline primary batteries, consumer electronics (ambient-temperature systems)
Lithium ion	High specific energy and energy density, long cycle life	Portable and consumer electronic equipment, electric vehicles, and space applications

Lead-Acid Batteries

The lead-acid battery system has many of these characteristics. The charge-discharge process is essentially reversible, the system does not suffer from deleterious chemical action, and while its energy density and specific energy are low, the lead-acid battery performs reliably over a wide temperature range. A key factor for its popularity and dominant position is its low cost with good performance and cycle-life.

The lead-acid battery is designed in many configurations, as listed in Table 2, from small sealed cells with a capacity of 1 Ah to large cells, up to 12,000 Ah. The automotive SLI battery is by far the most popular and the one in widest use. Most significant of the advances in SLI battery design are the use of lighter-weight plastic containers, the improvement in shelf life, the ‘‘dry-charge’’ process, and the ‘‘maintenance-free’’ design. The latter, using calcium-lead or low-antimony grids, has greatly reduced water loss during charging (minimizing the need to add water) and has reduced the self-discharge rate so that batteries can be shipped or stored in a wet, charged state for relatively long periods.

The lead-acid industrial storage batteries are generally larger than the SLI batteries, with a stronger, higher-quality construction. Applications of the industrial batteries fall in several categories. The motive power traction types are used in materials-handling trucks, tractors, mining vehicles, and, to a limited extent, golf carts and personnel carriers, although the majority in use are automotive-type batteries. A second category is diesel locomotive engine starting and the rapid-transit batteries, replacing the nickel-iron battery in the latter application. Significant advances are the use of lighter-weight plastic containers in place of the hard-rubber containers, better seals, and changes in the tubular positive-plate designs. Another category is stationary service: telecommunications systems, electric utilities for operating power distribution controls, emergency and standby power systems, uninterruptible power systems (UPS), and in railroads, signaling and car power systems. The industrial batteries use three different types of positive plates: tubular and pasted flat plates for motive power, diesel engine cranking, and stationary applications, and Plante´ designs, forming the active materials from pure lead, mainly in the stationary batteries. The flat-plate batteries use either lead-antimony or lead-calcium grid alloys. A relatively recent development for the telephone industry has been the ‘‘round cell,’’ designed for trouble-free long-life service. This battery uses plates, conical in shape with pure lead grids, which are stacked one above the other in a cylindrical cell container, rather than the normal prismatic structure with flat, parallel plates.

An important development in lead-acid battery technology is the Valve-Regulated Lead-Acid battery (VRLA). These batteries operate on the principle of oxygen recombination, using a ‘‘starved’’ or immobilized electrolyte. The oxygen generated at the positive electrode during charge can, in these battery designs, diffuse to the negative electrode, where it can react, in the presence of sulfuric acid, with the freshly formed lead. The VRLA design reduces gas emission by over 95% as the generation of hydrogen is also suppressed. Oxygen recombination is facilitated by the use of a pressure-relief valve, which is closed during normal operation. When pressure builds up, the valve opens at a predetermined value, venting the gases. The valve reseals before the cell pressure decreases to atmospheric pressure. The VRLA battery is now used in about 70% of the telecommunication batteries and in about 80% of the uninterrupted power source (UPS) applications. Smaller sealed lead-acid cells are used in emergency lighting and similar devices requiring backup power in the event of a utility power failure, portable instruments and tools, and various consumer-type applications. These small sealed lead-acid batteries are constructed in two configurations, prismatic cells with parallel plates, ranging in capacity from 1 to 30 Ah, and cylindrical cells similar in appearance to the popular primary alkaline cells and ranging in capacity up to 25 Ah. The acid electrolyte in these cells is either gelled or absorbed in the plates and in highly porous separators so they can be operated virtually in any position without the danger of leakage. The grids generally are of lead-calcium-tin alloy; some use grids of pure lead or a lead-tin alloy. The cells also include the features for oxygen recombination and are considered to be VRLA batteries.

Lead-acid batteries also are used in other types of applications, such as in submarine service, for reserve power in marine applications, and in areas where engine-generators cannot be used, such as indoors and in mining equipment. New applications, to take advantage of the cost effectiveness of this battery, include load leveling for utilities and solar photovoltaic systems. These applications will require improvements in the energy and power density of the lead-acid battery.

Alkaline Secondary Batteries

Most of the other conventional types of secondary batteries use an aqueous alkaline solution (KOH or NaOH) as the electrolyte. Electrode materials are less reactive with alkaline electrolytes than with acid electrolytes. Furthermore, the charge-discharge mechanism in the alkaline electrolyte involves only the transport of oxygen or hydroxyl ions from one electrode to the other; hence the composition or concentration of the electrolyte does not change during charge and discharge.

Nickel-Cadmium Batteries. The nickel-cadmium secondary battery is the most popular alkaline secondary battery and is available in several cell designs and in a wide range of sizes. The original cell design used the pocket-plate construction. The vented pocket-type cells are very rugged and can withstand both electrical and mechanical abuse. They have very long lives and require little maintenance beyond occasional topping with water. This type of battery is used in heavy-duty industrial applications, such as materials-handling trucks, mining vehicles, railway signaling, emergency or standby power, and diesel engine starting. The sintered-plate construction is a more recent development, having higher energy density. It gives better performance than the pocket-plate type at high discharge rates and low temperatures but is more expensive. It is used in applications, such as aircraft engine starting and communications and electronics equipment, where the lighter weight and superior performance are required. Higher energy and power densities can be obtained by using nickel foam, nickel fiber, or plastic-bonded (pressed-plate) electrodes. The sealed cell is a third design. It uses an oxygen-recombination feature similar to the one used in sealed lead acid batteries to prevent the buildup of pressure caused by gassing during charge. Sealed cells are available in prismatic, button, and cylindrical configurations and are used in consumer and small industrial applications.

