Handbook of
Rechargeable Batteries

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Rechargeable Battery

A rechargeable lithium polymer Nokia mobile phone battery

Energizer AA size 2500 mA·h (1.2 V, 3.0 W·h, NiMH) rechargeable cell

A battery bank used for an Uninterruptible power supply in a data center

A **rechargeable battery** or **storage battery** is a group of one or more electrochemical cells. They are known as **secondary cells** because their electrochemical reactions are electrically reversible. Rechargeable batteries come in many different shapes and sizes, ranging anything from a button cell to megawatt systems connected to stabilize an electrical distribution network. Several different combinations of chemicals are commonly used, including: lead-acid, nickel cadmium (NiCd), nickel metal hydride (NiMH), lithium ion (Li-ion), and lithium ion polymer (Li-ion polymer).

Rechargeable batteries have lower total cost of use and environmental impact than disposable batteries. Some rechargeable battery types are available in the same sizes as disposable types. Rechargeable batteries have higher initial cost, but can be recharged very cheaply and used many times.

Usage and applications

Rechargeable batteries are used for automobile starters, portable consumer devices, light vehicles (such as motorized wheelchairs, golf carts, electric bicycles, and electric forklifts), tools, and uninterruptible power supplies. Emerging applications in hybrid electric vehicles and electric vehicles are driving the technology to reduce cost and weight and increase lifetime.

Normally, new rechargeable batteries have to be charged before use; newer low self-discharge batteries hold their charge for many months, and are supplied charged to about 70% of their rated capacity.

Grid energy storage applications use rechargeable batteries for load leveling, where they store electric energy for use during peak load periods, and for renewable energy uses, such as storing power generated from photovoltaic arrays during the day to be used at night. By charging batteries during periods of low demand and returning energy to the grid during periods of high electrical demand, load-leveling helps eliminate the need for expensive peaking power plants and helps amortize the cost of generators over more hours of operation.

The US National Electrical Manufacturers Association has estimated that U.S. demand for rechargeable batteries is growing twice as fast as demand for nonrechargeables.

Charging and discharging

During charging, the positive active material is oxidized, producing electrons, and the negative material is reduced, consuming electrons. These electrons constitute the current flow in the external circuit. The electrolyte may serve as a simple buffer for ion flow between the electrodes, as in lithium-ion and nickel-cadmium cells, or it may be an active participant in the electrochemical reaction, as in lead-acid cells.

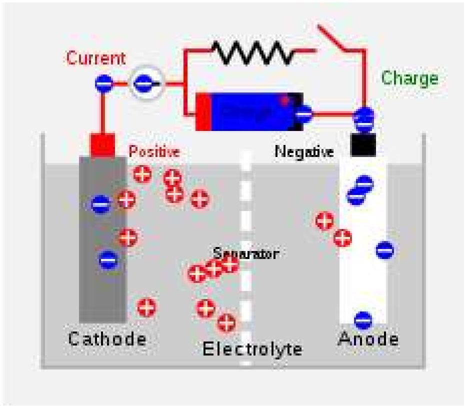


Diagram of the charging of a secondary cell battery

Battery charger

A solar-powered charger for rechargeable AA batteries

The energy used to charge rechargeable batteries usually comes from a battery charger using AC mains electricity. Chargers take from a few minutes (rapid chargers) to several hours to charge a battery. Most batteries are capable of being charged far faster than simple battery chargers are capable of; there are chargers that can charge consumer sizes of NiMH batteries in 15 minutes. Fast charges must have multiple ways of detecting full charge (voltage, temperature, etc.) to stop charging before onset of harmful overcharging.

Rechargeable multi-cell batteries are susceptible to cell damage due to reverse charging if they are fully discharged. Fully integrated battery chargers that optimize the charging current are available.

Attempting to recharge non-rechargeable batteries with unsuitable equipment may cause battery explosion.

Flow batteries, used for specialised applications, are recharged by replacing the electrolyte liquid.

Battery manufacturers' technical notes often refer to VPC; this is volts per cell, and refers to the individual secondary cells that make up the battery. For example, to charge a 12 V battery (containing 6 cells of 2 V each) at 2.3 VPC requires a voltage of 13.8 V across the battery's terminals.

Non-rechargeable alkaline and zinc-carbon cells output 1.5V when new, but this voltage gradually drops with use. Most NiMH AA and AAA batteries rate their cells at 1.2 V, and can usually be used in equipment designed to use alkaline batteries up to an end-point of 0.9 to 1.2V.

Reverse charging

Subjecting a discharged cell to a current in the direction which tends to discharge it further, rather than charge it, is called reverse charging; this damages cells. Reverse charging can occur under a number of circumstances, the two most common being:

- When a battery or cell is connected to a charging circuit the wrong way round.
- When a battery made of several cells connected in series is deeply discharged.

When one cell completely discharges ahead of the rest, the live cells will apply a reverse current to the discharged cell ("cell reversal"). This can happen even to a "weak" cell that is not fully discharged. If the battery drain current is high enough, the weak cell's internal resistance can experience a reverse voltage that is greater than the cell's remaining internal forward voltage. This results in the reversal of the weak cell's polarity while the current is flowing through the cells. This can significantly shorten the life of the affected cell and therefore of the battery. The higher the discharge rate of the battery needs to be, the better matched the cells should be, both in kind of cell and state of charge. In some extreme cases, the reversed cell can begin to emit smoke or catch fire.

In critical applications using Ni-Cad batteries, such as in aircraft, each cell is individually discharged by connecting a load clip across the terminals of each cell, thereby avoiding cell reversal, then charging the cells in series.

Depth of discharge

Depth of discharge (DOD) is normally stated as a percentage of the nominal ampere-hour capacity; 0% DOD means no discharge. Since the usable capacity of a battery system depends on the rate of discharge and the allowable voltage at the end of discharge, the depth of discharge must be qualified to show the way it is to be measured. Due to variations during manufacture and aging, the DOD for complete discharge can change over time or number of discharge cycles. Generally a rechargeable battery system will tolerate more charge/discharge cycles if the DOD is lower on each cycle.

Active components

The active components in a secondary cell are the chemicals that make up the positive and negative active materials, and the electrolyte. The positive and negative are made up of different materials, with the positive exhibiting a reduction potential and the negative having an oxidation potential. The sum of these potentials is the standard cell potential or voltage.

In primary cells the positive and negative electrodes are known as the cathode and anode, respectively. Although this convention is sometimes carried through to rechargeable systems — especially with lithium-ion cells, because of their origins in primary lithium cells — this practice can lead to confusion. In rechargeable cells the positive electrode is the cathode on discharge and the anode on charge, and vice versa for the negative electrode.

Table of rechargeable battery technologies

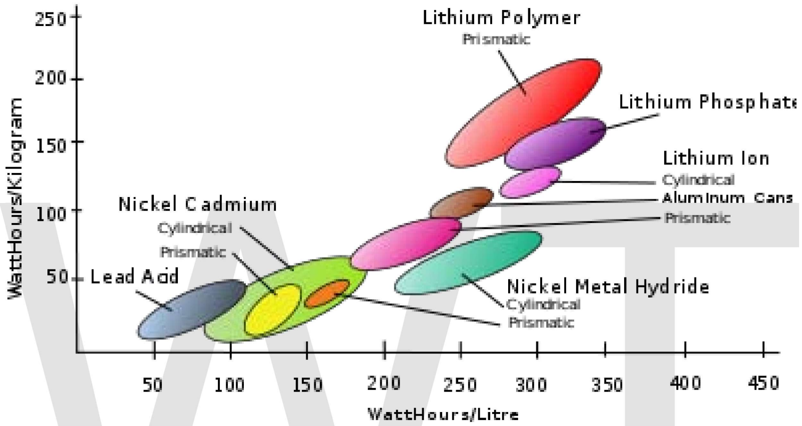
Type	Voltage[a]	Energy density[b]			Power[c]	Effi.[d]	E/$[e]	Disch.[f]	Cycles[g]	Life[h]
	(V)	(MJ/kg)	(Wh/kg)	(Wh/L)	(W/kg)	(%)	(Wh/$)	(%/month)	(#)	(years)
Lead-acid	2.1	0.11-0.14	30-40	60-75	180	70%-92%	5-8	3%-4%	500-800	5-8 (car battery), 20 (stationary)
VRLA[i]	2.105									
Alkaline	1.5	0.31	85	250	50	99.9%	7.7	<0.3	100-1000	<5
Ni-iron	1.2	0.18	50		100	65%	5-7.3	20%-40%		50+
Ni-cadmium	1.2	0.14-0.22	40-60	50-150	150	70%-90%	1.25-2.5	20%	1500	
NiH2	1.5		75						20,000	15+
NiMH	1.2	0.11-0.29	30-80	140-300	250-1000	66%	2.75	30%	500-1000	
Ni-zinc	1.7	0.22	60	170	900		2-3.3		100-500	
Li ion	3.6	0.58	150-250	250-360	1800	80-90%	2.8-5	5%-10%	1200	2-3
Li polymer	3.7	0.47-0.72	130-200	300	3000+		2.8-5.0		500~1000	2-3
$LiFePO_4$	3.25		80-120	170	1400		0.7-3.0		2000+	
Li sulfur	2.0	0.94-1.44	400	350					~100	
Li titanate	2.3		90		4000+	87-95%[r]	0.5-1.0		9000+	20+
Thin film Li	?			350	959	?	?[p]		40000	
ZnBr			75-85							
V redox	1.15-1.55		25-35			80%		20%	14,000	10(stationary)
NaS			150			89%-92%				

Molten salt	2.58		70-110	160	150-220		4.54		3000+	8+
Silver zinc (Ag-zinc)	1.86		130	240						

Notes

For brevity, entries in the table had to be abbreviated. For a full description, please refer to the individual article about each type.

- [a] Nominal cell voltage in V.



Graph of mass and volume energy densities of several secondary cells

- [b] Energy density = energy/weight or energy/size, given in three different units
- [c] Specific power = power/weight in W/kg
- [d] Charge/discharge efficiency in %
- [e] Energy/consumer price in W·h/US$ (approximately)
- [j] Safe Depth of Discharge to maintain lifecycles
- [f] Self-discharge rate in %/month
- [g] Cycle durability in number of cycles
- [h] Time durability in years
- [i] VRLA or recombinant includes gel batteries and absorbed glass mats
- [p] Pilot production
- [r] Depending upon charge rate

Common rechargeable battery types

Nickel-cadmium battery (NiCd)

Created by Waldemar Jungner of Sweden in 1899, based on Thomas Edison's first alkaline battery. Using nickel oxide hydroxide and metallic cadmium as electrodes. Cadmium is a toxic element, and was banned for most uses by the European Union in

2004. Nickel-cadmium batteries have been almost completely superseded by nickel-metal hydride (NiMH) batteries.

Nickel-metal hydride battery (NiMH)

First commercial types were available in 1989. These are now a common consumer and industrial type. The battery has a hydrogen-absorbing alloy for the negative electrode instead of cadmium.

Lithium-ion battery

The technology behind lithium-ion battery has not yet fully reached maturity. However, the batteries are the type of choice in many consumer electronics and have one of the best energy-to-mass ratios and a very slow loss of charge when not in use.

Lithium-ion polymer battery

These batteries are light in weight and can be made in any shape desired.

Less common types

Lithium sulfur battery

A new battery chemistry developed by Sion Power since 1994. Claims superior energy to weight than current lithium technologies on the market. Also lower material cost may help this product reach the mass market.

Thin film battery (TFB)

An emerging refinement of the lithium ion technology by Excellatron. The developers claim a very large increase in recharge cycles, around 40,000 cycles. Higher charge and discharge rates. At least 5*C* charge rate. Sustained 60*C* discharge, and 1000*C* peak discharge rate. And also a significant increase in specific energy, and energy density.

Also Infinite Power Solutions makes thin film batteries (TFB) for micro-electronic applications, that are flexible, rechargeable, solid-state lithium batteries.

Smart battery

A smart battery has the voltage monitoring circuit built inside.

Carbon foam-based lead acid battery

Firefly Energy has developed a carbon foam-based lead acid battery with a reported energy density of 30-40% more than their original 38 W·h/kg, with long life and very high power density.

Potassium-ion battery

This type of rechargeable battery can deliver the best known cycleability, in order of a million cycles, due to the extraordinary electrochemical stability of potassium insertion/extraction materials such as Prussian blue.

Developments since 2005

In 2007 Yi Cui and colleagues at Stanford University's Department of Materials Science and Engineering discovered that using silicon nanowires as the anode of a lithium-ion battery increases the volumetric charge density of the anode by up to a factor of 10, the nanowire battery.

Another development is the paper-thin flexible self-rechargeable battery combining a thin-film organic solar cell with an extremely thin and highly flexible lithium-polymer battery, which recharges itself when exposed to light.

Ceramatec, a research and development subcompany of CoorsTek, as of 2009 was testing a battery comprising a chunk of solid sodium metal mated to a sulfur compound by a paper-thin ceramic membrane which conducts ions back and forth to generate a current. The company claimed that it could fit about 40 kilowatt hours of energy into a package about the size of a refrigerator, and operate below 90 °C; and that their battery would allow about 3,650 discharge/recharge cycles (or roughly 1 per day for one decade.)

Alternatives

Several alternatives to rechargeable batteries exist or are under development. For uses such as portable radios, rechargeable batteries may be replaced by clockwork mechanisms which are wound up by hand, driving dynamos, although this system may be used to charge a battery rather than to operate the radio directly. Flashlights may be driven by a dynamo directly. For transportation, uninterruptible power supply systems and laboratories, flywheel energy storage systems store energy in a spinning rotor for conversion to electric power when needed; such systems may be used to provide large pulses of power that would otherwise be objectionable on a common electrical grid. Ultracapacitors are also used; an electric screwdriver which charges in 90 seconds and will drive about half as many screws as a device using a rechargeable battery was introduced in 2007, and similar flashlights have been produced.

Ultracapacitors—capacitors of extremely high value—are being developed for transportation, using a large capacitor to store energy instead of the rechargeable battery banks used in hybrid vehicles. One drawback to capacitors compared with batteries is that the terminal voltage drops rapidly; a capacitor that has 25% of its initial energy left in it will have one-half of its initial voltage. Battery systems tend to have a terminal voltage that does not decline rapidly until nearly exhausted. This characteristic complicates the design of power electronics for use with ultracapacitors. However, there are potential benefits in cycle efficiency, lifetime, and weight compared with rechargeable systems. China started using ultracapacitors on two commercial bus routes in 2006; one of them is route 11 in Shanghai.

Chapter- 2

Lead–Acid Battery

Lead–acid battery

lead acid car battery

specific energy	30-40 Wh/kg
energy density	60-75 Wh/l
specific power	180 W/kg
Charge/discharge efficiency	50%-92%
Energy/consumer-price	7(sld)-18(fld) Wh/US$
Self-discharge rate	3%-20%/month
Cycle durability	500-800 cycles
Nominal cell voltage	2.105 V

Lead-acid batteries, invented in 1859 by French physicist Gaston Planté, are the oldest type of rechargeable battery. Despite having a very low energy-to-weight ratio and a low energy-to-volume ratio, their ability to supply high surge currents means that the cells maintain a relatively large power-to-weight ratio. These features, along with their low cost, make them attractive for use in motor vehicles to provide the high current required by automobile starter motors.

Electrochemistry

In the charged state, each cell contains electrodes of elemental lead (Pb) and lead(IV) oxide (PbO_2) in an electrolyte of approximately 33.5% *v*/*v* (4.2 Molar) sulfuric acid (H_2SO_4).

In the discharged state both electrodes turn into lead(II) sulfate ($PbSO_4$) and the electrolyte loses its dissolved sulfuric acid and becomes primarily water. Due to the freezing-point depression of water, as the battery discharges and the concentration of sulfuric acid decreases, the electrolyte is more likely to freeze during winter weather.

The chemical reactions are (discharged to charged):

Anode (oxidation):

$$\mathrm{PbSO_4}(s) + 5\mathrm{H_2O}(l) \leftrightarrow \mathrm{PbO_2}(s) + 3\mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq) + 2e^- \quad \epsilon^o = 1.685\ \mathrm{V}$$

Cathode (reduction):

$$\mathrm{PbSO_4}(s) + \mathrm{H_3O^+}(aq) + 2e^- \leftrightarrow \mathrm{Pb}(s) + \mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \quad \epsilon^o = -0.356\ \mathrm{V}$$

Because of the open cells with liquid electrolyte in most lead-acid batteries, overcharging with high charging voltages generates oxygen and hydrogen gas by electrolysis of water, forming an explosive mix. The acid electrolyte is also corrosive.

Practical cells are usually not made with pure lead but have small amounts of antimony, tin, calcium or selenium alloyed in the plate material to add strength and simplify manufacture.

Voltages for common usages

These are general voltage ranges for *six-cell* lead-acid batteries:

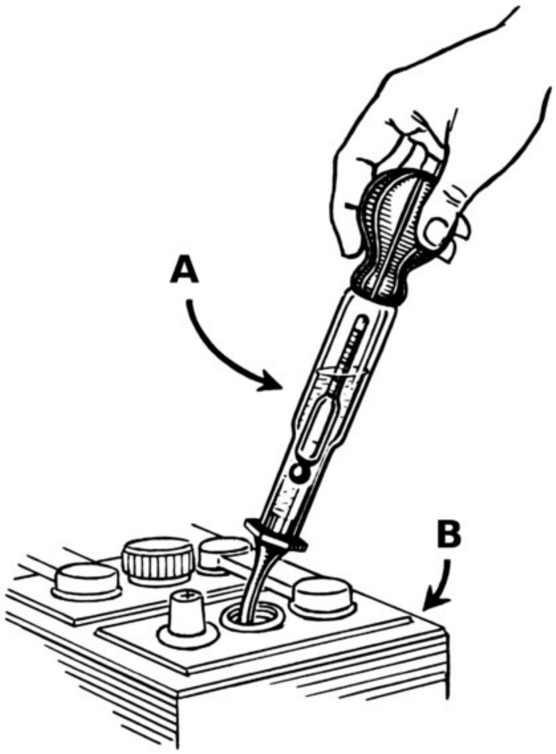
- Open-circuit (quiescent) at full charge: 12.6 V to 12.8 V (2.10-2.13V per cell)
- Open-circuit at full discharge: 11.8 V to 12.0 V
- Loaded at full discharge: 10.5 V.
- Continuous-preservation (float) charging: 13.4 V for gelled electrolyte; 13.5 V for AGM (absorbed glass mat) and 13.8 V for flooded cells

1. All voltages are at 20 °C (68 °F), and must be adjusted -0.022V/°C for temperature changes.
2. Float voltage recommendations vary, according to the manufacturer's recommendation.
3. Precise float voltage (±0.05 V) is critical to longevity; insufficient voltage (causes sulfation) which is almost as detrimental as excessive voltage (causing corrosion and electrolyte loss)

- Typical (daily) charging: 14.2 V to 14.5 V (depending on manufacturer's recommendation)
- Equalization charging (for flooded lead acids): 15 V for no more than 2 hours. Battery temperature must be monitored.
- Gassing threshold: 14.4 V
- After full charge, terminal voltage drops quickly to 13.2 V and then slowly to 12.6 V.

