

Recent Developments in Batteries for Portable Consumer Electronics Applications

by Ralph J. Brodd

The engine that powers the growth in batteries, especially primary and small rechargeable varieties, has been, and will continue to be, the proliferation of portable electronic devices

that find use in our daily lives. The worldwide battery market in 1997 was about \$34 billion of which the primary market segment was about \$10 billion. The growth in primary batteries has closely followed the increased use of "boom" boxes, Walkman portable cassette and disc players, and the like.

The worldwide rechargeable market segment in 1997 was about \$24 billion with lead acid accounting for over half of this value. The double-digit growth of small rechargeable cells has paralleled the spectacular growth of cellular phones and laptop computers. These devices demanded greater performance than was available from rechargeable nickel cadmium (Ni-Cd) and alkaline primary cells. In response to this demand and the environmental pressure on Ni-Cd, the lithium-ion (Li-ion) and nickel metal hydride (Ni-MH) rechargeable battery systems have been developed. Figure 1 depicts the growth in the rechargeable market and the shift from Ni-Cd to Li-ion and Ni-MH. The market for Ni-Cd has remained fairly constant while Ni-MH and Li-ion have supplied the growth. In 1997, the sales value of the Li-ion surpassed that of Ni-Cd although

the production volume was lower. This is a remarkable growth rate for a new battery system. The alkaline primary battery was introduced in about 1960 and it took over 15 years to equal the sales

medium drain applications but lack the high current capability, shelf life, and leakage resistance of the alkaline cell. Worldwide, there were about 15 billion carbon-zinc cells produced in 1998. In

the U.S., there has been a shift away from the traditional carbon zinc (Zn-MnO₂ with NH₄Cl or ZnCl₂ electrolyte) dry cell constructions to the higher performance alkaline (Zn-MnO₂ with KOH electrolyte) cells. Both the Leclanché and zinc chloride are now imported into the U.S. (the last major producer of carbon zinc in the U.S. has just discontinued production). This shift to alkaline cells has been slower to occur in Europe and Japan

where the consumer is more conscious of the cost-performance ratio.

Alkaline cells now dominate the U.S. market for primary cells with the U.S. producers setting the standard for quality and performance. There has been a shift in product mix away from the larger D- and C-cells to the smaller AA- and AAA-size cells. Strong competition has led the major producers to institute significant service improvements to meet the competition. Service life has increased over 30% compared to 10 years ago. The high current pulse capability has also been improved. These improvements were accomplished by a major redesign of the internal structure and composition of the components of the alkaline cell. The

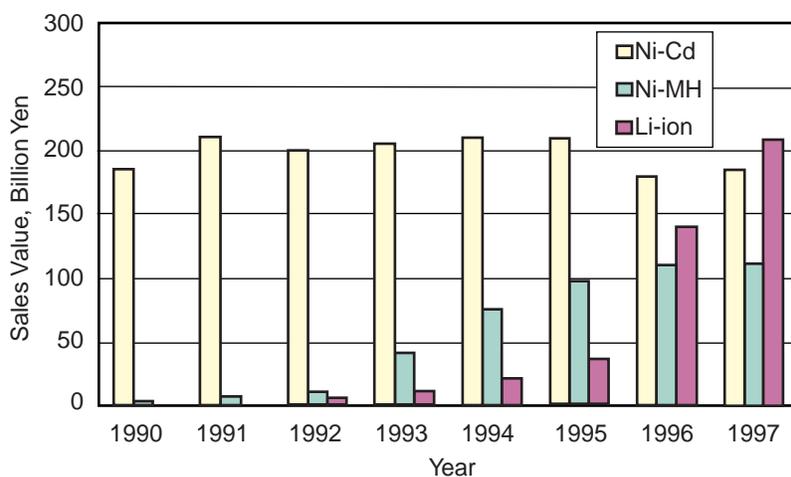


FIG. 1. Growth of the small rechargeable cell market segment. H. Takeshita, Proceedings of Power '98, Giga Information Group and Arthur D. Little, Santa Clara CA, October 4-6, 1998.

value of the carbon-zinc in the U.S. Japan dominates the production of the rechargeable cells and sets the standard for quality and performance.