Nickel-Iron Batteries. The nickel-iron battery was important from its introduction in 1908 until the 1970s, when it lost its market share to the industrial lead-acid battery. It was used in materials-handling trucks, mining and underground vehicles, railroad and rapid-transit cars, and in stationary applications. The main advantages of the nickel-iron battery, with major cell components of nickel-plated steel, are extremely rugged construction, long life, and durability. Its limitations, namely, low specific energy, poor charge retention, and poor low-temperature performance, and its high cost of manufacture compared with the lead-acid battery led to a decline in usage.

Silver Oxide Batteries. The silver-zinc (zinc / silver oxide) battery is noted for its high energy density, low internal resistance desirable for high-rate discharge, and a flat second discharge plateau. This battery system is useful in applications where high energy density is a prime requisite, such as electronic news gathering equipment, submarine and training target propulsion, and other military and space uses. It is not employed for general storage battery applications because its cost is high, its cycle life and activated life are limited, and its performance at low temperatures falls off more markedly than with other secondary battery systems.
The silver-cadmium (cadmium/ silver oxide) battery has significantly longer cycle life and better low-temperature performance than the silver-zinc battery but is inferior in these characteristics compared with the nickel-cadmium battery. Its energy density, too, is between that of the nickel-cadmium and the silver-zinc batteries. The battery is also very expensive, using two of the more

costly electrode materials. As a result, the silver-cadmium battery was never developed commercially but is used in special applications, such as nonmagnetic batteries and space applications. Other silver battery systems, such as silver-hydrogen and silver-metal hydride couples, have been the subject of development activity but have not reached commercial viability.

Nickel-Zinc Batteries. The nickel-zinc (zinc /nickel oxide) battery has characteristics midway between those of the nickel-cadmium and the silver-zinc battery systems. Its energy density is about twice that of the nickel-cadmium battery, but the cycle life previously has been limited due to the tendency of the zinc electrode toward shape change which reduces capacity and dendrite formations, which cause internal short-circuiting. Recent development work has extended the cycle life of nickel-zinc batteries through the use of additives in the negative electrode in conjunction with the use of a reduced concentration of KOH to repress zinc solubility in the electrolyte. Both of these modifications have extended the cycle life of this system so that it is now being marketed for use in electric bicycles, scooters and trolling motors in the United States and Asia.

Hydrogen Electrode Batteries. Another secondary battery system uses hydrogen for the active negative material (with a fuel-cell-type electrode) and a conventional positive electrode, such as nickel oxide. These batteries are being used exclusively for the aerospace programs which require long cycle life at low depth of discharge. The high cost of these batteries is a disadvantage which limits their application. A further extension is the sealed nickel /metal hydride battery where the hydrogen is absorbed, during charge, by a metal alloy forming a metal hydride. This metal alloy is capable of undergoing a reversible hydrogen absorption-desorption reaction as the battery is charged and discharged respectively. The advantage of this battery is that its specific energy and energy density are significantly higher than that of the nickel-cadmium battery. The sealed nickel-metal hydride battery, manufactured in small prismatic and cylindrical cells, is being used for portable electronic applications and are being employed for other applications including hybrid electric vehicles. Larger sizes are finding use in electric vehicles.

Zinc/Manganese Dioxide Batteries. Several of the conventional primary battery systems have been manufactured as rechargeable batteries, but the only one currently being manufactured is the cylindrical cell using the zinc /alkaline-manganese dioxide chemistry. Its major advantage is a higher capacity than the conventional secondary batteries and a lower initial cost, but its cycle life and rate capability are limited.

Lithium Ion Batteries. Lithium ion batteries have emerged in the last decade to capture over half of the sales value of the secondary consumer market, with applications such as laptop computers, cell phones and camcorders (known as the ‘‘Three-C’’ market). Production capacity has recently been estimated to be 75 million / cells per month, These cells provide high energy density and specific energy (see Figure 1) and long cycle life, typically greater than 1000 cycles @ 80% depth of discharge. When built into batteries, battery management circuitry is required to prevent over charge and over discharge, both of which are deleterious to performance. The circuits may also provide an indication of state-of-charge and safety features in the case of an over-current or an over-heating condition.

COMPARISON OF PERFORMANCE CHARACTERISTICS FOR SECONDARY BATTERY SYSTEMS

The characteristics of the major secondary systems are summarized in Table 3. It should be noted that these types of data and comparisons as well as the performance characteristics are necessarily approximations, with each system being presented under favorable discharge conditions. The specific performance of a battery system is very dependent on the cell design and all the detailed and specific conditions of the use and discharge-charge of the battery. A qualitative comparison of the various secondary battery systems is presented in Table 4. The different ratings given to the various designs of the same electrochemical system are an indication of the effects of the design on the performance characteristics of a battery.