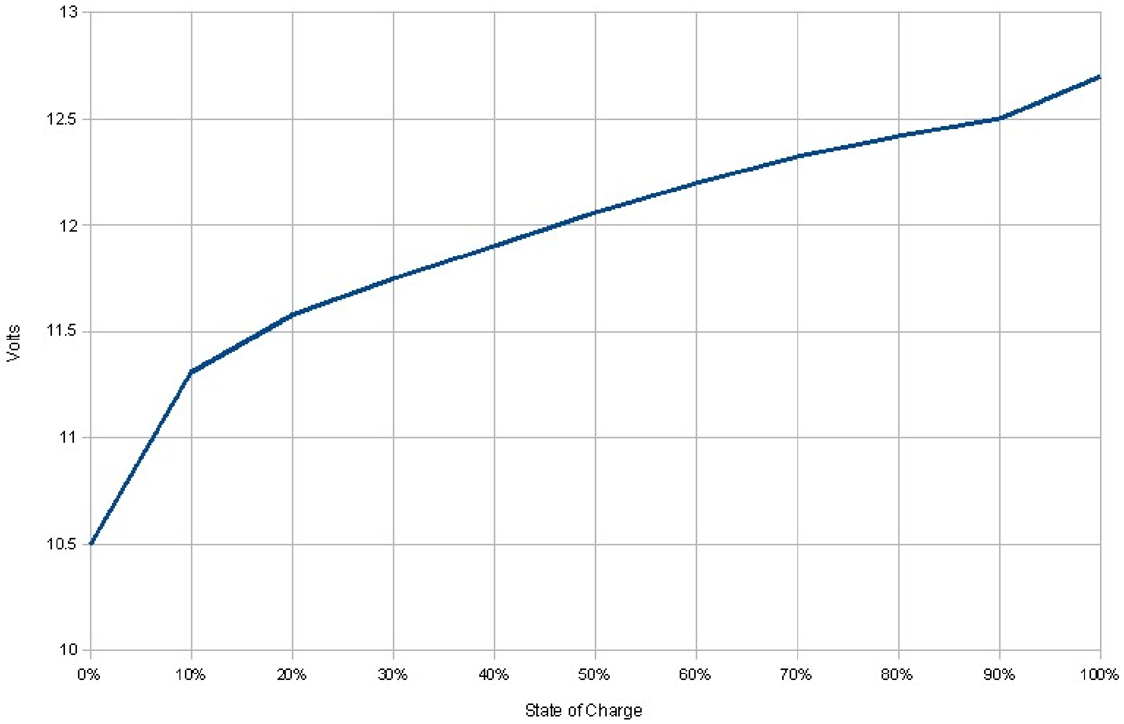
Portable batteries, such as for miners' cap lamps (headlamps) typically have two cells, and use one third of these voltages.

Measuring the charge level



A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge.

Because the electrolyte takes part in the charge-discharge reaction, this battery has one major advantage over other chemistries. It is relatively simple to determine the state of charge by merely measuring the specific gravity (S.G.) of the electrolyte, the S.G. falling as the battery discharges. Some battery designs include a simple hydrometer using colored floating balls of differing density. When used in diesel-electric submarines, the S.G. was regularly measured and written on a blackboard in the control room to indicate how much longer the boat could remain submerged.



A battery's open-circuit voltage can be used to estimate the state of charge, in this case for a 12 volt battery.

Construction

Plates

The lead acid cell can be demonstrated using sheet lead plates for the two electrodes. However such a construction produces only around one ampere for roughly postcard sized plates, and for only a few minutes.

Gaston Planté found a way to provide a much larger effective surface area. In Planté's design, the positive and negative plates were formed of two spirals of lead foil, separated with a sheet of cloth and coiled up. The cells initially had low capacity, so a slow process of "forming" was required to corrode the lead foils, creating lead dioxide on the plates and roughen them to increase surface area. Initially this process used electricity from primary batteries; when generators became available after 1870, the cost of production of batteries greatly declined. Planté plates are still used in some stationary applications, where the plates are mechanically grooved to increase their surface area.

Faure pasted-plate construction is typical of automotive batteries. Each plate consists of a rectangular lead grid alloyed with antimony or calcium to improve the mechanical characteristics. The holes of the grid are filled with a paste of red lead and 33% dilute sulfuric acid. (Different manufacturers vary the mixture). The paste is pressed into the holes in the grid which are slightly tapered on both sides to better retain the paste. This porous paste allows the acid to react with the lead inside the plate, increasing the surface area many fold. At this stage the positive and negative plates are similar, however expanders and additives vary their internal chemistry to assist in operation. Once dry, the plates are stacked with suitable separators and inserted in the battery container. An odd number of plates is usually used, with one more positive plate than negative. Each alternate plate is connected.

The positive plates are the chocolate brown color of Lead(IV) Oxide, and the negative are the slate gray of 'spongy' lead at the time of manufacture. In this charged state the plates are called 'formed'.

One of the problems with the plates is that the plates increase in size as the active material absorbs sulfate from the acid during discharge, and decrease as they give up the sulfate during charging. This causes the plates to gradually shed the paste. It is important that there is room underneath the plates to catch this shed material. If it reaches the plates, the cell short-circuits.

The paste contains carbon black, *blanc fixe* (barium sulfate) and lignosulfonate. The blanc fixe acts as a seed crystal for the lead–to–lead sulfate reaction. The blanc fixe must be fully dispersed in the paste in order for it to be effective. The lignosulfonate prevents the negative plate from forming a solid mass during the discharge cycle, instead enabling the formation of long needle–like crystals. The long crystals have more surface area and are easily converted back to the original state on charging. Carbon black counteracts the effect of inhibiting formation caused by the lignosulfonates. Sulfonated naphthalene condensate dispersant is a more effective expander than lignosulfonate and speeds up formation. This dispersant improves dispersion of barium sulfate in the paste, reduces hydroset time, produces a more breakage-resistant plate, reduces fine lead particles and thereby improves handling and pasting characteristics. It extends battery life by increasing end–of–charge voltage. Sulfonated naphthalene requires about one-third to one-half the amount of lignosulfonate and is stable to higher temperatures.

About 60% of the weight of an automotive-type lead-acid battery rated around 60 Ah (8.7 kg of a 14.5 kg battery) is lead or internal parts made of lead; the balance is electrolyte, separators, and the case.

Separators

Separators between the positive and negative plates prevent short-circuit through physical contact, mostly through dendrites (‘treeing’), but also through shedding of the active material. Separators obstruct the flow of ions between the plates and increase the internal resistance of the cell. Wood, rubber, glass fiber mat, cellulose, and PVC or polyethylene plastic have been used to make separators. Wood was the original choice, but deteriorated in the acid electrolyte. Rubber separators were stable in the battery acid.

An effective separator must possess a number of mechanical properties; such as permeability, porosity, pore size distribution, specific surface area, mechanical design and strength, electrical resistance, ionic conductivity, and chemical compatibility with the electrolyte. In service, the separator must have good resistance to acid and oxidation. The area of the separator must be a little larger than the area of the plates to prevent material shorting between the plates. The separators must remain stable over the battery's operating temperature range.

Applications

Wet cell stand-by (stationary) batteries designed for deep discharge are commonly used in large backup power supplies for telephone and computer centers, grid energy storage, and off-grid household electric power systems . Lead-acid batteries are used in emergency lighting in case of power failure.

Traction (propulsion) batteries are used for in golf carts and other battery electric vehicles. Large lead-acid batteries are also used to power the electric motors in diesel-electric (conventional) submarines and are used on nuclear submarines as well. Motor vehicle starting, lighting and ignition (SLI) batteries (car batteries) provides current for starting internal combustion engines.

Valve-regulated lead acid batteries cannot spill their electrolyte. They are used in back-up power supplies for alarm and smaller computer systems (particularly in uninterruptible power supplies) and for electric scooters, electrified bicycles, marine applications, battery electric vehicles or micro hybrid vehicles, and motorcycles.

Lead-acid batteries were used to supply the filament (heater) voltage (usually between 2 and 12 volts with 2 V being most common) in early vacuum tube (valve) radio receivers.

Cycles

Starting batteries

Lead acid batteries designed for starting automotive engines are not designed for deep discharge. They have a large number of thin plates designed for maximum surface area, and therefore maximum current output, but which can easily be damaged by deep discharge. Repeated deep discharges will result in capacity loss and ultimately in premature failure, as the electrodes disintegrate due to mechanical stresses that arise from cycling. Starting batteries kept on continuous float charge will have corrosion in the electrodes and result in premature failure. Starting batteries should be kept open circuit but charged regularly (at least once every two weeks) to prevent sulfation.

Starting batteries are lighter weight than deep cycle batteries of the same battery dimensions, because the cell plates do not extend all the way to the bottom of the battery case. This allows loose disintegrated lead to fall off the plates and collect under the cells, to prolong the service life of the battery. If this loose debris rises high enough it can touch the plates and lead to failure of a cell, resulting in loss of battery voltage and capacity.

Deep cycle batteries

Specially designed deep-cycle cells are much less susceptible to degradation due to cycling, and are required for applications where the batteries are regularly discharged, such as photovoltaic systems, electric vehicles (forklift, golf cart, electric cars and other) and uninterruptible power supplies. These batteries have thicker plates that can deliver less *peak current*, but can withstand frequent discharging.

Some batteries are designed as a compromise between starter (high-current) and deep cycle batteries. They are able to be discharged to a greater degree than automotive batteries, but less so than deep cycle batteries. They may be referred to as "Marine/Motorhome" batteries, or "leisure batteries".

Fast and slow charge and discharge

Charge current needs to match the ability of the battery to absorb the energy. Using too large of a charge current on a small battery can lead to boiling and venting of the electrolyte. In this image a VRLA battery case has ballooned due to the high gas pressure developed during overcharge.

The capacity of a lead-acid battery is not a fixed quantity but varies according to how quickly it is discharged. An empirical relationship exists between discharge rate and capacity, known as Peukert's law.

When a battery is charged or discharged, this initially affects only the reacting chemicals, which are at the interface between the electrodes and the electrolyte. With time, the charge stored in the chemicals at the interface, often called "interface charge", spreads by diffusion of these chemicals throughout the volume of the active material.

If a battery has been completely discharged (e.g. the car lights were left on overnight) and next is given a fast charge for only a few minutes, then during the short charging time it develops only a charge near the interface. The battery voltage may rise to be close to the charger voltage so that the charging current decreases significantly. After a few hours this interface charge will spread to the volume of the electrode and electrolyte, leading to an interface charge so low that it may be insufficient to start the car.

On the other hand, if the battery is given a slow charge, which takes longer, then the battery will become more fully charged. During a slow charge the interface charge has time to redistribute to the volume of the electrodes and electrolyte, while being replenished by the charger. The battery voltage remains below the charger voltage throughout this process allowing charge to flow into the battery.

Similarly, if a battery is subject to a fast discharge (such as starting a car, a current draw of more than 100 amps) for a few minutes, it will appear to go dead, exhibiting reduced voltage and power. However, it may have only lost its interface charge. If the discharge is halted for a few minutes the battery may resume normal operation at the appropriate voltage and power for its state of discharge. On the other hand, if a battery is subject to a slow, deep discharge (such as leaving the car lights on, a current draw of less than 7 amps) for hours, then any observed reduction in battery performance is likely permanent.

Valve regulated

In a valve regulated lead acid (VRLA) battery the hydrogen and oxygen produced in the cells largely recombine into water. Leakage is minimal, although some electrolyte still escapes if the recombination cannot keep up with gas evolution. Since VRLA batteries do not require (and make impossible) regular checking of the electrolyte level, they have been called *maintenance free batteries*. However, this is somewhat of a misnomer. VRLA cells do require maintenance. As electrolyte is lost, VRLA cells "dry-out" and lose capacity. This can be detected by taking regular internal resistance, conductance or impedance measurements. Regular testing reveals whether more involved testing and maintenance is required. Recent maintenance procedures have been developed allowing "rehydration", often restoring significant amounts of lost capacity.

VRLA types became popular on motorcycles around 1983, because the acid electrolyte is absorbed into the separator, so it cannot spill. The separator also helps them better withstand vibration. They are also popular in stationary applications such as telecommunications sites, due to their small footprint and installation flexibility.

The electrical characteristics of VRLA batteries differ somewhat from wet-cell lead-acid batteries, requiring caution in charging and discharging.

Sulfation

Lead-acid batteries lose the ability to hold a charge when discharged for too long due to *sulfation*, the crystallization of lead sulfate. They generate electricity through a double sulfate chemical reaction. Lead and Lead(IV) Oxide, which are the active materials on the battery's plates, react with sulfuric acid in the electrolyte to form lead sulfate. The lead sulfate first forms in a finely divided, amorphous state, and easily reverts to lead, lead oxide and sulfuric acid when the battery recharges. As batteries cycle through numerous discharge and charges, the lead sulfate slowly converts to a stable crystalline form that no longer dissolves on recharging. Thus, not all the lead is returned to the battery plates, and the amount of usable active material necessary for electricity generation declines over time.

Sulfation occurs in all lead-acid batteries during normal operation. It clogs the grids, impedes recharging and ultimately expands, cracking the plates and destroying the battery. In addition, the sulfate portion (of the lead sulfate) is not returned to the electrolyte as sulfuric acid. The large crystals physically block the electrolyte from entering the pores of the plates. Sulfation can be avoided if the battery is fully recharged immediately after a discharge cycle.

Sulfation also affects the charging cycle, resulting in longer charging times, less efficient and incomplete charging, and higher battery temperatures.

The process can often be at least partially prevented and/or reversed by a desulfation technique called pulse conditioning, in which short but powerful current surges are repeatedly sent through the damaged battery. Over time, this procedure tends to break down and dissolve the sulfate crystals, restoring some capacity.

Higher temperature speeds both desulfation and sulfation, although too much heat damages the battery by accelerating corrosion.

Stratification

A typical lead-acid battery contains a mixture with varying concentrations of water and acid. There is a slight difference in density between water and acid, and if the battery is allowed to sit idle for long periods of time, the mixture can separate into distinct layers with the water rising to the top and the acid sinking to the bottom. This results in a difference of acid concentration across the surface of the plates, and can lead to greater corrosion of the bottom half of the plates.

Frequent charging and discharging tends to stir up the mixture, since the electrolysis of water during charging forms hydrogen and oxygen bubbles that rise and displace the liquid as the bubbles move upward. Batteries in moving vehicles are also subject to sloshing and splashing in the cells, as the vehicle accelerates, brakes, and turns.

Risk of explosion

Car battery after explosion

Excessive charging electrolyzes some of the water emitting hydrogen and oxygen. This process is known as "gassing". Wet cells have open vents to release any gas produced, and VRLA batteries rely on valves fitted to each cell. Wet cells come with catalytic caps to recombine any emitted hydrogen. A VRLA cell normally recombines any hydrogen and oxygen produced inside the cell, but malfunction or overheating may cause gas to build up. If this happens (e.g., by overcharging) the valve vents the gas and normalizes the pressure, producing a characteristic acid smell. Valves can sometimes fail however, if dirt and debris accumulate, allowing pressure to build up.

If the accumulated hydrogen and oxygen within either a VRLA or wet cell is ignited, an explosion results. The force can burst the plastic casing or blow the top off the battery, spraying acid and casing shrapnel. An explosion in one cell may ignite the combustible gas mixture in remaining cells.

The cell walls of VRLA batteries typically swell when the internal pressure rises. The deformation varies from cell to cell, and is greater at the ends where the walls are unsupported by other cells. Such over-pressurized batteries should be carefully isolated and discarded. Personnel working near batteries at risk for explosion should protect their eyes and exposed skin from burns due to spraying acid and fire by wearing a face shield, overalls, and gloves. Using goggles instead of a face shield sacrifices safety by leaving one's face exposed to acid and heat from a potential explosion.

Environment

Environmental concerns

According to a 2003 report entitled, "Getting the Lead Out," by Environmental Defense and the Ecology Center of Ann Arbor, Mich., the batteries of vehicles on the road contained an estimated 2,600,000 metric tons (2,560,000 LT; 2,870,000 ST) of lead. Lead is extremely toxic. Long-term exposure to even tiny amounts of lead can cause brain and kidney damage, hearing impairment, and learning problems in children. The auto industry uses over 1,000,000 metric tons (980,000 LT; 1,100,000 ST) every year, with 90% going to conventional lead-acid vehicle batteries. While lead recycling is a well-established industry, more than 40,000 metric tons (39,000 LT; 44,000 ST) ends up in landfills every year. According to the federal Toxic Release Inventory, another 70,000 metric tons (69,000 LT; 77,000 ST) are released in the lead mining and manufacturing process.

Attempts are being made to develop alternatives (particularly for automotive use) because of concerns about the environmental consequences of improper disposal and of lead smelting operations, among other reasons. Alternatives are unlikely to displace them for applications such as engine starting or backup power systems, since the batteries are low-cost although heavy.

Recycling

Lead–acid battery recycling is one of the most successful recycling programs in the world. In the United States 97% of all battery lead was recycled between 1997 and 2001. An effective pollution control system is a necessity to prevent lead emission. Continuous improvement in battery recycling plants and furnace designs is required to keep pace with emission standards for lead smelters.

Additives

Since the 1950's chemical additives have been used to reduce lead sulfate build up on plates and improve battery condition when added to the electrolyte of a vented lead-acid battery. Such treatments are rarely, if ever, effective.

Two compounds used for such purposes are Epsom salts and EDTA. Epsom salts reduces the internal resistance in a weak or damaged battery and may allow a small amount of extended life. EDTA can be used to dissolve the sulfate deposits of heavily discharged plates. However, the dissolved material is then no longer available to participate in the normal charge/discharge cycle, so a battery temporarily revived with EDTA should not be expected to have normal life expectancy. Residual EDTA in the lead-acid cell forms organic acids which will accelerate corrosion of the lead plates and internal connectors.

Active material changes physical form during discharge, resulting in plate growth, distortion of the active material, and shedding of active material. Once the active material has fallen out of the plates, it cannot be restored into position by any chemical treatment. Similarly, internal physical problems such as cracked plates, corroded connectors, or damaged separators cannot be restored chemically.

Corrosion problems

Corrosion of the external metal parts of the lead-acid battery results from a chemical reaction of the battery terminals, lugs and connectors. It can be caused by the following:

The corrosion on the positive terminal is caused by electrolysis, due a mismatch of metal alloys used in the manufacture of the battery terminal and cable connector. White corrosion is usually lead or zinc sulfate crystals. Aluminum connectors corrode to aluminum sulfate. Copper connectors produce blue and white corrosion crystals. Minimize corrosion by coating with a suitable rubber or plastic spray or using a commercially available product.

If the battery is over-filled with water and electrolyte, thermal expansion can force some of the liquid out of the battery vents onto the top of the battery. This solution can then react with the lead and other metals in the battery connector and cause corrosion.

The electrolyte can weep from the plastic-to-lead seal where the battery terminals penetrate the plastic case.

Acid fumes that vaporize through the vent caps, often caused by overcharging, and insufficient battery box ventilation can allow the sulfuric acid fumes to build up and react with the exposed metals.

Maintenance precautions

Ammonia can neutralize spilled battery acid. Surplus ammonia and water evaporate, leaving an ammonium sulfate residue. Sodium bicarbonate (baking soda) is also commonly used for this purpose.

Chapter- 3

VRLA Battery

A sealed lead-acid battery

A **VRLA battery** (valve-regulated lead-acid battery) is the designation for low-maintenance lead-acid rechargeable batteries. Because of their construction, VRLA batteries do not require regular addition of water to the cells. VRLA batteries are commonly further classified as:

- Absorbed glass mat battery
- Gel battery (gel cell)

These batteries are often colloquially called *sealed* lead-acid batteries, but they always include a safety pressure relief valve. As opposed to *vented* (also called *flooded*) batteries, a VRLA cannot spill its electrolyte if it is inverted. Because VRLA batteries use much less electrolyte (battery acid) than traditional lead-acid batteries, they are also occasionally referred to as an "acid-starved" design.

The name "valve regulated" does not wholly describe the technology; these are really "recombinant" batteries, which means that the oxygen evolved at the positive plates will largely recombine with the hydrogen ready to evolve on the negative plates, creating water and so preventing water loss. The valve is a safety feature in case the rate of hydrogen evolution becomes dangerously high. In flooded cells, the gases escape before they have a chance to recombine, so water must be periodically added.

One result of this design is a much higher ratio of power to "floorspace" than large, flooded type battery systems; another is a high-rate power capacity, though of relatively short duration. As a result, VRLA batteries are frequently employed in UPS (uninterruptible power supply) or other high-rate applications.