Primary Batteries

Figure 2 illustrates the energy storage capability of the common primary battery. Since the energy delivered by a battery varies depending on the design, current drain, temperature, etc., the energy storage capability in Fig. 2 is depicted as a field, rather than the single "best" value, to illustrate the variation in performance in its area of application. The carbon zinc cells, both Leclanché and zinc chloride versions, are more cost effective for low to

outside label has remained intact so the public perception is that little change has occurred over the past ten years.

The three major components of the alkaline cell—the anode, cathode, and separator—all have undergone significant changes. The specifications of the composition of the manganese dioxide cathode active material now require control of critical impurities to less than parts-per-million level with improved current carrying capability. The internal structure of the cathode active mass has been modified to improve the diffusion into the mass and to increase the surface area for better performance at high currents. New zinc powder anode compositions have eliminated mercury. Other zinc alloying agents and added organic corrosion inhibitors provide the control of zinc corrosion (hydrogen gas generation) to essentially the same levels as when mercury was the main corrosion inhibitor. The particle size distribution of the zinc powders has also changed. The composition and stability of the KOH gelling agents, which hold the zinc powders in the anode compartment, has also been modified. Although the basic overall manufacturing processes for the new cells are the same, these changes in materials and internal construction have required extensive modifications to the unit manufacturing processes. The state of charge indicator on the label of alkaline cells, that was introduced as a marketing feature, will likely be removed in the future. It is inaccurate and of questionable usefulness to the average consumer. Also, when activated, it discharges the cell and lowers the service life.

The zinc-air (Zn-air) button cell has the highest energy storage capability of all consumer cells. It has captured almost 95% of the hearing aid market. Zn-air cells have twice the capacity of the same size zinc-silver button cells. A new construction concept described in U.S. Patent 5,691,074 restricts airflow to the oxygen electrode. New constructions, based on this development, could open the way to commercialize Zn-air cells in cylindrical format or in battery pack construc-

tions. Mercury cells have been phased out from consumer applications. Only a few highly specialized medical and military applications still use the mercury cell to power the devices.

Lithium metal anode primary cells have high energy storage capability but lack high power capability. The thin (4-

wrap constructions of the lithium manganese dioxide (Li-MnO₂) and lithium carbon monofluoride (Li-CF_x) cell systems have captured the camera market while coin cells service the memory protection applications. Both Li-MnO₂ and Li-CF_x coin cells are widely used as memory protection in CMOS circuitry applications. Electrolyte modifications have improved the high temperature performance in response to higher operating temperatures found in the newer high performance devices. The thin postage stamp sized lithium cells have found a niche market in security cards, but their envisioned use in powered "smart cards" has not yet occurred.

The Li-FeS₂ AA-size cell has been developed for photoflash applications. This system was originally developed to provide a low cost alternate to silver-zinc cells. Although the lithium metal anodes do not have good high current capability, the combination of thin electrodes with large geometric surface area, combined with an innovative opposite-end current collection, yields a cell design with very uniform current distribution. This gives the cell excellent pulse capability. The fact that the cathode decreases in resistance during discharge gives the cell low internal resistance and uniform fast response, even to the end of the service life.

Rechargeable Cells

Rechargeable batteries can be discharged and then restored to their original condition for reuse. The energy storage capability of the common rechargeable cells is shown in Fig. 3. A rule-of-thumb states that a cell should be capable of delivering 300 complete discharge-charge cycles to 80% of its original capacity for it to be classified as a rechargeable battery system. In the past, the energy storage capability of rechargeable cells was significantly lower than that of primary cells. The advantage of the rechargeable batteries is their high current capability and their ability to accept recharging to restore their capacity to the original level. For the first time, the energy

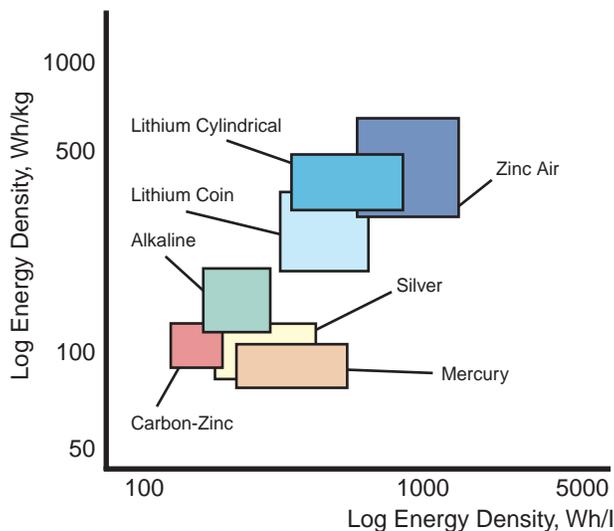


FIG. 2. Comparison of the energy storage capability of various primary battery systems. Please note the different scales in Figures 2 and 3.