Voltage and Discharge Profiles

The discharge curves of the conventional secondary battery systems, at the *C*/5 rate, are compared in Figure 2. The lead-acid battery has the highest cell voltage of the aqueous systems. The average voltage of the alkaline systems ranges from about 1.65 V for the nickel-zinc system to about 1.1 V. At the *C*/5 discharge rate at 20^{o}C there is relatively little difference in the shape of the discharge curve for the various designs of a given system. However, at higher discharge rates and at lower temperatures, these differences could be significant, depending mainly on the internal resistance of the cell. Most of the conventional rechargeable battery systems have a flat discharge profile, except for the silver oxide systems, which show the double plateau due to the two-stage discharge of the silver oxide electrode, and the rechargeable zinc /manganese dioxide battery. The discharge curve of a lithium ion battery, the carbon/ lithiated cobalt oxide system, is shown for comparison. The cell voltages of the lithium ion batteries are higher than those of the conventional aqueous cells because of the characteristics of these systems. The discharge profile of the lithium ion batteries are usually not as flat due to the lower conductivity of the nonaqueous electrolytes that must be used and to the thermodynamics of intercalation electrode reactions. The average discharge voltage for a lithium ion cell is 3.6 V, which allows one unit to replace three Nicad or NiMH cells in a battery configuration.

Effect of Discharge Rate on Performance

The effects of the discharge rate on the performance of these secondary battery systems are compared again in Figure 3. This figure is similar to a Ragone plot, except that the abscissa is expressed in hours of service instead of specific energy (Wh/ kg). This figure shows that hours of service each battery type (unitized to 1 kg battery weight) will deliver at various power (discharge current *x* midpoint voltage) levels. The higher slope is indicative of superior retention of capacity with increasing discharge load. The specific energy can be calculated by the following equation:

$$\text{specific energy} = \text{specific power} \times \text{hours of service}$$

or

$$\text{Wh/kg} = \text{W/kg} \times \text{h} = \frac{\text{A} \times \text{V} \times \text{h}}{\text{kg}}$$

Table 3: Characteristics of the Major Secondary Battery Systems

	Lead-acid				Nickel-cadmium			
Common name	SLI	Traction	Stationary	Portable	Vented pocket plate	Vented sintered plate	Sealed	FNC
Chemistry: Anode Cathode Electrolyte	Pb PbO_2 H_2SO_4 (aqueous solution)	Pb PbO_2 H_2SO_4 (aqueous solution)	Pb PbO_2 H_2SO_4 (aqueous solution)	Pb PbO_2 H_2SO_4 (aqueous solution)	Cd NiOOH KOH (aqueous solution)	Cd NiOOH KOH (aqueous solution)	Cd NiOOH KOH (aqueous solution)	Cd NiOOH KOH (aqueous solution)
Cell voltage (typical), V: Nominal Open circuit Operating End	2.0 2.1 2.0–1.8 1.75 (lower operating and end voltage during cranking operation)	2.0 2.1 2.0–1.8 1.75	2.0 2.1 2.0–1.8 1.75 (except when on float service)	2.0 2.1 2.0–1.8 1.75 (where cycled)	1.2 1.29 1.25–1.00 1.0	1.2 1.29 1.25–1.00 1.0	1.2 1.29 1.25–1.00 1.0	1.2 1.35 1.25–0.85 1.00–0.65
Operating temperatures, °C	−40 to 55	−20 to 40	−10 to 40[c]	−40 to 60	−20 to 45	−40 to 50	−40 to 45	−50 to 60
Specific energy and energy density (at 20°C) Wh/kg Wh/L	35 70	25 80	10–20 50–70	30 90	20 40	30–37 58–96	35 100	10–40 15–80
Discharge profile (relative)	Flat	Flat	Flat	Flat	Flat	Very flat	Very flat	Flat
Power density	High	Moderately high	Moderately high	High	High	High	Moderate to high	Very high
Self-discharge rate (at 20°C), % loss per month[b]	20–30 (Sb-Pb) 2–3 (maintenance-free)	4–6	—	4–8	5	10	15–20	10–15
Calendar life, years	3–6	6	18–25	2–8	8–25	3–10	2–5	5–20
Cycle life, cycles[c]	200–700	1500	—	250–500	500–2000	500–2000	300–700	500–10,000
Advantages	Low cost, ready availability, good high-rate, high- and low-temperature operation (good cranking service), good float service, new maintenance-free designs	Lowest cost of competitive systems (also see SLI)	Designed for "float" service lowest cost of competitive systems (also see SLI)	Maintenance-free: long life on float service; low- and high-temperature performance; no "memory" effect; operates in any position	Very rugged, can withstand physical and electrical abuse; good charge retention, storage and cycle life lowest cost of alkaline batteries	Rugged; excellent storage; good specific energy and high-rate and low-temperature performance	Sealed, no maintenance, good low-temperature and high-rate performance; long life cycle; operates in any position	Sealed, no maintenance, high power capability even at low temperature, long cycle life at low depth of discharge, fast charging
Limitations	Relatively low cycle life; limited energy density; poor charge retention and storability; hydrogen evolution	Low energy density; less rugged than competitive systems; hydrogen evolution	Hydrogen evolution	Cannot be stored in discharged condition; lower cycle life than sealed nickel-cadmium; difficult to manufacture in very small sizes	Low energy density	High cost; "memory" effect; thermal runaway problem	Sealed lead-acid battery better at high temperature and float service, "memory" effect	Lower energy density than sintered plate design
Major battery types available	Prismatic cells; 30–200 Ah at 20-h rate	Based on positive plate designs; 45–200 Ah per positive plate	Based on positive plate design: 5–400 Ah per positive to 1440 Ah plate	Sealed cylindrical cells; 2.5–25 Ah; prismatic cells; to 1440 Ah	Prismatic cells; 5–1300 Ah	Prismatic cells; 1.5–100 Ah	Button cells to 0.5 Ah; cylindrical cells to 10 Ah	Prismatic designs to 450 Ah

[a] Based on $C/LiCoO_2$ lithium-ion battery (see Chap. 35) (characteristics vary with battery system and design).
[b] Self-discharge rate usually decreases with increasing storage time.
[c] Dependent on depth of discharge.
[d] High rate Zn/AgO battery.
[e] Low rate Zn/AgO battery.