Construction

These batteries have a pressure relief valve which will activate when the battery is recharged at high voltage, typically greater than 2.30 volts per cell. (A 12 volt battery has six cells.) Valve activation allows some of the gas or electrolyte to escape, thus decreasing the overall capacity of the battery. Rectangular cells may have valves set to operate as low as 1 or 2 psi; round spiral cells, with metal external containers, can have valves set as high as 40 psi.

The cell covers typically have gas diffusers built into them that allow safe dispersal of any excess hydrogen that may be formed during overcharge. They are not permanently sealed, but are maintenance free; and they can be oriented in any manner, unlike normal lead-acid batteries, which must be kept upright to avoid acid spills and to keep the plates' orientation vertical. Cells may be operated with the plates horizontal (*pancake* style), which may improve cycle life.

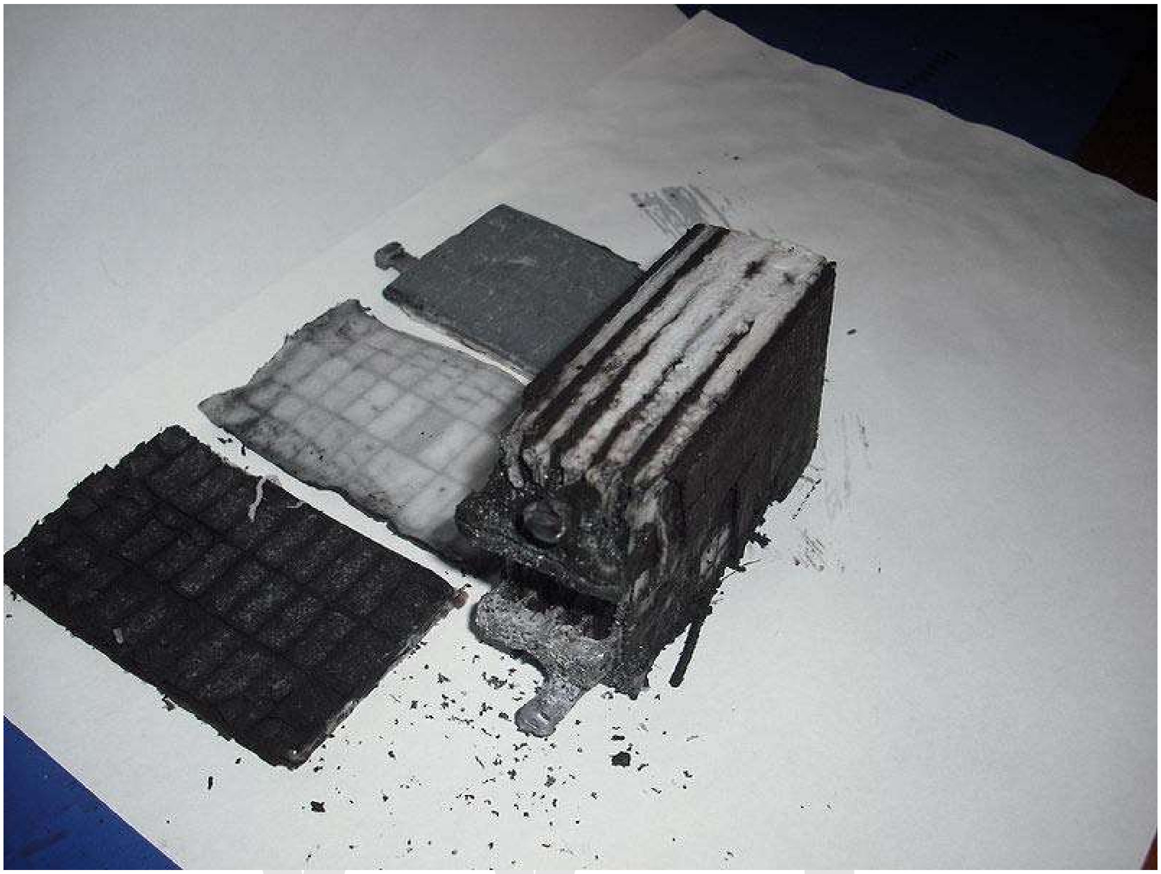
VRLA cells may be made of flat plates similar to a conventional flooded lead-acid battery, or may be made in a spiral roll form to make cylindrical cells.

At high overcharge currents, electrolysis of water occurs, expelling hydrogen and oxygen gas through the battery's valves. Care must be taken to prevent short circuits and rapid charging. Constant-voltage charging is the usual, most efficient and fastest charging method for VRLA batteries, although other methods can be used. VRLA batteries may be continually "float" charged at around 2.35 volts per cell at 25°C. Some designs can be fast charged (1 hour) at high rates. Sustained charging at 2.7 V per cell will damage the cells. Constant-current overcharging at rates higher than C/3 will exceed the capacity of the cell to recombine hydrogen and oxygen.

Comparison with flooded lead-acid cells

Compared with flooded lead-acid cells, VRLA batteries offer several advantages. The battery can be mounted in any position, since the valves only operate on over pressure faults. Since the battery system is designed to be recombinant and eliminate the emission of gases on overcharge, room ventilation requirements are reduced and no acid fume is emitted during normal operation. The volume of free electrolyte that could be released on damage to the case or venting is very small. There is no need (nor possibility) to check the level of electrolyte or to top up water lost due to electrolysis, reducing inspection and maintenance. Compared to flooded batteries, VRLA batteries are more sensitive to high temperature environments and more vulnerable to thermal run-away during abusive charging conditions.

Absorbed glass mat (AGM)



Disassembled AGM cell. From left: positive plate, glass mat separator, negative plate. On the right is the entire cell.

Absorbed glass mat (**AGM**) is a class of VRLA battery in which the electrolyte is held on the glass mat separator by way of capillary action.

History

AGM batteries were developed by Concorde Aircraft Battery, in the late 1980s in San Bernardino California. The AGM battery technology was developed to be a warm weather, vibration resistant, and chemical alternative to the expensive Ni-Cad batteries in both naval helicopters and fighter aircraft. As production was mechanized, Optima Battery patented a spiral wound method for producing an AGM battery. Due to the spiral wound cell configuration, they are also sometimes referred to as **spiral wound**. These two manufacturers maintain UL, CE, and Mil-Spec ratings on their batteries.

Manufacture

AGM batteries are just like flooded lead acid batteries, except the electrolyte is being held in the glass mats, as opposed to freely flooding the plates. Very thin glass fibers are woven into a mat to increase surface area enough to hold sufficient electrolyte on the cells for their lifetime. The fibers that comprise the fine glass fibers glass mat do not absorb nor are affected by the acidic electrolyte they reside in. These mats are wrung out 2-5% after being soaked in acids, prior to manufacture completion and sealing. The AGM battery can now accumulate more acid than is available, and never spill a drop.

The plates in an AGM battery may be any shape. Some are flat, others are bent or wound. AGM batteries, both deep cycle and starting, are built in a rectangular case to BCI battery code specifications. Optima Battery builds a patented cylindrical AGM series of batteries that are fashioned to fit the same BCI battery size specifications as any other battery.

Advantages

All AGM batteries boast some significant performance enhancement over traditional flooded lead acid cells:

- AGM construction allows purer lead in the plates as each plate no longer needs to support its own weight based on the sandwich construction with AGM matting. Traditional cells must support their own weight in the bath of acid.
- un-spillable
- high specific power or power density, holding roughly 1.5x the AH capacity as flooded batteries based on purer lead
- low internal resistance allowing them to be charged and discharged quite rapidly
- never requiring addition of water
- acid is encapsulated in the matting
- will operate well below 0°F or -18 °C.
- UL, DOT, CE, Coast Guard, and Mil-Spec approved types
- vibration resistant based on the sandwich construction.

Disadvantages

- Cost. AGM automobile batteries for example, are typically about twice the price of flooded-cell batteries in a given BCI size group.
- AGM batteries have up to a 10 year lifespan, but must be sized to discharge less deeply than the traditional flooded batteries. For an AGM battery, the depth of discharge for optimal performance is 50% but flooded batteries can be rated up to 80% depth of discharge.
- AGM batteries do not tolerate overcharging. Overcharging dissociates the water in the electrolyte, which is unable to be replaced, leading to premature failure.

Gel battery

A gel battery

A **gel battery** (also known as a "gel cell") is a VRLA battery with a gelified electrolyte; the sulfuric acid is mixed with silica fume, which makes the resulting mass gel-like and immobile. Unlike a flooded wet-cell lead-acid battery, these batteries do not need to be kept upright. Gel batteries reduce the electrolyte evaporation, spillage (and subsequent corrosion issues) common to the wet-cell battery, and boast greater resistance to extreme temperatures, shock, and vibration. Chemically they are the same as wet (non-sealed) batteries except that the antimony in the lead plates is replaced by calcium.

Applications

Many modern motorcycles on the market utilize AGM or factory-sealed AGM batteries for the combined benefits of reduced likelihood of acid spilling during accidents, and for packaging reasons (lighter, smaller battery to do the same job; the battery can be installed at an odd angle if needed for the design of the motorcycle).

Due to the higher manufacturing costs compared with flooded lead-acid batteries, AGM batteries are currently used on premium vehicles. As vehicles become heavier and equipped with more electronic devices such as navigation, stability control, and premium stereos, AGM batteries are being employed to lower vehicle weight and provide better electrical reliability compared with flooded lead-acid batteries.

New 5 series BMWs from March 2007 incorporate AGM batteries in conjunction with devices for recovering brake energy using regenerative braking and computer control to ensure the alternator charges the battery when the car is decelerating. Vehicles used in auto racing may use AGM batteries due to their vibration resistance.

Deep-cycle AGMs are also commonly used in large-scale amateur robotics. Two examples are the FIRST and IGVC competitions.

AGM batteries are routinely chosen for remote sensors such as ice monitoring stations in the Arctic. AGM batteries due to their lack of free electrolyte will not crack and leak in these cold environments.

Gel cell batteries are used extensively in power wheelchairs, as the extremely low gas and acid output makes them much safer for indoor use.

SLA "Gel" cells are also the standard power source in sailplanes, due to their ability to withstand a variety of flight attitudes and a relatively large ambient temperature range with no adverse effects. Both AGM and Gel cells are commonly used in powered aerobatic aircraft, for the same reasons.

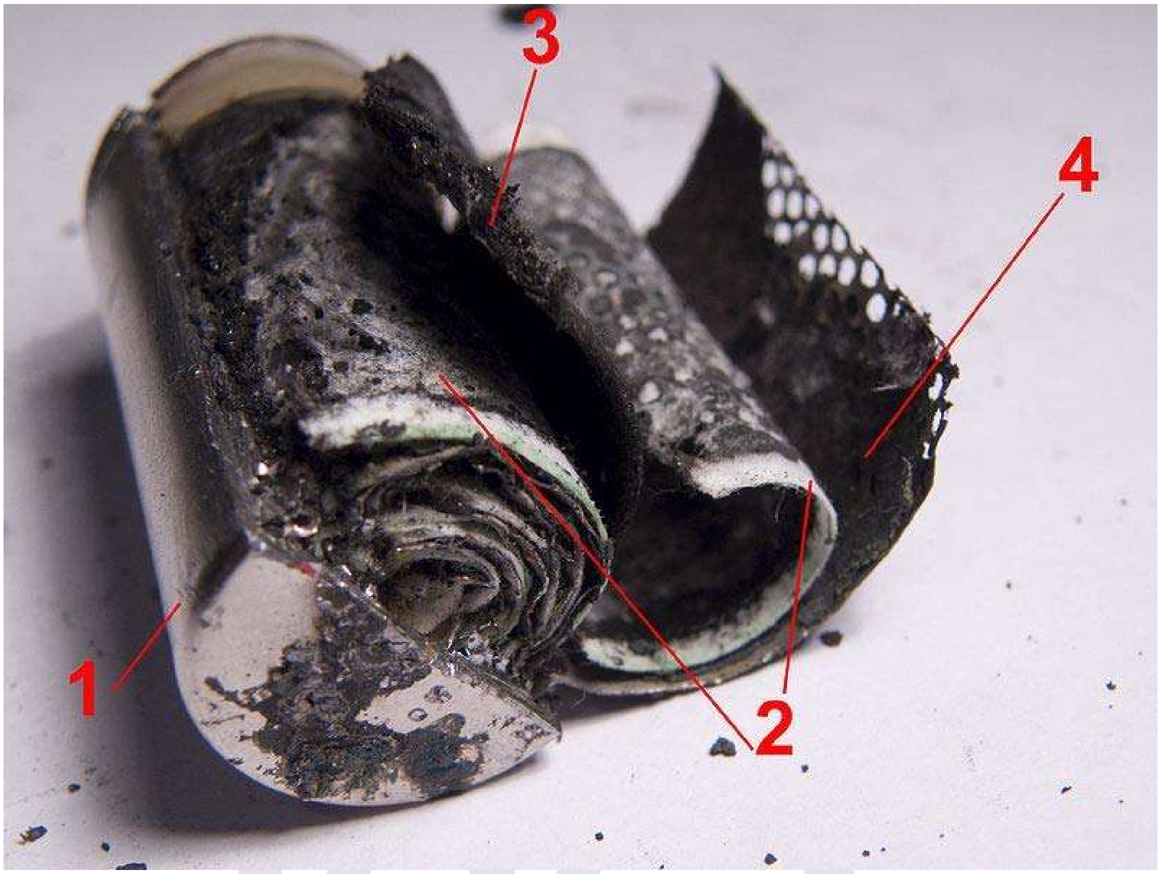
Chapter- 4

Nickel-Cadmium Battery

Nickel-cadmium battery

From top to bottom – "Gumstick", AA, and AAA NiCd batteries.

specific energy	40–60 Wh/kg
energy density	50–150 Wh/L
specific power	150W/kg
Charge/discharge efficiency	70%–90%
Energy/consumer-price	? US$ per Wh
Self-discharge rate	10%/month
Cycle durability	2,000 cycles
Nominal cell voltage	1.2 V



Disassembled Ni-Cd battery from cordless drill.1:outer metal casing (also negative terminal) 2: separator (between electrodes) 3: positive electrode 4: negative electrode with current collector (metal grid, connected to metal casing). Everything is rolled. Construction is very similar to NiMH cell.

Nickel-cadmium battery of a PSA Peugeot Citroën electric vehicle, Museum Autovision, Altlußheim, Germany

The **nickel-cadmium battery** (commonly abbreviated **NiCd** or **NiCad**) is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes.

The abbreviation *NiCad* is a registered trademark of SAFT Corporation, although this brand name is commonly used to describe all nickel-cadmium batteries. The abbreviation *NiCd* is derived from the chemical symbols of nickel (Ni) and cadmium (Cd).

Applications

Sealed NiCd cells may be used individually, or assembled into battery packs containing two or more cells. Small NiCd dry cells are used for portable electronics and toys, often using cells manufactured in the same sizes as primary cells. When NiCds are substituted for primary cells, the lower terminal voltage and smaller ampere-hour capacity may reduce performance as compared to primary cells. Miniature button cells are sometimes used in photographic equipment, hand-held lamps (flashlight or torch), computer-memory standby, toys, and novelties.

Specialty NiCd batteries are used in cordless and wireless telephones, emergency lighting, and other applications. With a relatively low internal resistance, a NiCd battery can supply high surge currents. This makes them a favourable choice for remote-controlled electric model airplanes, boats, and cars, as well as cordless power tools and camera flash units. Larger flooded cells are used for aircraft starting batteries, electric vehicles, and standby power.

Voltage

Nickel-cadmium cells have a nominal cell potential of 1.2 V. This is lower than the 1.5 V of alkaline and zinc-carbon primary cells, and consequently they are not appropriate as a replacement in all applications. However, the 1.5V of a primary alkaline cell refers to its initial, rather than average, voltage. Unlike alkaline and zinc-carbon primary cells, a NiCd cell's terminal voltage only changes a little as it discharges. Because many electronic devices are designed to work with primary cells that may discharge to as low as 0.90 to 1.0 V per cell, the relatively steady 1.2 V of a NiCd is enough to allow operation. Some would consider the near-constant voltage a drawback as it makes it difficult to detect when the battery charge is low.

NiCd batteries used to replace 9 V batteries usually only have six cells, for a terminal voltage of 7.2 volts. While most pocket radios will operate satisfactorily at this voltage, some manufacturers such as Varta made 8.4 volt batteries with seven cells for more critical applications.

12 V NiCd batteries are made up of 10 cells connected in series.

History

The first NiCd battery was created by Waldemar Jungner of Sweden in 1899. At that time, the only direct competitor was the lead-acid battery, which was less physically and chemically robust. With minor improvements to the first prototypes, energy density rapidly increased to about half of that of primary batteries, and significantly greater than lead-acid batteries. Jungner experimented with substituting iron for the cadmium in varying quantities, but found the iron formulations to be wanting. Jungner's work was largely unknown in the United States. Thomas Edison adapted the battery design where he introduced the nickel-iron battery to the US two years after Jungner had built one. In 1906, Jungner established a factory close to Oskarshamn, Sweden to produce flooded design NiCd batteries.

Production in the United States

The first production in the United States began in 1946. Up to this point, the batteries were "pocket type," constructed of nickel-plated steel pockets containing nickel and cadmium active materials. Around the middle of the twentieth century, sintered-plate NiCd batteries became increasingly popular. Fusing nickel powder at a temperature well below its melting point using high pressures creates sintered plates. The plates thus formed are highly porous, about 80 percent by volume. Positive and negative plates are produced by soaking the nickel plates in nickel- and cadmium-active materials, respectively. Sintered plates are usually much thinner than the pocket type, resulting in greater surface area per volume and higher currents. In general, the greater amount of reactive material surface area in a battery, the lower its internal resistance.

Recent developments

In the past few decades, NiCd batteries have had internal resistance as low as alkaline batteries. Today, all consumer NiCd batteries use the "swiss roll" or "jelly-roll" design. This design incorporates several layers of positive and negative material rolled into a cylindrical shape. This design reduces internal resistance as there is a greater amount of electrode in contact with the active material in each cell.

Popularity

Advances in battery-manufacturing technologies throughout the second half of the twentieth century have made batteries increasingly cheaper to produce. Battery-powered devices in general have increased in popularity. As of 2000, about 1.5 billion NiCd batteries were produced annually. Up until the mid 1990s, Ni-Cds had an overwhelming majority of the market share for rechargeable batteries in consumer electronics.

Battery characteristics

Comparison to other batteries

Recently, nickel-metal hydride (Ni-MH) and lithium-ion batteries (Li-ion) have become commercially available and cheaper, the former type now rivaling NiCd in cost. Where energy density is important, Ni-Cd batteries are now at a disadvantage compared to Ni-MH and Li-ion batteries. However, the Ni-Cd battery is still very useful in applications requiring very high discharge rates because the Ni-Cd can endure such discharge with no damage or loss of capacity, though recharging it without complete drain can have somewhat of the opposite effect.

Advantages

When compared to other forms of rechargeable battery, the NiCd battery has a number of distinct advantages.

- The batteries are more difficult to damage than other batteries, tolerating deep discharge for long periods. In fact, NiCd batteries in long-term storage are typically stored fully discharged. This is in contrast, for example, to lithium ion batteries, which are less stable and will be permanently damaged if discharged below a minimum voltage.

- NiCd batteries typically last longer, in terms of number of charge/discharge cycles, than other rechargeable batteries such as lead/acid batteries.

- Compared to lead-acid batteries, NiCd batteries have a much higher energy density. A NiCd battery is smaller and lighter than a comparable lead-acid battery. In cases where size and weight are important considerations (for example, aircraft), NiCd batteries are preferred over the cheaper lead-acid batteries.

- In consumer applications, NiCd batteries compete directly with alkaline batteries. A NiCd cell has a lower capacity than that of an equivalent alkaline cell, and costs more. However, since the alkaline battery's chemical reaction is not reversible, a reusable NiCd battery has a significantly longer total lifetime. There have been attempts to create rechargeable alkaline batteries, such as the rechargeable alkaline, or specialized battery chargers for charging single-use alkaline batteries, but none that has seen wide usage.