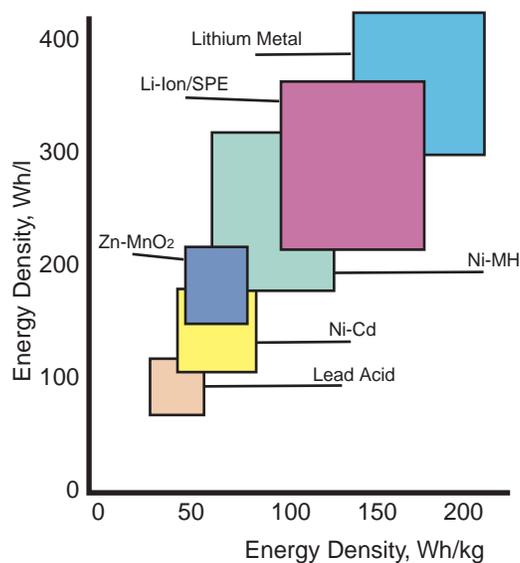


FIG. 3. Comparison of the energy storage capability of various rechargeable battery systems. Please note the different scales in Figs. 2 and 3.

8 Å) protective film that forms on the lithium surface by reaction with cell electrolyte results in a low exchange current density. As a result, although they have higher energy storage potential, lithium cells have not replaced alkaline cells for most applications. Lithium anode cells now provide the power for most camera and memory protect applications. Wound or spiral

storage capability of rechargeable batteries is almost equal to that of primary cells. The newer rechargeable Li-ion and Ni-MH systems have nearly the same volumetric energy storage capability as that of alkaline cells. The Li-ion cell is inherently lighter. The recycling of rechargeable batteries makes them even more environmentally friendly.

The rechargeable alkaline Zn-MnO₂ reappeared as the Renewal® brand in the U.S. The internal structure and design of the primary alkaline cell has been modified at the cost of capacity to produce the rechargeable version. It offers a low cost alternative to other rechargeable systems. It also has lower cycle life than the industry standard.

For many years the Ni-Cd was the major small rechargeable cell system. It used a simple charger and had better cycle life and high rate performance than the lead acid system. Since it is more costly than lead acid, it has found wide use only in the smaller spiral wound constructions. The Ni-Cd has a designed-in overcharge and overdischarge protection system based on a chemical shuttle mechanism. It is very robust and can tolerate abuse conditions. It can be stored in a discharged condition without serious damage.

The Ni-MH system was developed as an alternative to the Ni-Cd. The environmentally threatened cadmium negative electrode in Ni-Cd was replaced by a hydrogen absorbing alloy negative electrode. The voltage of the two systems is essentially the same. The change in chemistry allowed a new internal cell balance with significantly increased energy storage capability. New, high density, spherical nickel oxide cathode materials, coupled with non-woven nickel fiber current collectors, have significantly improved the performance of the nickel electrode for both Ni-Cd and Ni-MH. The same simple charging systems can be used with minor modifications for either system.

The hydrogen absorbing alloys used in the Ni-MH cells are based on two different alloy systems. One, termed AB₅, is based on misch metal alloys and the other, termed AB₂, is based on transition metal alloys. Both alloy systems contain numerous components to improve hydrogen storage, corrosion, structural stability, etc. Competition is strong and manufacturers have steadily increased the cell capacity as manufacturing and design improvements are instituted. It is estimated that the Ni-MH can deliver almost 400

Wh/l and 200 Wh/kg in the future. Considerable effort is being devoted to develop the Ni-MH for use in electric vehicles.