Common name	Nickel-iron (conventional)	Nickel-zinc	Zinc/silver oxide (silver-zinc)	Cadmium/silver oxide (silver-cadmium)	Nickel-hydrogen	Nickel-metal hydride	Rechargeable "primary" types, Zn/MnO_2	Lithium ion systems[a]
Chemistry: Anode Cathode Electrolyte	Fe NiOOH KOH (aqueous solution)	Zn NiOOH KOH (aqueous solution)	Zn AgO KOH (aqueous solution)	Cd AgO KOH (aqueous solution)	H_2 NiOOH KOH (aqueous solution)	MH NiOOH KOH (aqueous solution)	Zn MnO_2 KOH (aqueous solution)	C $LiCoO_2$ Organic solvent
Cell voltage (typical), V: Nominal Open circuit Operating End	1.2 1.37 1.25–1.05 1.0	1.65 1.73 1.6–1.4 1.2	1.5 1.86 1.7–1.3 1.0	1.1 1.41 1.4–1.0 0.7	1.4 1.32 1.3–1.15 1.0	1.2 1.4 1.25–1.10 1.0	1.5 1.5 1.3–1.0 1.0	4.0 4.1 4.0–3.0 3.0
Operating temperatures, °C	−10 to 45	−10 to 50	−20 to 60	−25 to 70	0 to 50	−20 to 50	−20 to 40	−20 to 50
Specific energy and energy density (at 20°C) Wh/kg Wh/L	30 55	50–60 80–120	105[d] 180	70 120	64 (CPV) 105 (CPV)	75 240	85 250	150 400
Discharge profile (relative)	Moderately flat	Flat	Double plateau	Double plateau	Moderately flat	Flat	Sloping	Sloping
Power density	Moderate to low	High	Very high (for high rate-design)	Moderate to high	Moderate	Moderate to high	Moderate	Moderate; high in prismatic designs
Self-discharge rate (at 20°C), % loss per month[b]	20–40	<20	5	5	Very high except at low temp.	15–25		2
Calendar life, years	8–25	—	2	3 (vented) 4 (sealed)	—	2–5		
Cycle life, cycles[c]	2000–4000	500	50–100	300–800	1500–6000 40,000 at 40% (DOD)	300–600	15–25	1000+
Advantages	Very rugged, can withstand physical and electrical abuse; long life (cycling or stand)	High energy density; relatively low cost; good low-temperature performance	High energy density; high discharge rate; low self-discharge	High-energy density; low self-discharge, good cycle life	High energy density; long cycle life at low DOD; can tolerate overcharge	High energy density; sealed, good cycle life	Good shelf life; low cost	High specific energy and energy density; low self-discharge; long cycle life
Limitations	Low power and energy density; high self-discharge; hydrogen evolution; high cost and high maintenance cost	Improved cycle life at reduced specific energy	High cost; low cycle life; decreased performances at low temperatures	High cost; decreased performance at low temperatures	High initial cost; self-discharge proportional to H_2 pressure and temperature	Intermediate in cost between NiCad and Li Ion	Limited cycle life; low drain applications; small size only	Lower rate (compared to aqueous systems)
Major battery types available	Decreasing significance in developed countries	In production for electric bicycles and scooters and trolling motors 2–100 Ah sizes	Prismatic cells <1 to 1000 Ah; special types to 5000 Ah	Prismatic cells <1 to 1000 Ah	Aerospace applications (up to 100 Ah)	Button and cylindrical cells to 4.1 Ah, large prismatics to 100 Ah	Cylindrical cells to 10 Ah	Cylindrical and prismatic cells to 100 Ah

Table 4: Comparison of Secondary Batteries*

System	Energy density	Power density	Flat discharge profile	Low-temp-erature operation	Charge retention	Charge acceptance	Effic-iency	Life	Mech-anical prop-erties	Cost
Lead-acid:										
Pasted	4	4	3	3	4	3	2	3	5	1
Tubular	4	5	4	3	3	3	2	2	3	2
Planté	5	5	4	3	3	3	2	2	4	2
Sealed	4	3	3	2	3	3	2	3	5	2
Lithium-metal	1	3	3	2	1	3	3	4	3	4
Lithium-ion	1	2	3	2	2	1	1	1	3	2
Nickel-cadmium:										
Pocket	5	3	2	1	2	1	4	2	1	3
Sintered	4	1	1	1	4	1	3	2	1	3
Sealed	4	1	2	1	4	2	3	3	2	2
Nickel-iron	5	5	4	5	5	2	5	1	1	3
Nickel-metal hydride	3	2	2	2	4	2	3	3	2	3
Nickel-zinc	2	3	2	3	4	3	3	4	3	3
Silver-zinc	1	1	4	3	1	3	2	5	2	4
Silver-cadmium	2	3	5	4	1	5	1	4	3	4
Nickel-hydrogen	2	3	3	4	5	3	5	2	3	5
Silver-hydrogen	2	3	4	4	5	3	5	2	3	5
Zinc-manganese dioxide	2	4	5	3	1	4	4	5	4	2

*Rating: 1 to 5, best to poorest.