- The terminal voltage of a NiCd battery declines more slowly as it is discharged, compared with carbon-zinc batteries. Since an alkaline battery's voltage drops significantly as the charge drops, most consumer applications are well equipped to deal with the slightly lower NiCd voltage with no noticeable loss of performance.

- The capacity of a nickel cadmium battery is not significantly affected by very high discharge currents. Even with discharge rates as high as 50C, a nickel cadmium will provide very nearly its rated capacity. By contrast, a lead acid battery will only provide approximately half its rated capacity when discharged at a relatively modest 1.5C.

- Nickel-metal hydride (NiMH) batteries are the newest, and most similar, competitor to NiCd batteries. Compared to NiCd, NiMH batteries have a higher capacity and are less toxic, and are now more cost effective. However, a NiCd battery has a lower self-discharge rate (for example, 20% per month for a NiCd, versus 30% per month for a traditional NiMH under identical conditions), although low self-discharge NiMH batteries are now available, which have substantially lower self-discharge than either NiCd or traditional NiMH. This results in a preference for NiCd over NiMH in applications where the current draw on the battery is lower than the battery's own self-discharge rate (for example, television remote controls). In both types of cell, the self-discharge rate is highest for a full charge state and drops off somewhat for lower charge states. Finally, a similarly sized NiCd battery has a slightly lower internal resistance, and thus can achieve a higher maximum discharge rate (which can be important for applications such as power tools).

Disadvantages

The primary trade-off with NiCd batteries is their higher cost and the use of cadmium. They are more costly than lead-acid batteries because nickel and cadmium are more costly materials.

One of the NiCd's biggest disadvantages is that the battery exhibits a very marked negative temperature coefficient. This means that as the cell temperature rises, the internal resistance falls. This can pose considerable charging problems, particularly with the relatively simple charging systems employed for lead-acid type batteries. Whilst lead-acid batteries can be charged by simply connecting a dynamo to them, with a simple electromagnetic cut-out system for when the dynamo is stationary or an over-current occurs, the NiCd under a similar charging scheme would exhibit thermal runaway, where the charging current would continue to rise until the over-current cut-out operated or the battery destroyed itself. This is the principal factor that prevents its use as engine-starting batteries. Today with alternator-based charging systems with solid-state regulators, the construction of a suitable charging system would be relatively simple, but the car manufacturers are reluctant to abandon tried-and-tested technology.

Availability

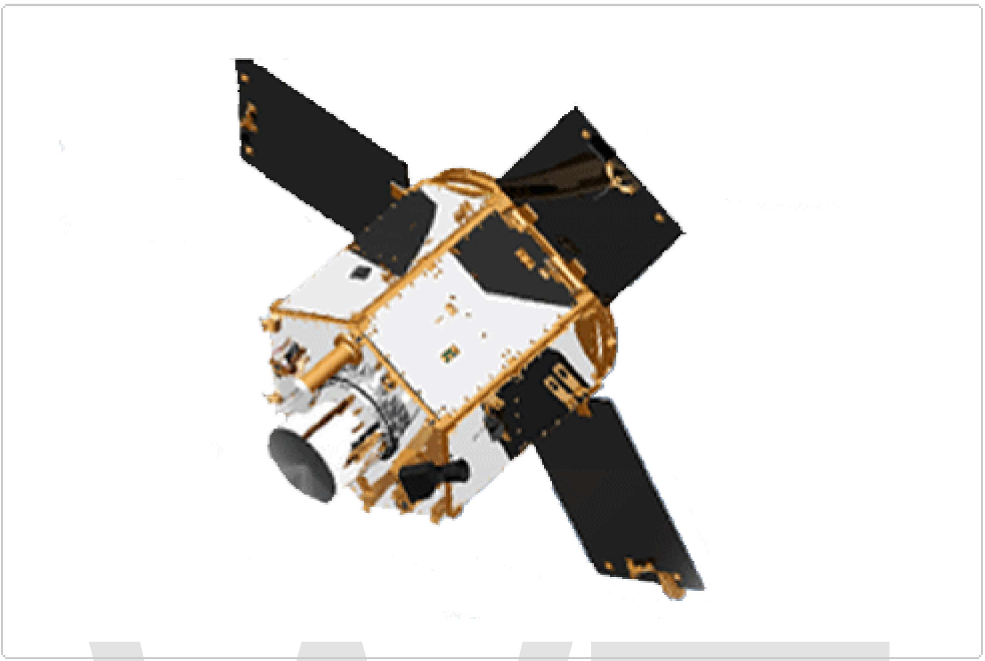
NiCd cells are available in the same sizes as alkaline batteries, from AAA through D, as well as several multi-cell sizes, including the equivalent of a 9 volt battery. A fully charged single NiCd cell, under no load, carries a potential difference of between 1.25 and 1.35 volts, which stays relatively constant as the battery is discharged. Since an alkaline battery near fully discharged may see its voltage drop to as low as 0.9 volts, NiCd cells and alkaline cells are typically interchangeable for most applications.

In addition to single cells, batteries exist that contain up to 300 cells (nominally 360 volts, actual voltage under no load between 380 and 420 volts). This many cells are mostly used in automotive and heavy-duty industrial applications. For portable applications, the number of cells is normally below 18 cells (24V). Industrial-sized flooded batteries are available with capacities ranging from 12.5Ah up to several hundred Ah.

Characteristics

The maximum discharge rate for a NiCd battery varies by size. For a common AA-size cell, the maximum discharge rate is approximately 18 amps; for a D size battery the discharge rate can be as high as 35 amps.

Model-aircraft or -boat builders often take much larger currents of up to a hundred amps or so from specially constructed small batteries, which are used to drive main motors. 5–6 minutes of model operation is easily achievable from quite small batteries, so a reasonably high power-to-weight figure is achieved, comparable to internal combustion motors, though of lesser duration.



The RazakSAT used NiCd

Charging

NiCd batteries can be charged at several different rates, depending on how the cell was manufactured. The charge rate is measured based on the percentage of the amp-hour capacity the battery is fed as a steady current over the duration of the charge. Regardless of the charge speed, more energy must be supplied to the battery than its actual capacity, to account for energy loss during charging, with faster charges being more efficient. For example, an "overnight" charge, might consist of supplying one tenth the amperehour rating (C/10) for 14–16 hours; that is, a 100 mAh battery takes 140 mAh to charge at this rate. At the rapid-charge rate, done at 100% of the rated capacity of the battery in 1 hour (1C), the battery holds roughly 80% of the charge, so a 100 mAh battery takes 120 mAh to charge (that is, approximately 1 hour and fifteen minutes). Some specialized NiCd cells can be charged in as little as 10–15 minutes at a 4C or 6C charge rate, but this is very uncommon. It also exponentially increases the risk of the cells overheating and venting due to an internal overpressure condition: the cell's rate of temperature rise is governed by its internal resistance and the square of the charging rate. At a 4C rate, the amount of heat generated in the cell is sixteen times higher than the heat at the 1C rate. The downside to faster charging is the higher risk of overcharging, which can damage the battery. and the increased temperatures the cell has to endure (which potentially shortens its life).

The safe temperature range for a NiCd battery in use is between −20°C and 45°C. During charging, the battery temperature typically stays low, around 0°C (the charging reaction absorbs heat), but as the battery nears full charge the temperature will rise to 45–50°C.

Some battery chargers detect this temperature increase to cut off charging and prevent over-charging.

When not under load or charge, a NiCd battery will self-discharge approximately 10% per month at 20°C, ranging up to 20% per month at higher temperatures. It is possible to perform a trickle charge at current levels just high enough to offset this discharge rate; to keep a battery fully charged. However, if the battery is going to be stored unused for a long period of time, it should be discharged down to at most 40% of capacity (some manufacturers recommend fully discharging and even short-circuiting once fully discharged), and stored in a cool, dry environment.

Inspecting

The battery should have no external damage, and depending on the number of cells it should have 1.3 –1.4 V per cell when fully charged and about 0.8–1 V when discharged.

Charge condition

High quality NiCd's have a thermal cut-off so if the battery gets too hot the charger stops. If a NiCd is still warm from discharging and been put on charge, it will not get the full charge possible. In that case, let the battery cool to room temperature, then charge. Watch for the correct polarity. Leave charger in a cool place when charging to get best results.

Charging method

A NiCd battery requires a charger with a slightly different voltage than for a lead-acid battery, especially if the NiCd has 11 or 12 cells. Also a charge termination method is needed if a fast charger is used. Often NiCd battery packs have a thermal cut-off inside that feeds back to the charger telling it to stop the charging once the battery has heated up and/or a voltage peaking sensing circuit. At room temperature during normal charge conditions the cell voltage increases from an initial 1.2 V to an end-point of about 1.45 V. The rate of rise increases markedly as the cell approaches full charge. The end-point voltage decreases slightly with increasing temperature.

Electrochemistry

A fully charged NiCd cell contains:

- a nickel(III) oxide-hydroxide positive electrode plate.
- a cadmium negative electrode plate.
- a separator.
- and an alkaline electrolyte (potassium hydroxide).

NiCd batteries usually have a metal case with a sealing plate equipped with a self-sealing safety valve. The positive and negative electrode plates, isolated from each other by the separator, are rolled in a spiral shape inside the case. This is known as the jelly-roll design and allows a NiCd cell to deliver a much higher maximum current than an equivalent size alkaline cell. Alkaline cells have a bobbin construction where the cell casing is filled with electrolyte and contains a graphite rod which acts as the positive electrode. As a relatively small area of the electrode is in contact with the electrolyte (as opposed to the jelly-roll design), the internal resistance for an equivalent sized alkaline cell is higher which limits the maximum current that can be delivered.

The chemical reactions in a NiCd battery during discharge are:

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

at the cadmium electrode, and

$$2\mathrm{NiO(OH)} + 2\mathrm{H}_2\mathrm{O} + 2\mathrm{e}^- \rightarrow 2\mathrm{Ni(OH)}_2 + 2\mathrm{OH}^-$$

at the nickel electrode. The net reaction during discharge is

$$2\mathrm{NiO(OH)} + \mathrm{Cd} + 2\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{Ni(OH)}_2 + \mathrm{Cd(OH)}_2.$$

During recharge, the reactions go from right to left. The alkaline electrolyte (commonly KOH) is not consumed in this reaction and therefore its Specific Gravity, unlike in lead-acid batteries, is not a guide to its state of charge.

When Jungner built the first NiCd batteries, he used nickel oxide in the positive electrode, and iron and cadmium materials in the negative. It was not until later that pure cadmium metal and nickel hydroxide were used. Until about 1960, the reaction in nickel-cadmium batteries was not completely understood. There were several speculations as to the reaction products. The debate was finally resolved by spectrometry, which revealed cadmium hydroxide and nickel hydroxide.

Another historically important variation on the basic nickel-cadmium cell is the addition of lithium hydroxide to the potassium hydroxide electrolyte. This was believed to prolong the service life by making the cell more resistant to electrical abuse. The nickel-cadmium battery in its modern form is extremely resistant to electrical abuse anyway, so this practice has been discontinued.

Problems with NiCd

Overcharging

Overcharging must be considered in the design of most rechargeable batteries. In the case of NiCds, there are two possible results of overcharging:

- If the negative electrode is overcharged, hydrogen gas is produced.

- If the positive electrode is overcharged, oxygen gas is produced.

For this reason, the negative electrode is always designed for a higher capacity than the positive, to avoid releasing hydrogen gas. There is still the problem of eliminating oxygen gas, to avoid rupture of the cell casing. NiCd cells are vented, with seals that fail at high internal gas pressures. The sealing mechanism must allow gas to escape from inside the cell, and seal again properly when the gas is expelled. This complex mechanism, unnecessary in alkaline batteries, contributes to their higher cost.

NiCd cells dealt with in here are of the sealed type. Cells of this type consist of a pressure vessel that is supposed to contain any generation of oxygen and hydrogen gasses until they can recombine back to water. Such generation typically occurs during rapid charge and discharge and exceedingly at overcharge condition. If the pressure exceeds the limit of the safety valve, water in the form of gas is lost. Since the vessel is designed to contain an exact amount of electrolyte this loss will rapidly affect the capacity of the cell and its ability to receive and deliver current. To detect all conditions of overcharge demands great sophistication from the charging circuit and a cheap charger will eventually damage even the best quality cells.

Cell reversal

Another potential problem is reverse charging. This can occur due to an error by the user, or more commonly, when a battery of several cells is fully discharged. Because there is a slight variation in the capacity of cells in a battery, one of the cells will usually be fully discharged before the others, at which point reverse charging begins seriously damaging that cell, reducing battery life. The by-product of reverse charging is hydrogen gas, which can be dangerous. Some commentators advise that one should never discharge multi-cell nickel-cadmium batteries to zero voltage; for example, incandescent lights should be turned off when they are yellow; before they go out completely.

A common form of this deprecation occurs when cells connected in series develop unequal voltages and discharge near zero voltage. The first cell that reaches zero is pushed beyond to negative voltage and gases generated open the seal and dry the cell.

In modern cells, an excess of *anti-polar material* (basically active material ballast at positive electrode) is inserted to allow for moderate negative charge without damage to the cell. This excess material slows down the start of oxygen generation at the negative plate. This means a cell can survive a negative voltage of about -0.2 to -0.4 volts. However if discharge is continued even further, this excess ballast is used up and both electrodes change polarity, causing destructive gassing (gas generation).

Battery packs with multiple cells in series should be operated well above 1 volt per cell to avoid placing the lowest capacity cell in danger of going negative. Battery packs that can be disassembled into cells should be periodically zeroed and charged individually to equalize the voltages. However, this does not help if old and new cells are mixed, since their different capacities will result in different discharge times and voltages.

Memory and lazy battery effects

NiCd batteries may suffer from a "memory effect" if they are discharged and recharged to the same state of charge hundreds of times. The apparent symptom is that the battery "remembers" the point in its charge cycle where recharging began and during subsequent use suffers a sudden drop in voltage at that point, as if the battery had been discharged. The capacity of the battery is not actually reduced substantially. Some electronics designed to be powered by NiCds are able to withstand this reduced voltage long enough for the voltage to return to normal. However, if the device is unable to operate through this period of decreased voltage, it will be unable to get enough energy out of the battery, and for all practical purposes, the battery appears "dead" earlier than normal.

There is controversy about whether the memory effect actually exists, or whether it is as serious a problem as is sometimes believed. Some critics claim it is used to promote competing NiMH batteries, which apparently do not suffer from it. Many NiCd battery manufacturers either deny the effect exists or are silent on the matter.

There is much evidence that the memory effect story originated from orbiting satellites, where they were typically charging for twelve hours out of twenty-four for several years. After this time, it was found that the capacities of the batteries had declined significantly, but were still perfectly fit for use. It is unlikely that this precise repetitive charging (e.g., 1000 charges / discharges with less than 2% variability) could ever be reproduced by consumers using electrical goods.

An effect with similar symptoms to the memory effect is the so-called *voltage depression* or *lazy battery effect*. (Some people use this term as a synonym for "memory effect".) This results from repeated overcharging; the symptom is that the battery appears to be fully charged but discharges quickly after only a brief period of operation. Larger cells may benefit from refilling with distilled water, or a complete electrolyte replacement. In rare cases, much of the lost capacity can be recovered by a few deep-discharge cycles, a function often provided by automatic NiCd battery chargers. However, this process may reduce the shelf life of the battery. If treated well, a NiCd battery can last for 1000 cycles or more before its capacity drops below half its original capacity.

Dendritic shorting

NiCd batteries, when not used regularly, tend to develop dendrites, which are thin, conductive crystals that may penetrate the separator membrane between electrodes. This leads to internal short circuits and premature failure, long before the 800–1000 charge/discharge cycle life claimed by most vendors. Sometimes, applying a brief, high-current charging pulse to individual cells can clear these dendrites, but they will typically reform within a few days or even hours. Cells in this state have reached the end of their useful life and should be replaced. Many battery guides, circulating on the Internet and online auctions, promise to restore dead cells using the above principle, but achieve very short-term results at best.

Environmental consequences of cadmium

NiCd batteries contain between 6% (for industrial batteries) and 18% (for consumer batteries) cadmium, which is a toxic heavy metal and therefore requires special care during battery disposal. In the United States, part of the price of a NiCd battery is a fee for its proper disposal at the end of its service lifetime. Under the so-called "batteries directive" (2006/66/EC), the sale of consumer nickel-cadmium batteries has now been banned within the European Union except for medical use; alarm systems; emergency lighting; and portable power tools. This last category is to be reviewed after 4 years. Under the same EU directive, used industrial nickel-cadmium batteries must be collected by their producers in order to be recycled in dedicated facilities.

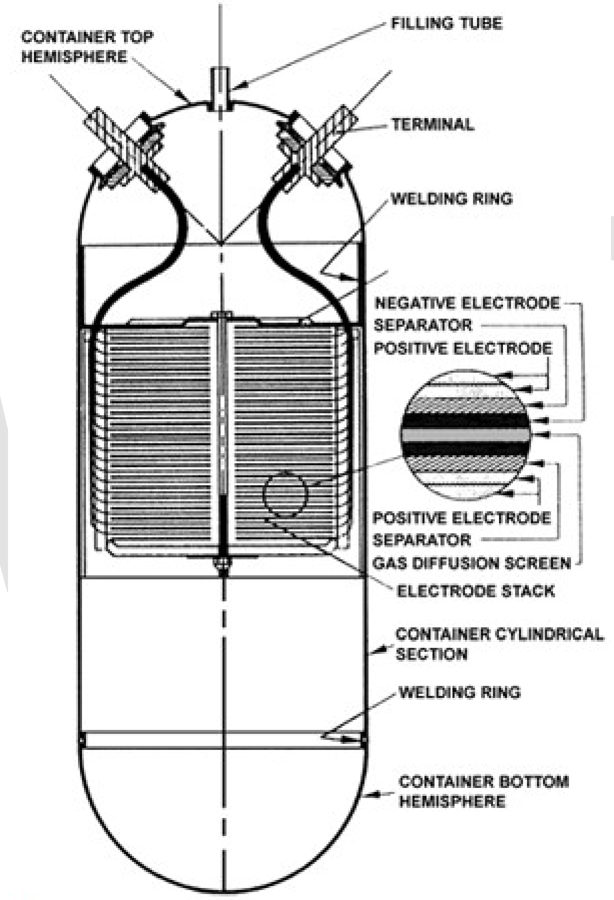
Cadmium, being a heavy metal, can cause substantial pollution when landfilled or incinerated. Because of this, many countries now operate recycling programs to capture and reprocess old NiCd batteries. However, it should be noted that the cadmium content of industrial batteries (approx 6%) is considerably lower than the heavy metal content which can be in excess of 60% in other technologies.

Safety

Manufacturers typically supply instructions for safe handling, use, and disposal of nickel-cadmium batteries. These warn against physically damaging the cells, short-circuiting when fully charged, and overcharging.

Chapter- 5

Nickel Hydrogen Battery



[D]

Figure 1. NiH2 CPV Positioned Vertically (only the upper of two stack sets is shown)

A **nickel hydrogen battery** (NiH_2 or $Ni\text{-}H_2$) is a rechargeable electrochemical power source based on nickel and hydrogen. The difference with a nickel-metal hydride battery is the use of hydrogen in a pressurized cell of up to 1200 psi (82.7 bar).

The cathode is made up of a dry sintered porous nickel plaque, which contains nickel hydroxide, the negative hydrogen electrode utilises a teflon-bonded platinum black catalyst, the separator is Zircar tricot knit zirconia cloth type ZYK-15.