The Li-ion battery system, first introduced by Sony in 1991, has enjoyed spectacular growth as noted in Fig. 1. Li-ion has been termed a "rocking chair" or "swing" battery system since the cell reactions essentially transport lithium ions from one electrode to the other and back again. During charge, the lithium ions from the lithium cobalt oxide (LiCoO₂) cathode active mass intercalate into the crystal structure of the carbon/graphite negative active materials. On discharge, the ions reverse direction, leave the carbon and re-enter the cathode structure. Although Li-ion is used to designate the cell chemistry, there is no lithium metal in the cell. Lithium refers to the Li⁺ ions intercalated into the crystal structure of the carbon and cobalt oxide active materials and the ions of the electrolyte that transport current during cell operation.

The cathode active material supplies the lithium for cell operation. Initially, the Li-ion system was developed using LiCoO₂ as the active material. Its crystal structure undergoes an irreversible change if the cell voltage exceeds 4.2 volts or falls below 2.7 volts. Electronic controls are required to limit charge and discharge voltages between these two levels on an individual cell basis. The electronic controls also function as a safety feature by stopping cell operation if the cell exceeds a current limit or a preset temperature.

Other transition metal oxides of nickel and manganese are also potential cathode active materials for the Li-ion system. The lithium nickel oxide (LiNiO₂) has a higher capacity but is difficult to prepare and may have potential safety problems. Recently, mixed oxides of cobalt and nickel (20% to 30% nickel) are employed to increase the cell capacity while avoiding the potential safety problems of the pure nickel oxide. The manganese spinels (LiMn₂O₄) have received intensive study and are in limited use. They possess lower capacity than the cobalt materials, but are lower in cost. Cells employing the spinel are reported to require simpler electronic controls.

During the first charge (formation) of the Li-ion cells, a portion of the lithium ions react with the electrolyte and the active oxygen species on the surface of the carbon to produce a

"solid electrolyte interface" often termed, SEI. These reactions consume a portion of the lithium ions and make them unavailable for use later in the energy producing battery reactions. This is often termed "first cycle loss." The graphitic materials tend to have a lower first cycle loss than the "hard" carbons or cokes.

The Li-ion is the system of choice to power many portable energy devices because of its lightweight and good overall performance. Li-ion polymer cells with a solid polymer electrolyte (gel) are now appearing on the market. These cells can be produced in large footprint (8" x 10") thin formats. The Li-ion polymer cells could satisfy the demand for a 100 Wh battery pack that would allow a traveler to use a notebook computer on cross-country flights. It would also allow additional "power-hungry" features to be incorporated in the notebook computer. At the present time, the Li-ion does not have the high power capability applications or the low temperature performance of either Ni-Cd or Ni-MH. Nonetheless, the light weight of the Li-ion has made it the system of choice for laptops and cellular phones. In situations where the phone is given away for agreeing to a service contract, the heavier but lower cost Ni-Cd still prevails.

A notable side benefit of the requirement for voltage and current control of the Li-ion system has been the advent of "power management" for all rechargeable systems. The circuitry and software developed to allow the exchange of information between the battery and the device has greatly enhanced safety and improved runtime. Power management is implemented by the incorporation of an IC package that monitors and controls the pack operation on a cell-by-cell basis for both discharge and charge. These same features also improve the operation of Ni-Cd and Ni-MH. As a result, the control circuitry and chargers for rechargeable batteries is an active technology development area. Power management has become a hot topic in over-all system design. With the advent of the Li-ion cell and its need for electronic control to prevent abuse conditions from developing, new concepts for charging have emerged.

The control circuitry has been extended to include charging operations of other rechargeable battery systems. The IC chip in "smart" chargers can identify the type of battery from its response to the pulse, and then

select the optimum charge regime. It may be possible to eliminate the memory effect of Ni-Cd by the choice of charging regime. Not surprisingly, the new chargers with power management capability also improve the performance of the older lead acid battery. Pulse charging techniques have been developed to rapidly and safely charge.

The principal use of lead acid batteries is for automotive starting, lighting, and ignition applications. While growth in lead acid batteries is slow and closely follows the GNP, a significant change is imminent in this area. The automotive industry is preparing to shift to higher voltage systems to handle the larger power needs of the new accessories. System voltages in the range of 36 to 48 volts are under consideration with the final decision on voltage to be made in the next year or two. Introduction of cars with the higher voltage systems is likely to occur by the year 2005. The voltage change will require completely new cell designs and sizes. This will open an opportunity for new concepts such as the small cylindrical lead acid cells and the Li-ion polymer battery system. The spiral-wrap lead acid cells incorporate very thin foil electrodes and are capable of delivering energy pulses of well over 1000 W/kg. The Li-ion polymer cells also offer very thin cell construction with one-third the weight and one-half the volume of the same energy lead acid battery.