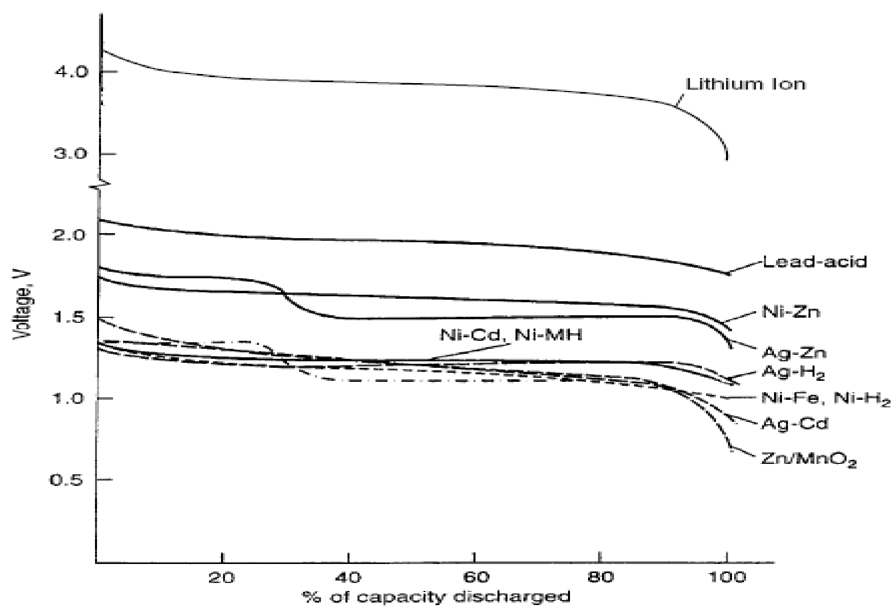


Figure 2: Discharge profiles of conventional secondary battery systems and rechargeable lithium ion battery at approximately *C*/ 5 discharge rate.

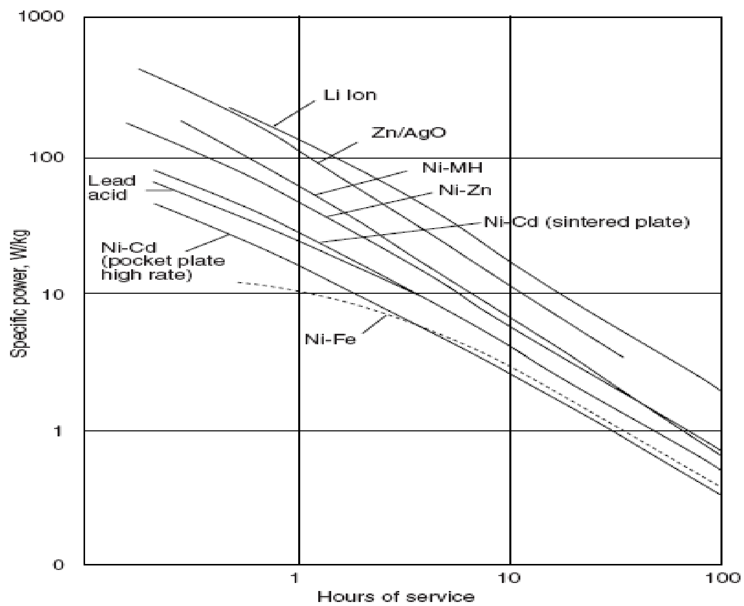


Figure 3: Comparison of performance of secondary battery systems at 20^{o}C.

Figure 4 is a Ragone plot on a semi-log scale comparing the performance of the nickel-cadmium and sealed nickel-metal hydride in AA size and the new lithium ion battery in a 14500 cylindrical configuration, on a gravimetric and volumetric basis at 20^{o}C.

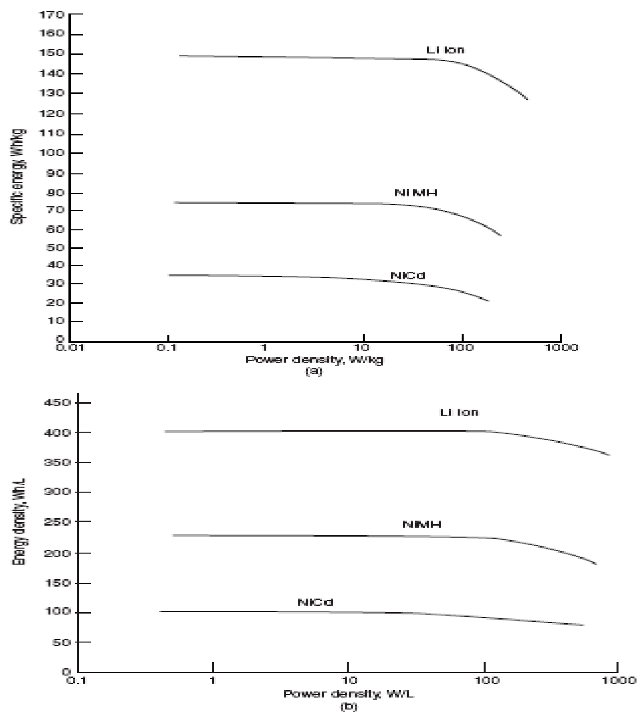


Figure 4: Comparison of rechargeable 14500 Li ion and AA-size NiMH and NiCd batteries at 20^{o}C. (*a*) Specific energy vs. power density. (*b*) Energy density vs. power density.