NiH_2 cells using 26% potassium hydroxide (KOH) as an electrolyte have shown a service life of 15 years or more at 80% depth of discharge (DOD) The energy density is 75 Wh/kg, 60 Wh/dm^3 specific power 220 W/kg. The open-circuit voltage is 1.55 V, discharge voltage 1.25 V, and the voltage under load 1.5 V. The cells handle more than 20,000 charge cycles on 85% efficiency.

NiH_2 rechargeable batteries possess good electrical properties which make them attractive for the energy storage of electrical energy in satellites and space probes. For example, the ISS, Mars Odyssey and the Mars Global Surveyor are equipped with nickel-hydrogen batteries. The Hubble Space Telescope, when its original batteries were changed in May 2009 more than 19 years after launch, led with the highest number of charge/discharge cycles of any NiH_2 battery in low earth orbit.

History

The development of the nickel hydrogen battery started in 1970 at Comsat and was used for the first time in 1977 aboard the U.S. Navy's Navigation technology satellite-2 (NTS-2).

Designs

Individual pressure vessel

The individual pressure vessel (IPV) design consists of a single unit of NiH_2 cells in a pressure vessel.

Common pressure vessel

The common pressure vessel (CPV) design consist of two NiH_2 cell stacks in series in a common pressure vessel. The CPV provides a slightly higher specific energy than the IPV.

Single pressure vessel

The single pressure vessel (SPV) design combines up to 22 cells in series in a single pressure vessel.

Bipolar

The bipolar design is based on thick electrodes, positive-to-negative back-to-back stacked in a SPV.

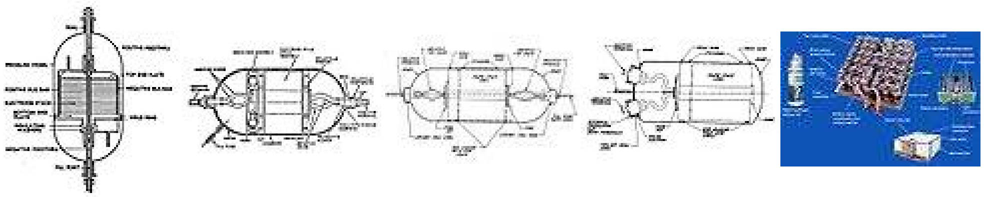
Dependent pressure vessel

The dependent pressure vessel (DPV) cell design offers higher specific energy and reduced cost .

Common/dependent-pressure-vessel

The common/dependent pressure vessel (C/DPV) is a hybrid of the common pressure vessel (CPV) and the dependent pressure vessel (DPV) with a high volumetric efficiency.

Schematics



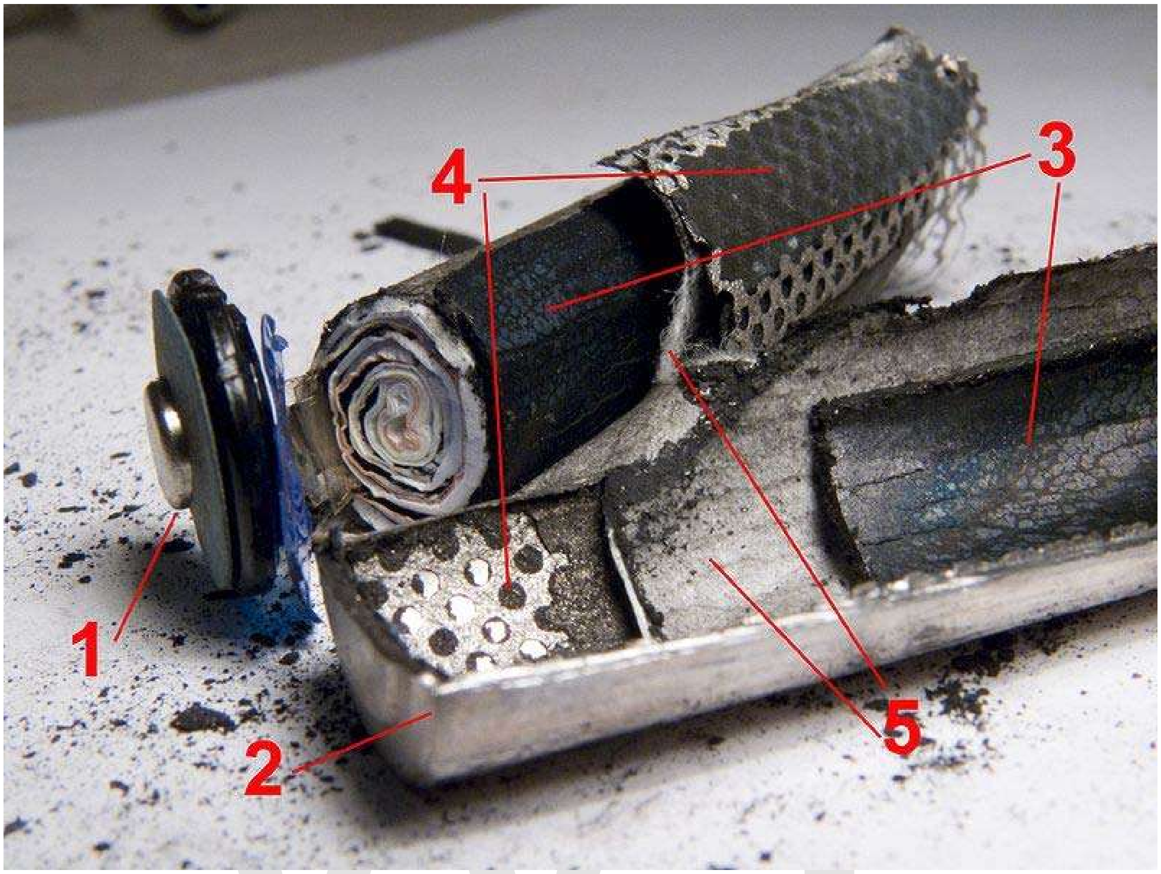
Chapter- 6

Nickel-Metal Hydride Battery

Nickel-metal hydride battery

Modern, high capacity NiMH rechargeable cells

specific energy	30–80(100) W·h/kg
energy density	140–300(385) W·h/L
specific power	250–1000 W/kg
Charge/discharge efficiency	66%
Energy/consumer-price	2.75(0.75-1) W·h/US$
Self-discharge rate	30%(1-2%)/month (temperature dependent)
Cycle durability	500–1,000(1500)
Nominal cell voltage	1.2 V



Disassembled NiMH AA cell:
1 - Positive terminal
2 - Outer metal casing (also negative terminal)
3 - Positive electrode
4 - Negative electrode with current collector (metal grid, connected to metal casing)
5 - Separator (between electrodes).

A **nickel-metal hydride cell**, abbreviated **NiMH**, is a type of rechargeable battery similar to the nickel-cadmium cell. The NiMH battery uses a hydrogen-absorbing alloy for the negative electrode instead of cadmium. As in NiCd cells, the positive electrode is nickel oxyhydroxide (NiOOH). A NiMH battery can have two to three times the capacity of an equivalent size nickel-cadmium battery. Compared to the lithium-ion cell, the volumetric energy density is similar but self-discharge is higher. (Compare: low self-discharge NiMH battery)

Common AA cells (penlight-size) NiMH batteries have nominal charge capacities (*C*) ranging from 1100 mA·h to 3100 mA·h at 1.2 V, measured at rate that discharges the cell in five hours. Useful discharge capacity is a decreasing function of the discharge rate, but up to a rate of around 1×*C* (full discharge in one hour), it does not differ significantly from the nominal capacity.

The specific energy for NiMH material is approximately 70 W·h/kg (250 kJ/kg), compared to 40–60 W·h/kg for Ni-Cd, or 100-160 W·h/kg for Li-ion. NiMH has a volumetric energy density of about 300 W·h/L (1080 MJ/m³), significantly better than nickel-cadmium at 50–150 Wh/L, and about the same as Li-ion at 250-360 W·h/L.

History

The first consumer grade NiMH cells for smaller applications appeared on the market in 1989, the culmination of over two decades of research and development.

The earliest pioneering work on NiMH batteries — essentially based on sintered Ti2Ni+TiNi+x alloys for the negative electrode and NiOOH-electrodes for the positives — was performed at the Battelle-Geneva Research Center starting after its invention in 1967. The development work was sponsored over nearly two decades by Daimler-Benz in Stuttgart, Germany, and by Volkswagen AG within the framework of Deutsche Automobilgesellschaft. The batteries showed high specific energy up to 50 W·h/kg (180 kJ/kg), power density up to 1000 W/kg and a reasonable deep cycle life of 500 cycles (DOD=100%). Patent applications were filed in European countries (priority: Switzerland), United States and Japan and the patents transferred to Daimler-Benz.

Interest grew in the 1970s with the commercialisation of the Nickel hydrogen battery for satellite applications. Hydride technology promised an alternative much less bulky way to store the hydrogen. Research carried out by Philips Laboratories and France's CNRS developed new high-energy hybrid alloys incorporating rare earth metals for the negative electrode. However, these suffered from the instability of the alloys in alkaline electrolyte and consequently insufficient cycle life.

Ovonic Battery Co. in Michigan altered and improved the Ti-Ni alloy structure and composition according to their patent and licensed NiMH batteries to over 50 companies worldwide. The "invented NiMH variation" of Ovonics consisted in special alloys with disordered alloy structure and specific multicomponent alloy compositions. Unfortunately linked to their composition, calendar and cycle life of such alloys always remain very low, and all NiMH batteries manufactured at the present time consist of AB_5-type rare earth metal alloys.

Positive electrode development was done by Dr. Masahiko Oshitani from GS Yuasa Company, who was the first to develop high-energy paste electrode technology. The association of this high-energy electrode with high-energy hybrid alloys for the negative electrode led to the new environmentally friendly high-energy NiMH cell.

Currently, more than 2 million hybrid cars worldwide are running with NiMH batteries, e.g., Prius, Lexus (Toyota), Civic, Insight (Honda), Fusion (Ford), and others. Many of these batteries are manufactured by PEVE (Panasonic) and Sanyo.

Applications

High power Ni-MH Battery of Toyota NHW20 Prius, Japan

Nickel-metal hydride battery made by VARTA, Museum Autovision, Altlussheim, Germany

Applications of NiMH electric vehicle batteries includes all-electric plug-in vehicles such as the General Motors EV1, Honda EV Plus, Ford Ranger EV and Vectrix scooter. Hybrid vehicles such as the Toyota Prius, Honda Insight, Ford Escape Hybrid, Chevrolet Malibu Hybrid, and Honda Civic Hybrid also use them. NiMH technology is used extensively in rechargeable batteries for consumer electronics, and it will also be used on the Alstom Citadis low floor tram ordered for Nice, France; as well as the humanoid prototype robot ASIMO designed by Honda.

Electrochemistry

The negative electrode reaction occurring in a NiMH cell is

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

The charge reaction is read left-to-right and the discharge reaction is read right-to-left.

On the positive electrode, nickel oxyhydroxide (NiOOH) is formed,

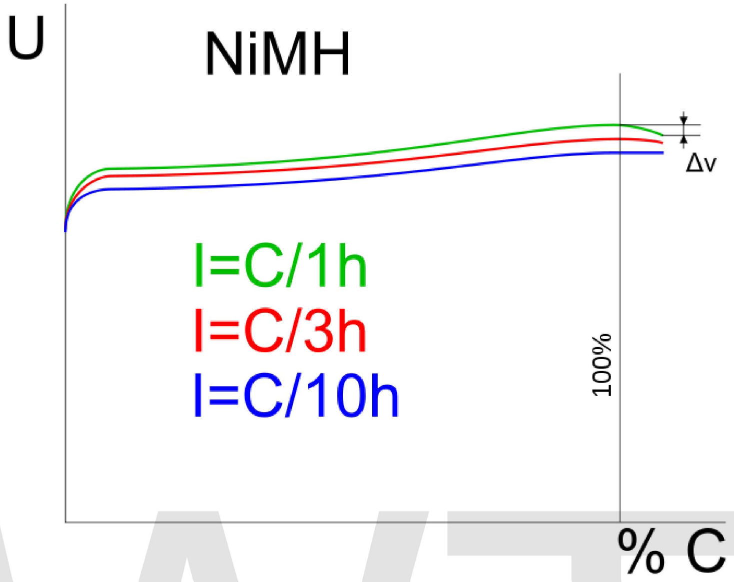
$$\mathrm{Ni(OH)_2 + OH^- \leftrightharpoons NiO(OH) + H_2O + e^-}$$

The "metal" M in the negative electrode of a NiMH cell is actually an intermetallic compound. Many different compounds have been developed for this application, but those in current use fall into two classes. The most common is AB_5, where A is a rare earth mixture of lanthanum, cerium, neodymium, praseodymium and B is nickel, cobalt, manganese, and/or aluminium. Very few cells use higher-capacity negative material electrodes based on AB_2 compounds, where A is titanium and/or vanadium and B is zirconium or nickel, modified with chromium, cobalt, iron, and/or manganese, due to the reduced life performances. Any of these compounds serve the same role, reversibly forming a mixture of metal hydride compounds.

When overcharged at low rates, oxygen produced at the positive electrode passes through the separator and recombines at the surface of the negative. Hydrogen evolution is suppressed and the charging energy is converted to heat. This process allows NiMH cells to remain sealed in normal operation and to be maintenance-free.

NiMH cells have an alkaline electrolyte, usually potassium hydroxide. For separation hydrophilic polyolefin nonwovens are used.

Charging



NiMH Charge curve

The charging voltage is in the range of 1.4–1.6 V/cell. In general, a constant-voltage charging method cannot be used for automatic charging. When fast-charging, it is advisable to charge the NiMH cells with a smart battery charger to avoid overcharging, which can damage cells and cause dangerous conditions. A NiCd charger should not be used as an automatic substitute for a NiMH charger.

Δ*V* charging method

According to Panasonic and other NiMH cell manufacturers, the Δ*V* method is one of the preferred methods for charging. The charger measures the rate of change (signified by the symbol Δ) of the voltage of the cell (signified by the letter *V*). This is illustrated in the "NiMH charge curve" figure. The cell or battery is rapidly charged at a constant current of 1 *C*/h, where *C* is the capacity of the battery (the capacity is expressed in ampere hours, or more commonly milliampere hours - mA·h). After the cell is fully charged, and as it begins to overcharge, the voltage polarity of the electrodes inside the battery will begin to reverse, and this will cause the battery voltage to decrease slightly. A Δ*V* type battery charger ends the charge cycle by switching off the charging current when it senses this drop in voltage. In some cases, a very small "trickle charge" may remain. The "charge curve" graph also shows that the charge voltage will change depending on the charge current (it also changes with temperature and battery age). This generally means that a constant-voltage charging method cannot be used automatically, because it will either be unsafe, or it will not charge batteries reliably and consistently. This is unlike a lead-acid cell for example, which can, in theory, be more easily charged at a suitably chosen constant voltage.

ΔT temperature charging method

The ΔT temperature change method is similar in principle to the ΔV method. Because the charging voltage is nearly constant, constant-current charging delivers energy at a near-constant rate. When the cell is not fully charged, most of this energy is converted to chemical energy. However, when the cell reaches full charge, most of the charging energy is converted to heat. This increases the rate of change of battery temperature, which can be detected by a sensor.

Trickle charging

Some equipment manufacturers consider that NiMH cells can be safely charged in simple fixed, low-current chargers with or without timers, and that permanent overcharging is permissible with currents up to 0.1 *C* (where *C* is the current equivalent to the capacity of the battery divided by one hour). According to the Panasonic NiMH charging manual, extensive trickle charging can cause battery deterioration due to overcharging, and it is the least preferred charging method concerning battery performance. If it is used, the trickle charge rate should be limited to between 0.033 *C* and 0.05 *C* for a maximum of 20 hours to avoid damaging the batteries.

For a slow charge, or "trickle charge" process, Duracell recommends "a maintenance charge of indefinite duration at 0.0033 *C*". Some chargers do this after the charge cycle, to offset the natural self-discharge rate of the battery. To maximize battery life, the preferred charge method of NiMH cells uses low duty cycle pulses of high current rather than continuous low current.

Safety

ni-mh which popped its cap due to failed safety valve

A good safety feature of a custom-built charger is to use a resettable fuse in series with the cell, particularly of the bimetallic strip type. This fuse will open if either the current or the temperature goes too high.

Modern NiMH cells contain catalysts to immediately deal with gases developed as a result of over-charging without being harmed ($2\ H_2 + O_2$ ---catalyst → $2\ H_2O$). However, this only works with overcharging currents of up to $0.1C$ (nominal capacity divided by 10 hours). As a result of this reaction, the batteries will heat up considerably, marking the end of the charging process. Some quick chargers have a fan to keep the batteries cool.

A method for very rapid charging called in-cell charge control involves an internal pressure switch in the cell, which disconnects the charging current in the event of overpressure.

There is an inherent risk with NiMH chemistry that overcharging will cause a buildup of hydrogen, causing the cell to rupture. Therefore, cells have a vent. Hydrogen will be emitted from the vent in the event of serious overcharging.

Discharging

A fully-charged cell measures 1.4–1.45 V (unloaded) , and supplies a nominal average 1.25 V/cell during discharge, down to about 1.0–1.1 V/cell (further discharge may cause permanent damage in the case of multi-cell packs, due to polarity reversal). This voltage varies depending on the discharge rate of the cell (lower discharge loads result in an increased voltage output for longer periods, approaching the 1.4 V unloaded cell voltage).

Under a light load (0.5 ampere), the starting voltage of a freshly charged AA NiMH cell in good condition is about 1.4 volts; some measure almost 1.5 volts . This voltage falls rapidly to about 1.25 volts at 10% depth of discharge (DOD) and then remains almost constant until the cell is over 80% discharged. The voltage then falls rapidly from about 1.2 volts down to 0.8–1.0 volts at which the cell is considered "flat" in most devices. Mid-discharge at a load of 1 ampere, the output is about 1.2 volts; at 2 amperes, about 1.15 volts; the total effective differential internal resistance is about 0.05 ohms. Nickel metal hydride batteries provide a relatively constant voltage for most of the discharge cycle, unlike a standard alkaline where the voltage falls steadily during discharge.

Over-discharging

A complete discharge of a cell until it goes into polarity reversal can cause permanent damage to the cell. This situation can occur in the common arrangement of four AA cells in series in a digital camera, where one will be completely discharged before the others due to small differences in capacity among the cells. When this happens, the good cells will start to drive the discharged cell in reverse, which can cause permanent damage to that cell. Some cameras, GPS receivers and PDAs detect the safe end-of-discharge voltage of the series cells and auto-shutdown, but devices like flashlights and some toys do not. A single cell driving a load can't suffer from polarity reversal, because there are no other cells to reverse-charge it when it becomes discharged.

Irreversible damage from polarity reversal is a particular danger in systems, even when a low voltage threshold cutout is employed, where cells in the battery are of different temperatures. This is because the capacity of NiMH cells significantly declines as the cells are cooled. This results in a lower voltage under load of the colder cells.

Self-discharge

NiMH cells historically had a somewhat higher self-discharge rate (equivalent to internal leakage) than NiCd cells. The self-discharge is 5–10% on the first day and stabilizes around 0.5–1% per day at room temperature. This is not a problem in the short term but makes them unsuitable for many light-duty uses, such as clocks, remote controls, or safety devices, where the battery would normally be expected to last many months or years. The rate is strongly affected by the temperature at which the batteries are stored with cooler storage temperatures leading to slower discharge rate and longer battery life. The highest capacity cells on the market (>8000 mA·h) are reported to have the highest self-discharge rates.

Low self-discharge cells

A new type of nickel-metal hydride cell was introduced in 2005 that reduces self-discharge and therefore lengthens shelf life. By using a new separator, manufacturers claim the cells retain 70% to 85% of their capacity after one year when stored at 20 °C (68 °F). These cells are marketed as "hybrid", "ready-to-use" or "pre-charged" rechargeables. Besides the longer shelf life, they are otherwise similar to normal NiMH batteries of equivalent capacity and can be charged in typical NiMH chargers.