New battery-like systems termed "double layer" capacitors or ultracapacitors have been under development for several years. The devices draw their character from the double layer and reaction capacitance that develops at the electrode-solution interface of all electrodes. Capacitances of up to 20 farads are possible in a common AA-size cell. The ultracapacitor can handle (smooth out) very high current pulses that occur in an electric circuit. They have specific power capability of over 10 kW/kg. It is reported that an ultracapacitor, in parallel with a primary alkaline cell, can extend the performance of an alkaline cell by 3 to 5 times for pulse applications such as are found in digital cellular phones. Research and development activity has accelerated as the usefulness of these devices has been recognized. Commercial systems are now on the market for use in memory protection, ground insulation, and uninterruptible power supplies. The main disadvantages are the low operating voltage, high equiv-

alent series resistance, and low energy storage capability of 5 to 10 Wh/kg. Most devices are based on high surface area carbon (250 to over 700 m²/g) electrode structures. Other materials, such as nitrides and carbides, show promise as electrode materials.

On the Horizon

Several issues face the battery industry. The first is the environmental impact of spent batteries. Lead acid batteries are an excellent example of the success of recycling. About 95% to 98% of spent lead acid batteries are recycled. The lead is refined and returned for use as the grid and active mass. The plastic is ground into small chunks and blended to mold new battery cases. New electrolytic processes with low or no lead emissions have been developed to replace the conventional hydrothermal refining techniques.

There is a move to require the recycling of all batteries in an effort to protect the environment. Several states in the U.S. already have laws in place but have delayed implementation. The cost and the reluctance, on the part of the consumer, to return batteries for collection and recycling are delaying action. The small rechargeable battery industry group recently formed an independent company, the Rechargeable Battery Recycling Corporation to recycle Ni-Cd batteries. Convenient collection centers have been established in major stores such as Radio Shack, Kmart and Wal-Mart as well as by municipalities. Eventually, the recycling of primary cells will also be required. Suitable technology appears to be available for economic recovery. The cost of recovering and recycling is almost equal to the initial manufacturing cost.

The second issue involves the shipping of lithium and Li-ion batteries. The shipping of all cells containing lithium metal are regulated by the Department of Transportation, the details of which are found in the Code of Federal Regulations, CFR49.185.173. The United Nations also has developed shipping regulations that have been adopted by various transport groups. The new proposed regulations include Li-ion batteries in the same category as lithium metal anode cells. These regulations will likely be modified over the next several years to reflect the good safety record of these systems.

Although the crystal ball is dim, several new high-energy battery sys-

tems will likely appear in the future. These include:

- Lithium metal anode rechargeable cells with polymer electrolyte. The lithium polymer battery now under development for use in electric vehicles is a forerunner of these new systems. The availability of solid electrolytes with good room temperature conductivity will spur this development for consumer applications.
- Very thin, large footprint rechargeable Li-ion polymer batteries. This freedom of format offered by the polymer cells will encourage designers to develop new, longer running devices. These will have about the same energy as the liquid electrolyte version but with a large footprint. For instance, a Li-ion polymer battery could deliver 100 Wh in a 8" x 12" x 0.5" configuration.
- Zinc-air primary cells with creative air management systems. The Zn-air system has the capability to equal or exceed the lithium systems in energy storage. A Zn-air D-cell could more than double the service life of the present alkaline Zn-MnO₂ D-size cell. ■

About the Author

Ralph J. Brodd is President of his consulting company, Broddarp of Nevada, Inc. He has over 30 years experience in the battery field and has worked on all the major primary and secondary battery systems. His work experience includes technical and marketing activities spanning a wide range of applications as bench chemist, technical manager, and vice president of marketing for various battery companies. He is Past President and Honorary Member of The Electrochemical Society.

Dr. Brodd has served as a National Secretary and Vice-President of the International Society of Electrochemistry, and Chairman of the 1979 Gordon Research Conference in Electrochemistry. Case Western Reserve University named him Centennial Fellow in 1980. He has served on several government advisory committees and has over 80 publications and patents.