Effect of Temperature

The performance of the various secondary batteries over a wide temperature range is shown in Figure 5 on a gravimetric basis. In this figure, the specific energy for each battery system is plotted from -40 to 60^oC at about the *C*/5 discharge rate. The lithium ion system has the highest energy density to -20^oC. The sintered-plate nickel-cadmium and nickel-metal hydride batteries show higher percentage retention. In general the low-temperature performance of the alkaline batteries is better than the performance of the lead-acid batteries, again with the exception of the nickel-iron system. The lead-acid system shows better characteristics at the higher temperatures. These data are necessarily generalized for the purposes of comparison and present each system under favorable discharge conditions. Performance is strongly influenced by the specific discharge conditions.

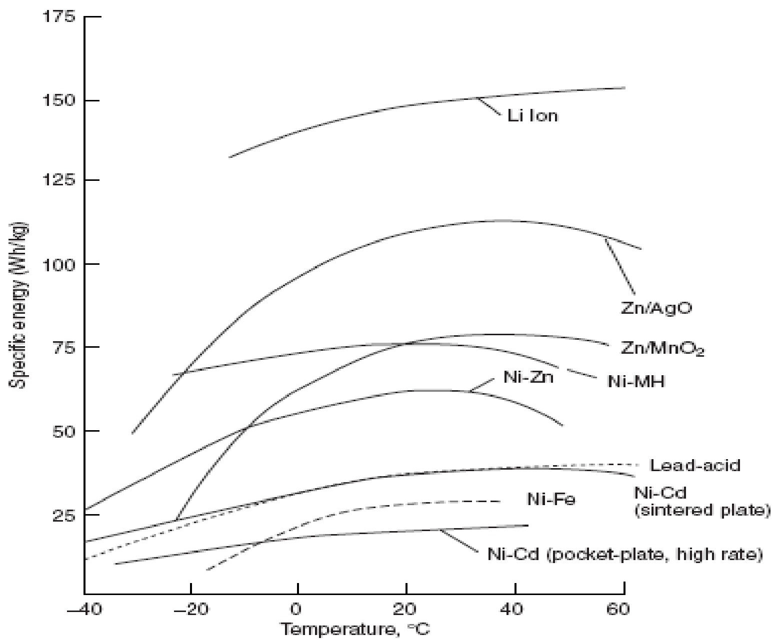


Figure 5: Effect of temperature on specific energy of secondary battery systems at approximately *C*/ 5 discharge rate.

Charge Retention

The charge retention of most of the conventional secondary batteries is poor compared with that of primary battery systems. Normally, secondary batteries are recharged on a periodic basis or maintained on ‘‘float’’ charge if they are to be in a state of readiness. Most alkaline secondary batteries, especially the nickel oxide batteries, can be stored for long periods of time even in a discharged state without permanent damage and can be recharged when required for use. The lead-acid batteries, however, cannot be stored in a discharged state because sulfation of the plates, which is detrimental to battery performance, will occur.

Figure 6 shows the charge retention properties of several different secondary battery systems. These data are also generalized for the purpose of comparison. There are wide variations of performance depending on design and many other factors, with the variability increasing with

increasing storage temperature. Typically, the rate of loss of capacity decreases with increasing storage time.
The silver secondary batteries, the Zn/MnO_2 rechargeable battery, and lithium-ion systems have the best charge retention characteristics of the secondary battery systems with typical lithium ion batteries, self discharge is typically 2% per month at ambient temperature. Low-rate silver cells may lose as little at 10 to 20% per year, but the loss with high-rate cells with large surface areas could be 5 to 10 times higher. The vented pocket- and sintered plate nickel-cadmium batteries and the nickel-zinc systems are next; the sealed cells and the nickel-iron batteries have the poorest charge retention properties of the alkaline systems.

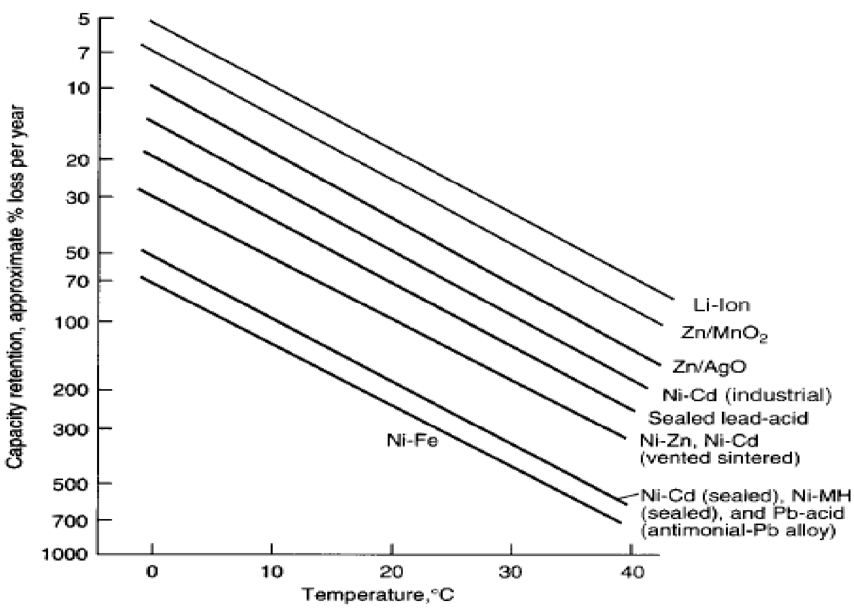


Figure 6: Capacity retention of secondary battery systems.