Low self-discharge cells have lower capacity than some standard NiMH cells due to the larger area of the separator. The highest capacity low-self-discharge cells have 2000–2450 mA·h and 850 mA·h capacities for AA and AAA cells respectively, compared to 2800 mA·h and 1000 mA·h for standard AA and AAA cells. C types are typically higher than their usual NiMH cousins, with 4000 mA·h and the D type being 8000 mA·h.

However, after only a few weeks of storage, the retained capacity of low-self-discharge batteries often exceeds that of traditional NiMH batteries of higher capacity.

Environmental impact

Improper disposal of NiMH batteries poses less environmental hazard than that of NiCd because of the absence of toxic cadmium. However, mining and processing the various alternate metals that form the negative electrode may be expected to pose other types of environmental impact, depending on the metal, mining method, and environmental practices of the mine.

Most industrial nickel is recycled, due to the relatively easy retrieval of the metal from scrap, and due to its high value.

Comparison with other battery types

NiMH cells and chargers are readily available in retail stores in the common sizes AAA and AA. Adapter sleeves are available to use the more common AA size in C and D applications. The sizes C and D cells are somewhat available, but are often just a AA core hidden in an outer shell, with a rating of about 2500 mA·h, much less than ordinary alkaline C and D batteries. Real NiMH C and D batteries are expensive (and the chargers are uncommon); they should be rated at least 5000 mA·h for C and 10,000 mA·h for D sizes.

PP3 (nine volt) NiMH batteries are available; these usually have an output voltage of 8.4 V (1.2 × 7) and a capacity of roughly 200 mA·h. Also available are eight-cell nine volt batteries with a nominal output voltage of 9.6 V (1.2 × 8).

NiMH cells are not expensive, and the voltage and performance is similar to primary alkaline cells in those sizes; they can be substituted for most purposes. Although alkaline cells are rated at 1.5 volts and NiMH cells at 1.2 volts, during discharge the alkaline voltage eventually drops below that of NiMH. NiMH batteries offer a flatter discharge curve, particularly at higher current draw.

NiMH cells are often used in digital cameras and other high drain devices, where over the duration of single charge use they outperform primary (such as alkaline) batteries. Applications that require frequent replacement of the battery, such as toys or video game controllers, also benefit from use of rechargeable batteries. With the development of low self-discharge NiMHs, many occasional-use and very low-power applications are now candidates for NiMH cells.

NiMH cells are particularly advantageous for high current drain applications, due in large part to their low internal resistance. Alkaline batteries, which might have approximately 3000 mA·h capacity at low current demand (200 mA), will have about 700 mA·h capacity with a 1000 mA load. Digital cameras with LCDs and flashlights can draw over 1000 mA, quickly depleting alkaline batteries. NiMH cells can deliver these current levels and maintain their full capacity.

Certain devices that were designed to operate using primary alkaline chemistry (or zinc-carbon/chloride) cells will not function when one uses NiMH cells as substitutes. However, this is rare, as most devices compensate for the voltage drop of an alkaline as it discharges down to about 1 volt. A good-quality freshly charged NiMH cell delivers 1.4–1.45 V, very close to the 1.5 V that these devices expect. Such devices would also likely have an extremely short runtime as the voltage from an alkaline falls to 1.4 V quite quickly from the 1.5 V starting voltage. Low internal resistance allows NiMH cells to deliver a near-constant voltage until they are almost completely discharged. This will cause a battery level indicator to overstate the remaining charge if it was designed to read only the voltage curve of alkaline cells. The voltage of alkaline cells decreases steadily during most of the discharge cycle.

Lithium ion batteries have a higher specific energy than nickel-metal hydride batteries, but they also have a much lower shelf-life and are significantly more expensive to produce. In October 2009, ECD Ovonics announced that their next-generation NiMH batteries will provide specific energy and power that are comparable to those of lithium ion batteries at a cost that is significantly lower than the cost of lithium ion batteries.

Patent encumbrance in electric vehicles

Stanford R. Ovshinsky invented and patented the NiMH battery and founded Ovonic Battery Company in 1982. General Motors purchased the patent from Ovonics in 1994. By the late 1990s, NiMH batteries were being used successfully in many fully electric vehicles, such as the General Motors EV1 and Dodge Caravan EPIC minivan. In October 2000, the patent was sold to Texaco and a week later Texaco was acquired by Chevron. Chevron's Cobasys subsidiary will only provide these batteries to large OEM orders. General Motors shut down production of the EV1 citing lack of battery availability as one of their chief obstacles. The Cobasys control of NiMH batteries has created a patent encumbrance of large automotive NiMH batteries.

Chapter- 7

Lithium-Ion Battery

Lithium-ion battery

Nokia Li-ion battery for powering a mobile phone

specific energy	100-250 W·h/kg (0.36-0.90 MJ/kg)
energy density	250-620 W·h/L (0.90-2.23 MJ/L)
specific power	~250-~340 W/kg
Charge/discharge efficiency	80-90%
Energy/consumer-price	2.5 Wh/US$
Self-discharge rate	8% at 21 °C 15% at 40 °C 31% at 60 °C (per month)
Cycle durability	400-1200 cycles

Nominal cell voltage	3.6 / 3.7 V

A **lithium-ion battery** (sometimes **Li-ion battery** or **LIB**) is a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging. Chemistry, performance, cost, and safety characteristics vary across LIB types. Unlike lithium primary batteries (which are disposable), lithium-ion electrochemical cells use an intercalated lithium compound as the electrode material instead of metallic lithium.

Lithium-ion batteries are common in consumer electronics. They are one of the most popular types of rechargeable battery for portable electronics, with one of the best energy densities, no memory effect, and a slow loss of charge when not in use. Beyond consumer electronics, LIBs are also growing in popularity for military, electric vehicle, and aerospace applications. Research is yielding a stream of improvements to traditional LIB technology, focusing on energy density, durability, cost, and intrinsic safety.

Charge and discharge

During discharge, lithium ions Li^+ carry the current from the negative to the positive electrode, through the non-aqueous electrolyte and separator diaphragm.

During charging, an external electrical power source (the charging circuit) applies a higher voltage (but of the same polarity) than that produced by the battery, forcing the current to pass in the reverse direction. The lithium ions then migrate from the positive to the negative electrode, where they become embedded in the porous electrode material in a process known as intercalation.

Construction

Cylindrical 18650 cell before closing

The three primary functional components of a lithium-ion battery are the anode, cathode, and electrolyte. The anode of a conventional lithium-ion cell is made from carbon, the cathode is a metal oxide, and the electrolyte is a lithium salt in an organic solvent.

The most commercially popular anode material is graphite. The cathode is generally one of three materials: a layered oxide (such as lithium cobalt oxide), a polyanion (such as lithium iron phosphate), or a spinel (such as lithium manganese oxide).

The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions. These non-aqueous electrolytes generally use non-coordinating anion salts such as lithium hexafluorophosphate ($LiPF_6$), lithium hexafluoroarsenate monohydrate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), and lithium triflate ($LiCF_3SO_3$).

Depending on materials choices, the voltage, capacity, life, and safety of a lithium-ion battery can change dramatically. Recently, novel architectures using nanotechnology have been employed to improve performance.

Pure lithium is very reactive. It reacts vigorously with water to form lithium hydroxide and hydrogen gas is liberated. Thus a non-aqueous electrolyte is typically used, and a sealed container rigidly excludes water from the battery pack.

Lithium ion batteries are more expensive than NiCd batteries but operate over a wider temperature range with higher energy densities, while being smaller and lighter. They are fragile and so need a protective circuit to limit peak voltages.

Formats

Nissan Leaf's lithium-ion battery pack

Li-Ion cells are available in various formats, which can generally be divided into four groups:

- Small cylindrical (solid body without terminals, such as those used in laptop batteries)
- Large cylindrical (solid body with large threaded terminals)
- Pouch (soft, flat body, such as those used in cell phones)
- Prismatic (semi-hard plastic case with large threaded terminals, often used in vehicles' traction packs)

The lack of case gives pouch cells the highest energy density; however, pouch cells (and prismatic cells) require an external means of containment to prevent expansion when their SOC level is high.

History

Varta Lithium-ion battery, Museum Autovision, Altlussheim, Germany

Lithium-ion batteries were first proposed by M.S. Whittingham at Binghamton University, at Exxon, in the 1970s. Whittingham used titanium(II) sulfide as the cathode and lithium metal as the anode.

The electrochemical properties of lithium intercalation in graphite were first discovered in 1980 by Rachid Yazami et al., at the Grenoble Institute of Technology (INPG) and French National Centre for Scientific Research (CNRS) in France. They showed the reversible intercalation of lithium into graphite in a lithium/polymer electrolyte/graphite half cell. Their work was published in 1982 and 1983. It covered both thermodynamics (staging) and kinetics (diffusion) together with reversibility.

Primary lithium batteries in which the anode is made from metallic lithium pose safety issues. As a result, lithium-ion batteries were developed in which both anode and cathode are made of a material containing lithium ions. In 1981, Bell Labs developed a workable graphite anode to provide an alternative to the lithium metal battery. Following cathode research performed by a team led by John Goodenough, in 1991 Sony released the first commercial lithium-ion battery. Their cells used layered oxide chemistry, specifically lithium cobalt oxide.

In 1983, Dr. Michael Thackeray, Goodenough, and coworkers identified manganese spinel as a cathode material. Spinel showed great promise, given low-cost, good electronic and lithium ion conductivity, and three-dimensional structure which gives it good structural stability. Although pure manganese spinel fades with cycling, this can be overcome with chemical modification of the material. Manganese spinel is currently used in commercial cells.

In 1989, Goodenough and Arumugam Manthiram of the University of Texas at Austin showed that cathodes containing polyanions, e.g. sulfates, produce higher voltages than oxides due to the inductive effect of the polyanion.

In 1996, Goodenough, Akshaya Padhi and coworkers identified lithium iron phosphate ($LiFePO_4$) and other phospho-olivines (lithium metal phosphates with olivine structure) as cathode materials.

In 2002, Yet-Ming Chiang and his group at MIT showed a substantial improvement in the performance of lithium batteries by boosting the material's conductivity by doping it with aluminum, niobium and zirconium. The exact mechanism causing the increase became the subject of a debate.

In 2004, Chiang again increased performance by utilizing iron-phosphate particles of less than 100 nanometers in diameter. This decreased particle density by almost one hundredfold, increased the cathode's surface area and improved capacity and performance. Commercialization led to a competitive market and a patent infringement battle between Chiang and Goodenough.

Electrochemistry

The three participants in the electrochemical reactions in a lithium-ion battery are the anode, cathode, and electrolyte.

Both the anode and cathode are materials into which, and from which, lithium can migrate. During *insertion* (or *intercalation*) lithium moves into the electrode. During the reverse process, *extraction* (or *deintercalation*), lithium moves back out. When a lithium-based cell is discharging, the lithium is extracted from the anode and inserted into the cathode. When the cell is charging, the reverse occurs.

Useful work can only be extracted if electrons flow through a closed external circuit. The following equations are in units of moles, making it possible to use the coefficient x.

The positive electrode half-reaction (with charging being forwards) is:

$$\mathrm{LiCoO_2} \leftrightarrows \mathrm{Li}_{1-x}\mathrm{CoO_2} + x\mathrm{Li}^+ + x\mathrm{e}^-$$

The negative electrode half-reaction is:

$$x\mathrm{Li}^+ + x\mathrm{e}^- + 6\mathrm{C} \leftrightarrows \mathrm{Li_xC_6}$$

The overall reaction has its limits. Overdischarge supersaturates lithium cobalt oxide, leading to the production of lithium oxide, possibly by the following irreversible reaction:

$$\mathrm{Li}^+ + \mathrm{LiCoO_2} \rightarrow \mathrm{Li_2O} + \mathrm{CoO}$$

Overcharge up to 5.2 Volts leads to the synthesis of cobalt(IV) oxide, as evidenced by x-ray diffraction

$$\mathrm{LiCoO_2} \rightarrow \mathrm{Li}^+ + \mathrm{CoO_2}$$

In a lithium-ion battery the lithium ions are transported to and from the cathode or anode, with the transition metal, cobalt (Co), in $\mathrm{Li}_x\mathrm{CoO_2}$ being oxidized from Co^{3+} to Co^{4+} during charging, and reduced from Co^{4+} to Co^{3+} during discharge.

Positive electrodes

Electrode material	Average potential difference	Specific capacity	Specific energy
$\mathrm{LiCoO_2}$	3.7 V	140 mA·h/g	0.518 kW·h/kg
$\mathrm{LiMn_2O_4}$	4.0 V	100 mA·h/g	0.400 kW·h/kg
$\mathrm{LiNiO_2}$	3.5 V	180 mA·h/g	0.630 kW·h/kg
$\mathrm{LiFePO_4}$	3.3 V	150 mA·h/g	0.495 kW·h/kg
$\mathrm{Li_2FePO_4F}$	3.6 V	115 mA·h/g	0.414 kW·h/kg
$\mathrm{LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2}$	3.6 V	160 mA·h/g	0.576 kW·h/kg
$\mathrm{Li(Li}_a\mathrm{Ni}_x\mathrm{Mn}_y\mathrm{Co}_z\mathrm{)O_2}$	4.2 V	220 mA·h/g	0.920 kW·h/kg

Negative electrodes

Electrode material	Average potential difference	Specific capacity	Specific energy
Graphite ($\mathrm{LiC_6}$)	0.1-0.2 V	372 mA·h/g	0.0372-0.0744 kW·h/kg
Hard Carbon ($\mathrm{LiC_6}$)	? V	? mA·h/g	? kW·h/kg
Titanate ($\mathrm{Li_4Ti_5O_{12}}$)	1-2 V	160 mA·h/g	0.16-0.32 kW·h/kg
Si ($\mathrm{Li_{4.4}Si}$)	0.5-1 V	4212 mA·h/g	2.106-4.212 kW·h/kg

Ge ($Li_{4.4}Ge$)	0.7-1.2 V	1624 mA·h/g	1.137-1.949 kW·h/kg

Electrolytes

The cell voltages given in the Electrochemistry section are larger than the potential at which aqueous solutions can electrolyze, in addition lithium is highly reactive to water, therefore, nonaqueous or aprotic solutions are used.

Liquid electrolytes in lithium-ion batteries consist of lithium salts, such as $LiPF_6$, $LiBF_4$ or $LiClO_4$ in an organic solvent, such as ethylene carbonate, dimethyl carbonate, and diethyl carbonate. A liquid electrolyte conducts lithium ions, acting as a carrier between the cathode and the anode when a battery passes an electric current through an external circuit. Typical conductivities of liquid electrolyte at room temperature (20 °C (68 °F)) are in the range of 10 mS/cm (1 S/m), increasing by approximately 30–40% at 40 °C (104 °F) and decreasing by a slightly smaller amount at 0 °C (32 °F)

Unfortunately, organic solvents easily decompose on anodes during charging. However, when appropriate organic solvents are used as the electrolyte, the solvent decomposes on initial charging and forms a solid layer called the solid electrolyte interphase (SEI), which is electrically insulating yet provides sufficient ionic conductivity. The interphase prevents decomposition of the electrolyte after the second charge. For example, ethylene carbonate is decomposed at a relatively high voltage, 0.7 V vs. lithium, and forms a dense and stable interface.

A good solution for the interface instability is the application of a new class of composite electrolytes based on PEO (poly(oxyethylene)) developed by Syzdek et al. It can be either solid (high molecular weight) and be applied in dry Li-polymer cells, or liquid (low molecular weight) and be applied in regular Li-ion cells.

Another issue that Li-ion technology is facing is safety. Large scale application of Li cells in Electric Vehicles needs a dramatic decrease in the failure rate. One of the solutions is the novel technology based on reversed-phase composite electrolytes, employing porous ceramic material filled with electrolyte .

Advantages and disadvantages

Note that both advantages and disadvantages depend on the materials and design that make up the battery. This summary reflects older designs that use carbon anode, metal oxide cathodes, and lithium salt in an organic solvent for the electrolyte.

Advantages

A lithium-ion battery from a laptop computer

- Wide variety of shapes and sizes efficiently fitting the devices they power.
- Much lighter than other energy-equivalent secondary batteries.
- High open circuit voltage in comparison to aqueous batteries (such as lead acid, nickel-metal hydride and nickel-cadmium). This is beneficial because it increases the amount of power that can be transferred at a lower current.
- No memory effect.
- Self-discharge rate of approximately 5-10% per month, compared to over 30% per month in common nickel metal hydride batteries, approximately 1.25% per month for Low Self-Discharge NiMH batteries and 10% per month in nickel-cadmium batteries. According to one manufacturer, lithium-ion cells (and, accordingly, "dumb" lithium-ion batteries) do not have any self-discharge in the usual meaning of this word. What looks like a self-discharge in these batteries is a permanent loss of capacity. On the other hand, "smart" lithium-ion batteries do self-discharge, due to the drain of the built-in voltage monitoring circuit.
- Components are environmentally safe as there is no free lithium metal.

Disadvantages

Cell life

- Charging forms deposits inside the electrolyte that inhibit ion transport. Over time, the cell's capacity diminishes. The increase in internal resistance reduces the cell's ability to deliver current. This problem is more pronounced in high-current applications. The decrease means that older batteries do not charge as much as new ones (charging time required decreases proportionally).

- High charge levels and elevated temperatures (whether from charging or ambient air) hasten capacity loss. Charging heat is caused by the carbon anode (typically replaced with lithium titanate which drastically reduces damage from charging, including expansion and other factors).
- A Standard (Cobalt) Li-Ion cell that is full most of the time at 25 °C (77 °F) irreversibly loses approximately 20% capacity per year. Poor ventilation may increase temperatures, further shortening battery life. Loss rates vary by temperature: 6% loss at 0 °C (32 °F), 20% at 25 °C (77 °F), and 35% at 40 °C (104 °F). When stored at 40%–60% charge level, the capacity loss is reduced to 2%, 4%, and 15%, respectively. In contrast, the calendar life of LiFePO4 cells is not affected by being kept at a high state of charge.

Internal resistance

- The internal resistance of standard (Cobalt) lithium-ion batteries is high compared to both other rechargeable chemistries such as nickel-metal hydride and nickel-cadmium, and LiFePO4 and lithium-polymer cells. Internal resistance increases with both cycling and age. Rising internal resistance causes the voltage at the terminals to drop under load, which reduces the maximum current draw. Eventually increasing resistance means that the battery can no longer operate for an adequate period.

- To power larger devices, such as electric cars, connecting many small batteries in a parallel circuit is more effective and efficient than connecting a single large battery.

Safety requirements

If overheated or overcharged Li-ion batteries may suffer thermal runaway and cell rupture. In extreme cases this can lead to combustion. Deep discharge may short-circuit the cell, in which case recharging would be unsafe. To reduce these risks, Lithium-ion battery packs contain fail-safe circuitry that shuts down the battery when its voltage is outside the safe range of 3–4.2 V per cell. When stored for long periods the small current draw of the protection circuitry itself may drain the battery below its shut down voltage; normal chargers are then ineffective. Many types of lithium-ion cell cannot be charged safely below 0°C.

Other safety features are required in each cell:

- shut-down separator (for overtemperature)
- tear-away tab (for internal pressure)
- vent (pressure relief)
- thermal interrupt (overcurrent/overcharging)

These devices occupy useful space inside the cells, add additional points of failure and irreversibly disable the cell when activated. They are required because the anode produces heat during use, while the cathode may produce oxygen. These devices and improved electrode designs reduce/eliminate the risk of fire or explosion.

These safety features increase costs compared to nickel metal hydride batteries, which require only a hydrogen/oxygen recombination device (preventing damage due to mild overcharging) and a back-up pressure valve.

Specifications and design

- Specific energy density: 150 to 250 W·h/kg (540 to 900 kJ/kg)
- Volumetric energy density: 250 to 620 W·h/l (900 to 1900 J/cm^3)
- Specific power density: 300 to 1500 W/kg (@ 20 seconds and 285 W·h/l)

Because lithium-ion batteries can have a variety of cathode and anode materials, the energy density and voltage vary accordingly.

Lithium-ion batteries with a lithium iron phosphate cathode and graphite anode have a nominal open-circuit voltage of 3.2 V and a typical charging voltage of 3.6 V. Lithium nickel manganese cobalt (NMC) oxide cathode with graphite anodes have a 3.7 V nominal voltage with a 4.2 V max charge. The charging procedure is performed at constant voltage with current-limiting circuitry (i.e., charging with constant current until a voltage of 4.2 V is reached in the cell and continuing with a constant voltage applied until the current drops close to zero). Typically, the charge is terminated at 3% of the initial charge current. In the past, lithium-ion batteries could not be fast-charged and needed at least two hours to fully charge. Current-generation cells can be fully charged in 45 minutes or less. Some lithium-ion varieties can reach 90% in as little as 10 minutes.

Charging procedure

Stage 1: Apply charging current until the voltage limit per cell is reached.

Stage 2: Apply maximum voltage per cell limit until the current declines below 3% of rated charge current.

Stage 3: Periodically apply a top-off charge about once per 500 hours.

The charge time is about three to five hours, depending on the charger used. Generally, cell phone batteries can be charged at 1*C* and laptop-types at 0.8*C*, where *C* is the current that would discharge the battery in one hour. Charging is usually stopped when the current goes below 0.03*C* but it can be left indefinitely depending on desired charging time. Some fast chargers skip stage 2 and claim the battery is ready at 70% charge. Laptop battery chargers sometimes gamble, and try to charge up to 4.35 V then disconnects the battery. This helps to compensate for the battery's internal resistance and charges up to 100% in short time.

Top-off charging is recommended when voltage goes below 4.05 V/cell.

Typically, lithium-ion cells are charged with 4.2 ± 0.05 V/cell, except for military long-life cells where 3.92 V is used for extending battery life. Most protection circuits cut off if either 4.3 V or 90 °C is reached. If the voltage drops below 2.50 V per cell, the battery protection circuit may also render it unchargeable with regular charging equipment. Most battery protection circuits stop at 2.7–3.0 V per cell.

For safety reasons it is recommended the battery be kept at the manufacturer's stated voltage and current ratings during both charge and discharge cycles.

Variations in materials and construction

The increasing demand for batteries has led vendors and academics to focus on improving the power density, operating temperature, safety, durability, charging time, output power, and cost of LIB solutions.

LIB types

Area	Technology	Researchers	Target application	Date	Benefit
Cathode	Manganese spinel (LMO)	Lucky Goldstar Chemical, NEC, Samsung, Hitachi, Nissan/AESC	Hybrid electric vehicle, cell phone, laptop	1996	durability, cost
	Lithium iron phosphate	University of Texas/Hydro-Québec,/Phostech Lithium Inc., Valence Technology, A123Systems/MIT	Segway Personal Transporter, power tools, aviation products, automotive hybrid systems, PHEV conversions	1996	moderate density (2 A·h outputs 70 amperes) operating temperature >60 °C (140 °F)
	Lithium nickel manganese cobalt (NMC)	Imara Corporation, Nissan Motor		2008	density, output, safety
	LMO/NMC	Sony, Sanyo			power, safety (although limited durability)
	Lithium iron fluorophosphate	University of Waterloo		2007	durability, cost (replace Li with Na or Na/Li)
	Lithium air	University of Dayton	automotive	2009	density, safety

		Research Institute			
	5% Vanadium-doped Lithium iron phosphate olivine	Binghamton University		2008	output
Anode	Lithium-titanate battery (LT)	Altairnano	automotive (Phoenix Motorcars), electrical grid (PJM Interconnection Regional Transmission Organization control area, United States Department of Defense), bus (Proterra)	2008	output, charging time, durability (20 years, 9,000 cycles), safety, operating temperature (-50–70 °C (-58–158 °F)
	Lithium vanadium oxide	Samsung/Subaru.	automotive	2007	density (745Wh/l)
	Cobalt-oxide nano wires from genetically modified virus	MIT		2006	density, thickness
	Iron-phosphate nano wires from genetically modified virus	MIT		2009	density, thickness
	Silicon/titanium dioxide composite nano wires from genetically modified tobacco virus	University of Maryland	explosive detection sensors, biomimetic structures, water-repellent surfaces, micro/nano scale heat pipes	2010	density, low charge time
	Porous silicon/carbon nanocomposite spheres	Georgia Institute of Technology	portable electronics, electrical vehicles, electrical grid	2010	high stability, high capacity, low charge time
	nano-sized wires on stainless steel	Stanford University	wireless sensors networks,	2007	density (shift from anode- to cathode-limited), durability (wire cracking)
	Metal hydrides	Laboratoire de Réactivité et de		2008	density (1480 mA·h/g)

	Chimie des Solides, General Motors		
Electrode LT/LMO	Ener1/Delphi,	2006	durability, safety (limited density)
Nanostructure	Université Paul Sabatier/Université Picardie Jules Verne	2006	density

Usage guidelines

Prolonging battery pack life

- Depletion below the low-voltage threshold (2.4 to 2.8 V/cell, depending on chemistry) results in a dead battery which does not even appear to charge because the protection circuit (a type of electronic fuse) disables it. This can be reversed in many modern batteries, especially single-cell ones, by applying a charging voltage for long enough to make the cell voltage rise above the low-voltage threshold; however this behaviour varies by manufacturer.
- Lithium-ion batteries should be kept cool; they may be stored in a refrigerator.
- The rate of degradation of Lithium-ion batteries is strongly temperature-dependent; they degrade much faster if stored or used at higher temperatures.

Multicell devices

Li-Ion batteries require a Battery Management System to prevent operation outside each cell's Safe Operating Area (over-charge, under-charge, safe temperature range) and to balance cells to eliminate SOC mismatches, significantly improving battery efficiency and increasing overall capacity. As the number of cells and load currents increase, the potential for mismatch also increases. There are two kinds of mismatch in the pack: state-of-charge (SOC) and capacity/energy ("C/E") mismatch. Though SOC is more common, each problem limits pack capacity (mA·h) to the capacity of the weakest cell.

Safety

Lithium-ion batteries can rupture, ignite, or explode when exposed to high temperature. Short-circuiting a battery will cause the cell to overheat and possibly to catch fire. Adjacent cells may also then heat up and fail, in some cases, causing the entire battery to ignite or rupture. In the event of a fire, the device may emit dense irritating smoke.

Replacing the lithium cobalt oxide cathode material in lithium-ion batteries with a lithium metal phosphate such as lithium iron phosphate, improves cycle counts, shelf life and safety, but lowers capacity. Currently, these 'safer' lithium-ion batteries are mainly used in electric cars and other large-capacity battery applications, where safety issues are critical.

Lithium-ion batteries normally contain safety devices to protect the cells from disturbance. However, contaminants inside the cells can defeat these safety devices.

Recalls

In March 2007, Lenovo recalled approximately 205,000 batteries at risk of explosion. In August 2007, Nokia recalled over 46 million batteries at risk of overheating and exploding. One such incident occurred in the Philippines involving an Nokia N91, which uses the BL-5C battery.

In December 2006, Dell recalled approximately 22,000 laptop batteries from the U.S. market. Approximately 10 million Sony batteries used in Dell, Sony, Apple, Lenovo/IBM, Panasonic, Toshiba, Hitachi, Fujitsu and Sharp laptops were recalled in 2006. The batteries were found to be susceptible to internal contamination by metal particles. Under some circumstances, these particles could pierce the separator, causing a short-circuit.

In October 2004, Kyocera Wireless recalled approximately 1 million mobile phone batteries to identify counterfeits.

Transport restrictions

In January 2008, the United States Department of Transportation ruled that passengers on board commercial aircraft could carry lithium batteries in their checked baggage if the batteries are installed in a device. Types of batteries affected by this rule are those containing lithium, including Li-ion, lithium polymer, and lithium cobalt oxide chemistries. Lithium-ion batteries containing more than 25 grams (0.88 oz) equivalent lithium content (ELC) are exempt from the rule and are forbidden in air travel. This restriction greatly reduces the chances of the batteries short-circuiting and causing a fire.

Additionally, a limited number of replacement batteries may be transported in carry-on luggage. Such batteries must be sealed in their original protective packaging or in individual containers or plastic bags.

Some postal administrations restricted air shipping (including EMS) of lithium and lithium-ion batteries, and products containing these (e.g. laptops, cell phones etc.). Among these countries and regions are Hong Kong, Australia and Japan.

Chapter- 8

Lithium-Ion Polymer Battery

Lithium-ion polymer battery

A Lithium-Ion Polymer Battery used to power a mobile phone

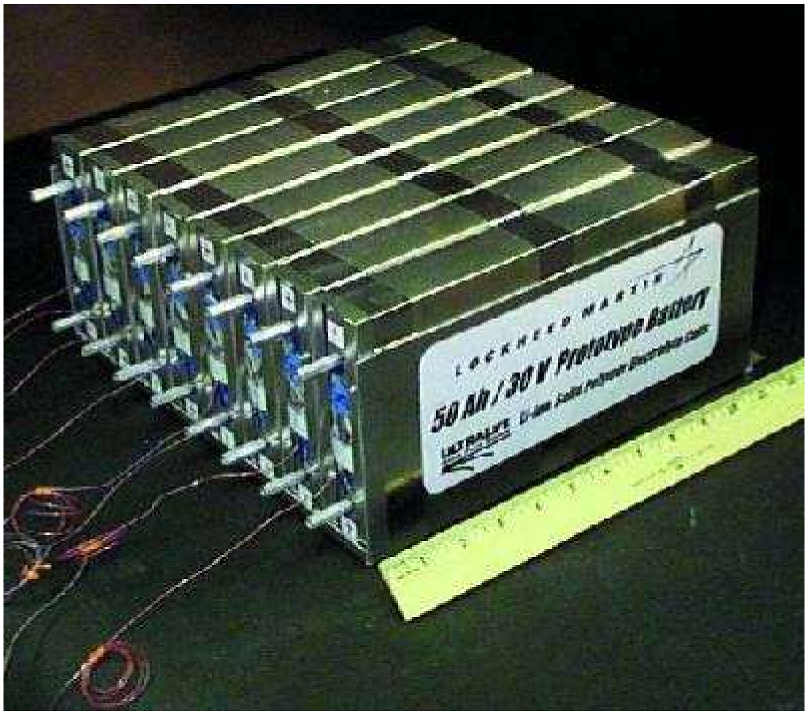
specific energy	130–200 W·h/kg
energy density	300 W·h/L
specific power	up to 7.1 kW/kg
Charge/discharge efficiency	99.8%
Energy/consumer-price	2.8–5 W·h/US$
Self-discharge rate	5%/month
Time durability	24–36 months
Cycle durability	>1000 cycles
Nominal cell voltage	3.7 V

Lithium-ion polymer batteries, **polymer lithium ion**, or more commonly **lithium polymer batteries** (abbreviated Li-poly, Li-Pol, LiPo, LIP, PLI or LiP) are rechargeable batteries (secondary cell batteries). Normally batteries are composed of several identical secondary cells in parallel addition to increase the discharge current capability.

Design origin

This type has technologically evolved from lithium-ion batteries. The primary difference is that the lithium-salt electrolyte is not held in an organic solvent but in a solid polymer composite such as polyethylene oxide or polyacrylonitrile. The advantages of Li-ion polymer over the lithium-ion design include potentially lower cost of manufacture, adaptability to a wide variety of packaging shapes, and ruggedness. Lithium-ion polymer batteries started appearing in consumer electronics around 1996.

Technology



An experimental Li Ion Polymer Battery made by Lockheed-Martin for NASA

Cells sold today as polymer batteries are pouch cells. Unlike lithium-ion cylindrical cells, which have a rigid metal case, pouch cells have a flexible, foil-type (polymer laminate) case. In cylindrical cells, the rigid case presses the electrodes and the separator onto each other; whereas in polymer cells this external pressure is not required because the electrode sheets and the separator sheets are laminated onto each other.

Since individual pouch cells have no strong metal casing, by themselves they are over 20% lighter than equivalent cylindrical cells. However, all Li-Ion cells expand at high levels of SOC; if uncontained, this may result in delamination, and reduction of reliability and cycle life; the case of cylindrical cells provides that containment, while pouch cells, by themselves, are not contained. Therefore, to achieve the rated performance, a battery composed of pouch cells must include an overall, strong, external casing to retain its shape.

The voltage of a Li-poly cell varies from about 2.7 V (discharged) to about 4.23 V (fully charged), and Li-poly cells have to be protected from overcharge by limiting the applied voltage to no more than 4.235 V per cell used in a series combination. Overcharging a Li-poly battery will probably cause explosion or fire. During discharge on load, the load has to be removed as soon as the voltage drops below approximately 3.0 V per cell (used in a series combination), or else the battery will subsequently no longer accept a full charge and may experience problems holding voltage under load. This can be achieved, as with other lithium-ion batteries, also harmed by under- and over-voltage, by circuitry that prevents overcharge and deep discharge.

Early in its development, lithium polymer technology had problems with internal resistance. Other challenges include longer charge times and slower maximum discharge rates compared to more mature technologies. Li-poly batteries typically require more than an hour for a full charge. Recent design improvements have increased maximum discharge currents from two times to 15 or even 30 times the cell capacity (discharge rate in amperes, cell capacity in ampere-hours). In December 2007 Toshiba announced a new design offering a much faster rate of charge (about 5 minutes to reach 90%). These cells were released onto the market in March 2008 and are expected to have a dramatic effect on the power tool and electric vehicle industries, and a major effect on consumer electronics.

When compared to the lithium-ion battery, Li-poly has a greater life cycle degradation rate. However, in recent years, manufacturers have been declaring upwards of 500 charge-discharge cycles before the capacity drops to 80% . Another variant of Li-poly cells, the "thin film rechargeable lithium battery", has been shown to provide more than 10,000 cycles.

Applications

A compelling advantage of Li-poly cells is that manufacturers can shape the battery almost however they please, which can be important to mobile phone manufacturers constantly working on smaller, thinner, and lighter phones.

3-Cell LiPo for RC-models

Li-poly batteries are also gaining favor in the world of radio-controlled aircraft as well as radio-controlled cars, where the advantages of both lower weight and greatly increased run times can be sufficient justification for the price. Some airsoft gun owners have switched to LiPo batteries due to the above reasons and the increased rate of fire they provide. However, lithium polymer-specific chargers are required to avoid fire and explosion. Explosions can also occur if the battery is short-circuited, as tremendous current passes through the cell in an instant. Radio-control enthusiasts take special precautions to ensure their battery leads are properly connected and insulated. Furthermore fires can occur if the cell or pack is punctured. Radio-controlled car batteries are often protected by durable plastic cases to prevent puncture. Specially designed electronic motor speed controls are used to prevent excessive discharge and subsequent battery damage. This is achieved using a low voltage cutoff (LVC) setting that is adjusted to maintain cell voltage greater than (typically) 3 V per cell.

Li-poly batteries are also gaining ground in PDAs and laptop computers, such as Apple's MacBook family, Amazon's Kindle, Lenovo's Thinkpad X300 and Ultrabay Batteries, the OQO series of palmtops, the HP Mini and Dell products featuring D-bay batteries. They can be found in small digital music devices such as iPods, Zunes, and other MP3 players and the Apple iPhone and iPad, as well as gaming equipment like Sony's Playstation 3 wireless controllers. They are desirable in applications where small form factors and energy density outweigh cost considerations.

Electric vehicles

These batteries may also power the next generation of battery electric vehicles. The cost of an electric car of this type is prohibitive, but proponents argue that with increased production, the cost of Li-poly batteries will go down.

Hyundai Motor Company plans to use this battery type in its hybrid electric vehicles. A Li-poly powered Audi A2 covered the record distance of 600 km without recharging on October 26, 2010.

Technical specifications

There are currently two commercialized technologies, both lithium-ion-polymer (where "polymer" stands for "polymer electrolyte/separator") cells. These are collectively referred to as "polymer electrolyte batteries".

The battery is constructed as:

- **Cathode**: $LiCoO_2$ or $LiMn_2O_4$
- **Separator**: Conducting polymer electrolyte
- **Anode**: Li or carbon-Li intercalation compound

Typical reaction:

- Anode: carbon–$Li_x \rightarrow C + xLi^+ + xe^-$
- Separator: Li+ conduction
- Cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2$

Polymer electrolytes/separators can be solid polymers (e.g., polyethyleneoxide, PEO) plus $LiPF_6$, or other conducting salts plus SiO_2, or other fillers for better mechanical properties (such systems are not available commercially yet). Some manufacturers like Avestor (since merged with Batscap) are using metallic Li as the anode (these are the **lithium-metal-polymer batteries**), whereas others wish to go with the proven safe carbon intercalation anode.

Both currently commercialized technologies use PVdF (a polymer) gelled with conventional solvents and salts, like EC/DMC/DEC. The difference between the two technologies is that one (Bellcore/Telcordia technology) uses $LiMn_2O_4$ as the cathode, and the other the more conventional $LiCoO_2$.

Other, more exotic (although not yet commercially available) Li-polymer batteries use a polymer cathode. For example, Moltech is developing a battery with a plastic conducting carbon-sulfur cathode. However, as of 2005 this technology seems to have had problems with self-discharge and manufacturing cost.

Yet another proposal is to use organic sulfur-containing compounds for the cathode in combination with an electrically conductive polymer such as polyaniline. This approach promises high power capability (i.e., low internal resistance) and high discharge capacity, but has problems with cycleability and cost.

Prolonging life in multiple cells through cell balancing

Analog front ends that balance cells and eliminate mismatches of cells in series or parallel significantly improve battery efficiency and increase the overall pack capacity. As the number of cells and load currents increase, the potential for mismatch also increases. There are two kinds of mismatch in the pack: state-of-charge (SOC) and capacity/energy (C/E) mismatch. Though the SOC mismatch is more common, each problem limits the pack capacity (mA·h) to the capacity of the weakest cell.

Battery pack cells are balanced when all the cells in the battery pack meet two conditions:

- If all cells have the same capacity, then they are balanced when they have the same relative state of charge (SOC). In this case, the open circuit voltage (OCV) is a good measure of the SOC. If, in an out-of-balance pack, all cells can be differentially charged to full capacity (balanced), then they will subsequently cycle normally without any additional adjustments.

- If the cells have different capacities, they are also considered balanced when the SOC is the same. But, since SOC is a relative measure, the absolute amount of capacity for each cell is different. To keep the cells with different capacities at the same SOC, cell balancing must provide differential amounts of current to cells in the series string during both charge and discharge on every cycle.

Capacity rating

Cell capacities are rated in ampere hours (A·h) or milliampere hours (mA·h). A 1000 mA·h battery is the same as a 1 A·h battery: both will supply 1 A for 1 hour. The C rating commonly associated with lithium ion batteries refers to the maximum current supply capability as a multiple of the cell's capacity: for instance, a 1 A·h, 20 C battery should be able to supply 20 A continuously without damage (1 A·h x 20 C = 20 A). A useful way to calculate how long a battery will last for under heavy load is to multiply the A·h capacity by 60 min to give A·min, so a 1 A·h battery is a 60 A·min battery; to calculate how many minutes the battery will last, just divide by the average current drawn (e.g. a 10 A average current draw will mean that a 60 A·min battery will last for 60 A·min / 10 A = 6 minutes).

Charging

LiPoly batteries must be charged carefully. The basic process is to charge at constant current until each cell reaches 4.2 V; the charger must then gradually reduce the charge current while holding the cell voltage at 4.2 V until the charge current has dropped to a small percentage of the initial charge rate, at which point the battery is considered 100% charged. Some manufacturers specify 2%, others 3%, but other values are also possible. The difference in achieved capacity is minute.

Balance charging simply means that the charger monitors the voltage of each cell in a pack and varies the charge on a per-cell basis so that all cells are brought to the same voltage.