The charge retention of the lead-acid batteries is dependent on the design, electrolyte concentration, and formulation of the grid alloy as well as other factors. The charge retention of the standard automotive SLI batteries, using the standard antimonial-lead grid, is poor, and these batteries have little capacity remaining after six-months' storage at room temperature. The low antimonial-lead designs and the maintenance-free batteries have much better charge retention with losses on the order of 20 to 40% per year. One of the potential advantages of the lithium metal rechargeable batteries is their good charge retention which, in many cases, should be similar to the charge retention characteristics of the lithium primary batteries.

Life

The cycle life and calendar life of the different secondary battery systems are also listed in Table 3. Again, these data are approximate because specific performance is dependent on the particular design and the conditions under which the battery is used. The depth of discharge (DOD), for example, as illustrated in Figure 7, and the charging regime strongly influences the battery's life.
Of the conventional secondary systems, the nickel-iron and the vented pocket-type nickel-cadmium batteries are best with regard to cycle life and total lifetime. The nickel-hydrogen battery developed mainly for aerospace applications, has demonstrated very long cycle life under

shallow depth of discharge. The lead-acid batteries do not match the performance of the best alkaline batteries. The pasted cells have the shortest life of the lead-acid cells; the best cycle life is obtained with the tubular design, and the Plante´ design has the best lifetime. One of the disadvantages of using zinc, lithium, and other metals with high negative standard potentials in rechargeable batteries is the difficulty of successful recharging and obtaining good cycle and calendar lives. The nickel-zinc battery has recently been improved to provide extended cycle life as seen in Figure 7. The lithium-ion system, however, has also been shown to have good cycle life.

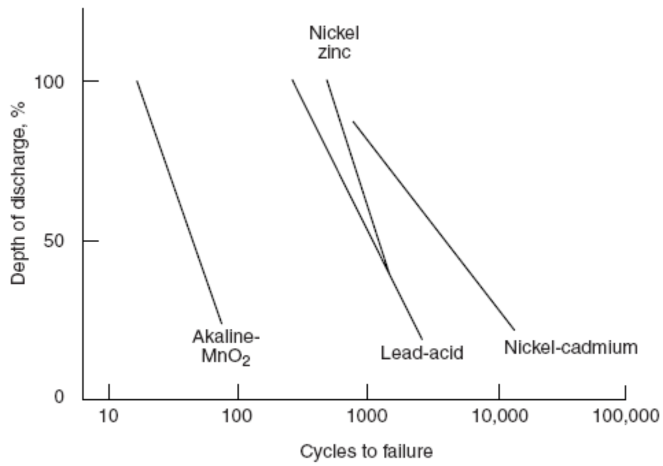
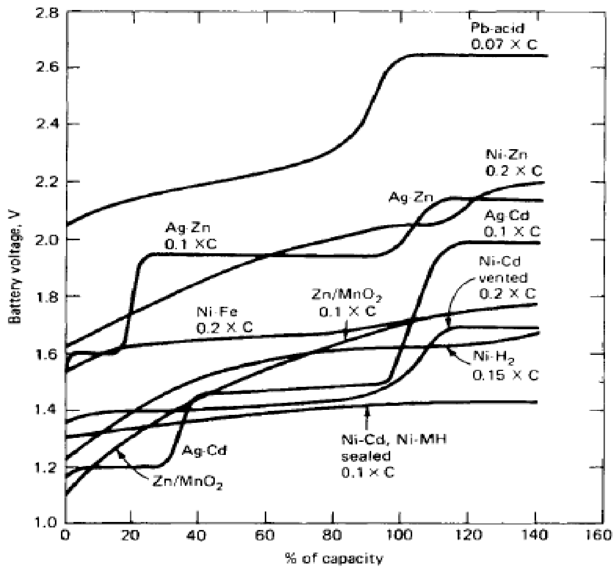


Figure 7: Effect of depth of discharge on cycle life of secondary battery systems.

Charge Characteristics

The typical charge curves of the various secondary aqueous-systems at normal constant current charge rates are shown in Figure 8. Most of the batteries can be charged under constant-current conditions, which is usually the preferred method of charging, although, in practice, constant-voltage or modified constant-voltage methods are used. Some of the sealed batteries, however, may not be charged by constant-voltage methods because of the possibility of thermal runaway. Generally the vented nickel-cadmium battery has the most favorable charge properties and can be charged by a number of methods and in a short time. These batteries can be charged over a wide temperature range and can be overcharged to some degree without damage. Nickel-iron batteries, sealed nickel-cadmium batteries, and sealed nickel /metal hydride batteries have good charge characteristics, but the temperature range is narrower for these systems. The nickel /metal hydride battery is more sensitive to overcharge, and charge control to prevent overheating is advisable. The lead-acid battery also has good charge characteristics, but care must be taken to prevent excessive overcharging.

The zinc /manganese dioxide and zinc / silver oxide batteries are most sensitive with regard to charging; overcharging is very detrimental to battery life. Figure 9 shows typical constant current–constant voltage charging characteristics of an 18650 lithium ion battery. Table 5 summarizes the typical conditions for charging the different systems.



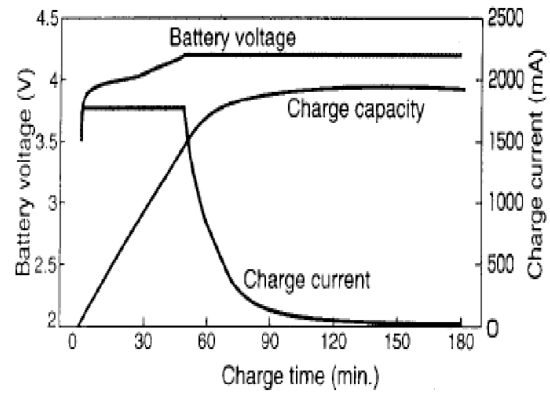


Figure 8: Typical charge characteristics of secondary battery systems, constant-current charge at 20^{o}C.

Figure 9: Charging characteristics of a typical cylindrical 18650 lithium ion battery at 20^{o}C.

Table 5: Charging Characteristics of Secondary Batteries

System	Charged methods*		Recommended constant-current charge rate, C (A)	Over-charge-ability	Temperature range for charging, °C	Efficiencies†	
	Preferred	Not recommended				Ah, %	Wh, %
Lithium ion	cc, cv		0.20	None	−20 to 50	99	95
Lead-acid							
Pasted, Planté	cc, cv		0.07	Fair	−40 to 50	90	75
Tubular	cc, cv		0.07	Fair	−40 to 50	80	70
Nickel-cadmium:							
Industrial vented	cc, cv		0.2	Very good	−50 to 40	70	60
Sintered vented	cc, cv		0.2	Very good	−55 to 75	70–80	60–70
Sealed	cc	cv	0.1–0.3‡	Very good	0 to 40	65–70	55–65
Nickel/metal hydride	cc	cv	0.1‡	Fair	0 to 40	65–70	55–65
Nickel-iron	cc	cv	0.2	Very good	0 to 45	80	60
Nickel-zinc	cc, cv		0.1–0.4	Fair	−20 to 40	85	70
Silver-zinc	cc		0.05–0.1	Poor	0 to 50	90	75
Silver-cadmium	cc		0.01–0.2	Fair	−40 to 50	90	70
Zn/MnO_2	cv	cc w/o v. limit		Fair	10–30		55–65

*Constant current (cc) includes two-rate charging, and constant voltage (cv) includes modified constant-voltage charging.
†All data are related to normal rates of charge and discharge and room-temperature operation.
‡Fast charge procedures can be used with charge control.

Many manufacturers are now recommending ‘‘fast’’ charge methods to meet consumer and application demand for recharging in less than 2 to 3 h. These methods require control to cut off the charge before an excessive rise in gassing, pressure, or temperature occurs. These could cause venting or a more serious safety hazard, or they could result in a deleterious effect on the battery’s performance or life. Pulse charging is also being employed with some systems to provide higher charge rates. In general, control techniques are useful for recharging most secondary batteries. They can be employed in several ways: to prevent overcharging, to facilitate ‘‘fast’’ charging, to sense when a potentially deleterious or unsafe condition may arise and cut off the charge or reduce the charging rate to safe levels. Similarly, discharge controls are also being used to maintain cell balance and to prevent overdischarge.

Another approach is the ‘‘smart’’ battery. These batteries incorporate features:

1. To control the charge so that the battery can be charged optimally and safely

2. For fuel gauging to indicate the remaining charge left in the battery

3. Safety devices to alert the user to unsafe or undesirable operation or to cut off the battery from the circuit when these occur.

Cost

The cost of a secondary battery may be evaluated on several bases, depending on the mode of operation. The initial cost is one of the bases for consideration. Other factors are the number of charge-discharge cycles that are available, or the number delivered in an application, during a battery’s lifetime, or the cost determined on a dollar-per-cycle or dollar per total kilowatt-hour basis. The cost of charging, maintenance, and associated equipment may also have to be considered in this evaluation.. In an emergency standby service or SLI-type application, the important factors may be the calendar life of the battery (rather than as cycle life) and the cost is evaluated on a dollar-per-operating-year basis.

The lead-acid battery system is by far the least costly of the secondary batteries, particularly the SLI type. The lead-acid traction and stationary batteries, having more expensive constructional features and not as broad a production base, are several times more costly, but are still less expensive than the other secondary batteries. The nickel-cadmium and the rechargeable zinc /manganese dioxide batteries are next lowest in cost, followed by the nickel /metal hydride battery. The cost is very dependent on the cell size or capacity, the smaller button cells being considerably more expensive than the larger cylindrical and prismatic cells. The nickel-iron battery is more expensive and, for this reason among others, lost out to the less expensive battery system.

The most expensive of the conventional-type secondary batteries are the silver batteries. Their higher cost and low cycle life have limited their use to special applications, mostly in the military and space applications, which require their high energy density. The nickel-hydrogen system is more expensive due to its pressurized design and a relatively limited production. However, their excellent cycle life under conditions of shallow discharge make them attractive for aerospace applications. The cost of cylindrical lithium ion batteries has been decreasing rapidly as production rates have increased and has recently been stated to be $1.22/Wh.

An important objective of the program for the development of secondary batteries for electric vehicles and energy storage is to reduce the cost of these battery systems.