It is important to note that trickle charging is not acceptable for lithium batteries; Li-ion chemistry cannot accept an overcharge without causing damage to the cell, possibly plating out lithium metal and becoming hazardous. Most manufacturers claim a maximum and minimum voltage of 4.23 and 3.0 volts per cell. Taking any cell outside these limits can reduce the cell's capacity and ability to deliver full rated current.

Most dedicated lithium polymer chargers use a charge timer for safety; this cuts the charge after a predefined time (typically 90 minutes).

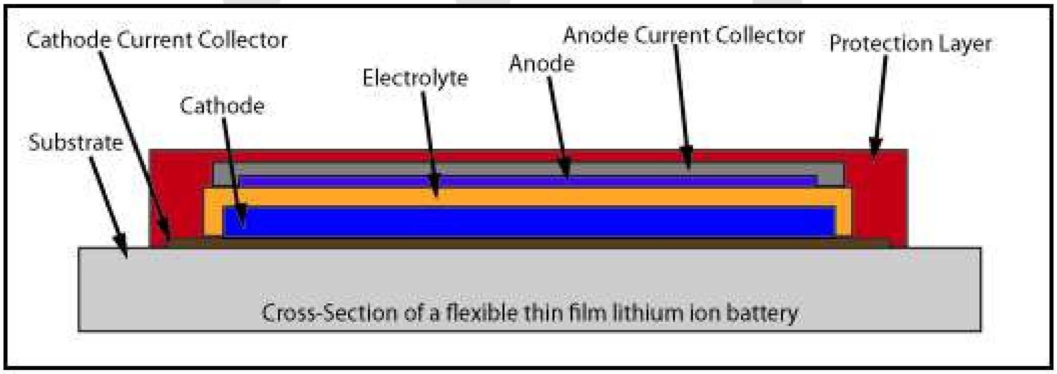
Storage

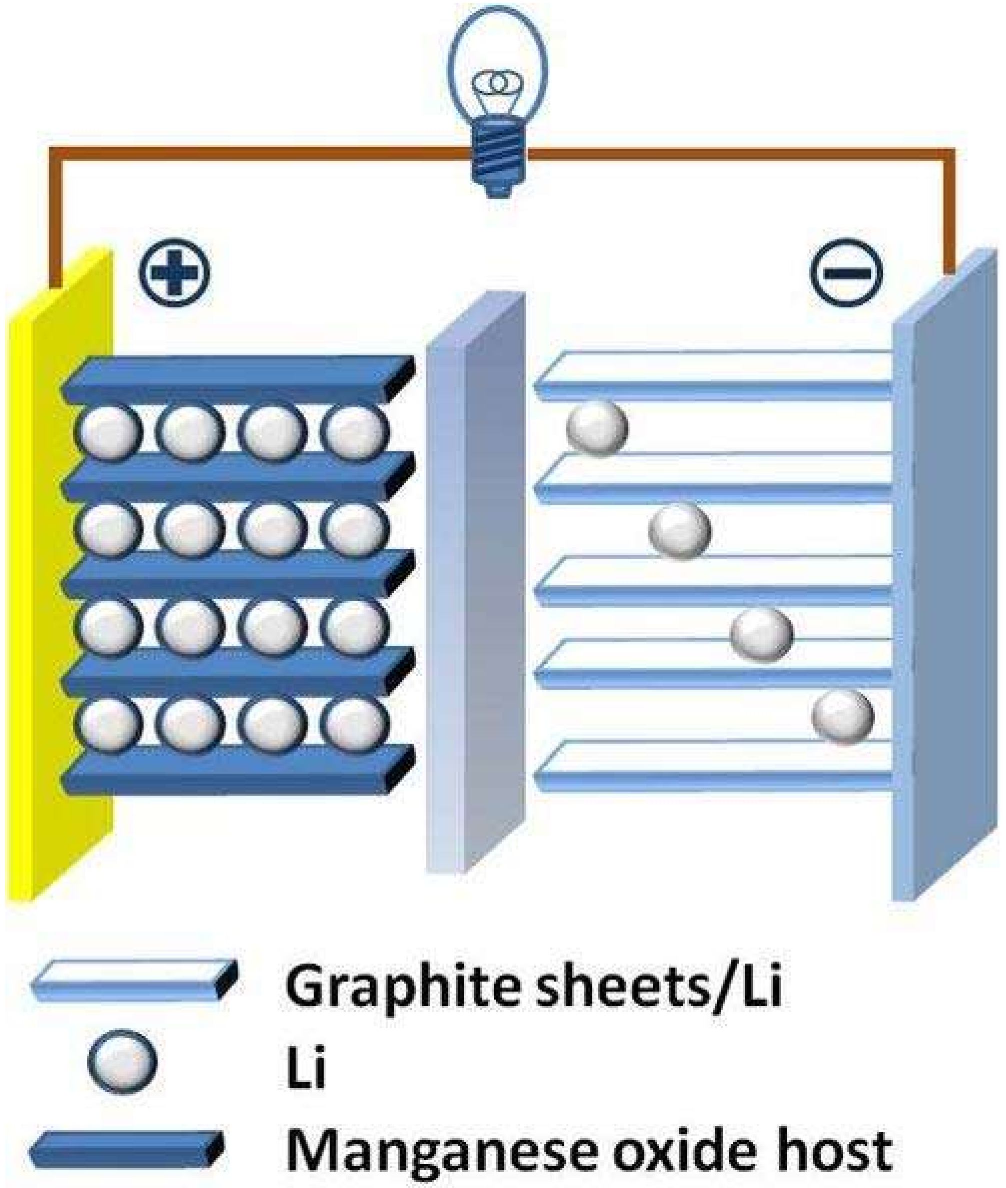
Unlike certain other types of batteries, lithium polymer batteries can be stored for one or two months without significantly losing charge. However, if storing for long periods, manufacturers recommend discharging the battery to 40% of full charge. In addition, other sources recommend refrigerating (but not freezing) the cell.

Chapter- 9

Thin Film Rechargeable Lithium Battery

Thin film lithium ion batteries are similar to lithium-ion batteries, but they are composed of thin materials, some only nanometers or micrometers thick, which allow for the finished battery to be just millimeters thick. They have been developed and advanced primarily within the last decade. These batteries consist of a substrate, electrolyte, current collector, anode, cathode, and a charge separator. There has been much research into the determination of the most effective components for this type of battery. It has been shown recently that even ordinary printer paper can be used as a charge separator and a substrate. . These thin film batteries are an improvement on the common secondary, or rechargeable, lithium ion batteries in many ways. These batteries exhibit the same voltage and current as their bulky counterparts, but their thinner dimensions allow for greater applications such as making thinner electronic devices, like cell phones and laptops and even implantable medical devices and reducing the weight of common devices that are run on battery power because of the batteries' high energy density. These batteries can be formed into any shape and they can be stacked, to be used in parallel, thus even further reducing the space needed for a battery.





Lithium Ion Battery Cell

Background

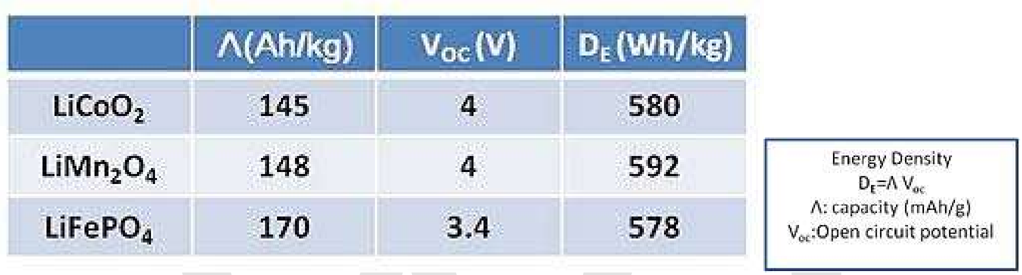
Lithium-ion batteries are a newer battery technology that is preferable due to their ability to be recharged. Also they have high energy density and last longer than many similar battery technologies. In the battery cell lithium ions flow through the electrolyte from the anode to the cathode while the battery is being discharged. Upon recharging the battery the lithium ions move back to the anode. This Li-ion battery design is effective for large devises. However, as a more mobile, technology driven society we rely heavily on portable electronics, which require thin batteries for power. Research into thin film batteries has developed over the recent years to accommodate for this demand.

Components of Thin Film Battery

Cathode materials

Cathode materials in thin film lithium ion batteries are the same of what is seen in classical lithium ion batteries. They are normally metal oxides that are deposited as a film by various methods.

Metal oxide materials are shown below as well as their relative specific capacities (Λ), open circuit voltages (V_{OC}), and energy densities (D_E).



	Λ(Ah/kg)	V_{OC}(V)	D_E(Wh/kg)
$LiCoO_2$	145	4	580
$LiMn_2O_4$	148	4	592
$LiFePO_4$	170	3.4	578

Energy Density
D_E=Λ V_{oc}
Λ: capacity (mAh/g)
V_{oc}:Open circuit potential

Deposition methods for cathode materials

There are various methods being used in order to deposit a thin film cathode material onto the current collector.

Pulsed Laser Deposition (PLD)

In Pulsed Laser Deposition materials are fabricated with varying parameters such as laser energy and fluence, substrate temperature, background pressure, and target-substrate distance.

Magnetron Sputtering

In Magnetron Sputtering the substrate is cooled for deposition.

Chemical Vapor Deposition (CVD)

In Chemical Vapor Deposition volatile precursor materials is deposited onto a substrate material.

Sol-Gel Processing

Sol-gel processing allows for homogeneous mixing of precursor materials at the atomic level.

Electrolyte

The greatest difference between classical lithium ion batteries and thin, flexible, lithium ion batteries is in the electrolyte material used. Progress in lithium ion batteries relies as much on improvements in the electrolyte as it does in the electrode materials, as the electrolyte plays a major role in safe battery operation. The concept of thin film lithium ion batteries was increasingly motivated by manufacturing advantages presented by the polymer technology for their use as electrolytes. Lipon, lithium phosphorus oxynitride, is an amorphous polymer material used as an electrolyte material in thin film flexible batteries. Layers of Lipon are deposited over the cathode material at ambient temperatures by RF magnetron sputtering. This forms the solid electrolyte used for ion conduction between anode and cathode. Solid polymer electrolytes offer several advantages in comparison to a classical liquid lithium ion battery. Rather than having separate components of electrolyte, binder, and separator, these solid electrolytes can act as all three. This increases the overall energy density of the assembled battery because the constituents of the entire cell are more tightly packed.

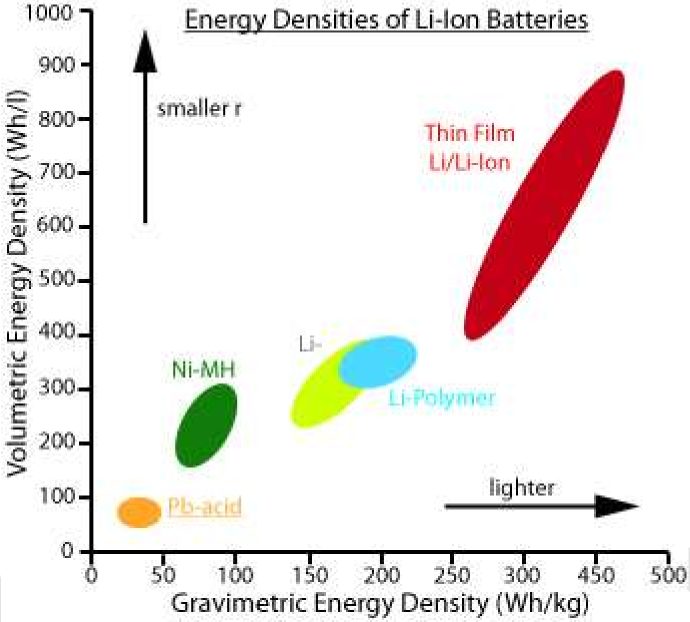
Separator Material

Separator materials in lithium ion batteries must have the ability to transport ions through their porous membranes while maintaining a physical separation between the anode and cathode materials in order to prevent short-circuiting. In a thin film based system, the electrolyte is normally a solid electrolyte, capable of conforming to the shape of the battery. Typically this material is a polymer based material and as mentioned above, this polymer commonly acts as both the separator and electrolyte. Since thin film batteries are made of all solid materials, this affords to use of simpler separator materials in these systems such as Xerox paper rather than in liquid based Li-ion batteries.

Current Collector

Current collectors in thin film batteries must be flexible, have high surface area, and cost-effective. Silver nanowires with improved surface area and loading weight have been shown to work as a current collector in these battery systems, but still are not as cost-effective as desired. Extending graphite technology to lithium ion batteries, solution processed carbon nanotubes (CNT) films are being looked into for use as both the current collector and anode material. CNTs have the ability to intercalate lithium and maintain high operating voltages, all with low mass loading and flexibility.

Advantages and Challenges



Thin film lithium ion batteries offer improved performance by having a higher average output voltage, lighter weights thus higher energy density, and longer cycling life than typical rechargeable batteries. In the thin film lithium ion battery, both electrodes are capable of reversible lithium insertion, thus forming a Li-ion transfer cell. Li-ion transfer cells are the most promising systems for satisfying the demand of high specific energy and high power. In order to construct a thin film battery it is necessary to fabricate all the battery components, as an anode, a solid electrolyte, a cathode and current leads into multi-layered thin films by suitable technologies.

In a thin film based system, the electrolyte is normally a solid electrolyte, capable of conforming to the shape of the battery. This is in contrast to classical lithium ion batteries, which normally have liquid electrolyte material. Liquid electrolytes can be challenging to utilized if they are not compatible with the separator. Also liquid electrolytes in general call for an increase in the overall volume of the battery, which is not ideal for designing a system that has high energy density. Additionally, in a thin film flexible Li-ion battery, the electrolyte, which is normally polymer-based, can act as the electrolyte, separator, and binder material. This provides the ability to have flexible systems since the issue of electrolyte leakage is circumvented. Finally, solid systems can be packed together tightly which affords an increase in energy density when compared to classical lithium ion batteries.

Separator materials in lithium ion batteries must have the ability to transport ions through their porous membranes while maintaining a physical separation between the anode and cathode materials in order to prevent short-circuiting. Furthermore, the separator must be resistant to degradation during the battery’s operation. In a thin film Li-ion battery, the separator must be a thin and flexible solid. Typically today, this material is a polymer-based material. Since thin film batteries are made of all solid materials, allows one to use simpler separator materials in these systems such as Xerox paper rather than in liquid based Li-ion batteries.

Scientific Development

Development of thin solid state batteries allows for roll to roll type production of batteries which would decrease production costs. Solid-state batteries can also afford increased energy density due to decrease in overall device weight. Where as the flexible nature allows for novel battery design and incorporation into electronics. Development is still required in cathode materials which will resist decreased capacity due to cycling.

Prior Technology	**Replacement Technology**	**Result**
Solution based electrolyte	Solid state electrolyte	Increased safety and cycle life
Polymer separators	Paper separator	Decreased cost increased increased rate of ion conduction
Metalic current collectors	Carbon nanotube current collectors	Decreased device weight, increased energy density
Graphite anode	Carbon nanotube anode	Decreased device complexity

Applications

The advancements made to the thin film lithium ion battery have allowed for many potential applications. The majority of these applications are aimed at improving the currently available consumer and medical products. Thin film lithium ion batteries can be used to make thinner portable electronics, because the thickness of the battery required to operate the device can be reduced greatly. These batteries have the ability to be an integral part of implantable medical devices, such as defibrillators and neural stimulators, “smart” cards , radio frequency identification, or RFID, tags and wireless sensors. They can also serve as a way to store energy collected from solar cells or other harvesting devices . Each of these applications is possible because of the flexibility in the size and shape of the batteries. The size of these devices doesn’t have to revolve around the size of the space needed for the battery anymore. The thin film batteries can be attached to the inside of the casing or in some other convenient way. The opportunities in which to use this type of batteries are endless.

Solar Cell Storage Devices

The thin film lithium ion battery can serve as a storage device for the energy collected from a solar cell. These batteries can be made to have a low self discharge rate, which means that these batteries can be stored for long periods of time without a major loss of the energy that was used to charge it. These fully charged batteries could then be used to power some or all of the other potential applications listed below.

Smart Cards

Smart cards are basically the same size as a credit card, but they contain a microchip that can be used to access information, give authorization, or process an application. These cards can go through harsh production conditions, with temperatures in the range of 130 to 150°C, in order to complete the high temperature, high pressure lamination processes . These conditions can cause other batteries to fail because of degassing or degradation of organic components within the battery. Thin film lithium ion batteries have been shown to withstand temperatures of -40 to 150°C . This use of thin film lithium ion batteries is hopeful for other extreme temperature applications.

RFID tags

Radio Frequency Identification (RFID) tags can be used in many different applications. These tags can be used in packaging, inventory control, used to verify authenticity and even allow or deny access to something. These ID tags can even have other integrated sensors to allow for the physical environment to be monitored, such as temperature or shock during travel or shipping. Also, the distance required to read the information in the tag depends on the strength of the battery. The farther away you want to be able to read the information, the stronger the output will have to be and thus the greater the power supply to accomplish this output. As these tags get more and more complex, the battery requirements will need to keep up. Thin film lithium ion batteries have shown that they can fit into the designs of the tags because of the flexibility of the battery in size and shape and are sufficiently powerful enough to accomplish the goals of the tag. Low cost production methods, like roll to roll lamination, of these batteries may even allow for this kind of RFID technology to be implemented in disposable applications.

Implantable Medical Devices

Thin films of $LiCoO_2$ have been synthesized in which the strongest x ray reflection is either weak or missing, indicating a high degree of preferred orientation. Thin film solid state batteries with these textured cathode films can deliver practical capacities at high current densities. For example, for one of the cells 70% of the maximum capacity between 4.2 V and 3 V (approximately 0.2 mAh/cm^2) was delivered at a current of 2 mA/cm^2. When cycled at rates of 0.1 mA/cm^2, the capacity loss was 0.001%/cycle or less. The reliability and performance of Li $LiCoO_2$ thin-film batteries make them attractive for application in implantable devices such as neural stimulators, pacemakers, and defibrillators.

Implantable medical devices require batteries that can deliver a steady, reliable power source for as long as possible. These applications call for a battery that has a low self-discharge rate, for when it's not in use, and a high power rate, for when it needs to be used, especially in the case of an implantable defibrillator. Also, users of the product will want a battery that can go through many cycles, so these devices won't have to be replaced or serviced often. Thin film lithium ion batteries have the ability to meet these requirements. The advancement from a liquid to a solid electrolyte has allowed these batteries to take almost any shape without the worry of leaking, and it has been shown that certain types of thin film rechargeable lithium batteries can last for around 50,000 cycles . Another advantage to these thin film batteries is that they can be stacked and used in parallel to give a larger voltage equal to the sum of the individual battery voltages. This fact can be used in reducing the "footprint" of the battery, or the size of the space needed for the battery, in the design of a device.

Wireless Sensors

Wireless sensors need to be in use for the duration of their application, whether that may be in package shipping or in the detection of some unwanted compound, or controlling inventory in a warehouse. If the wireless sensor can't transmit its data due to low or no battery power, the consequences could potentially be severe based on the application. Also, the wireless sensor must be adaptable to each application. Therefore the battery must be able to fit within the designed sensor. This means that the desired battery for these devices must be long-lasting, size specific, low cost, if they are going to be used in disposable technologies, and must meet the requirements of the data collection and transmission processes. Once again, thin film lithium ion batteries have shown the ability to meet all of these requirements.

Thinner Electronics

The reduction of the battery footprint can be the foothold to thinner and lighter electronics based on these thin film flexible lithium ion batteries. Since the batteries have such a high energy density in such a thin film, a thin film battery can replace a thicker, heavier, less energy dense battery in order to accomplish the same task. Today's society is fast-moving, technology driven and ever interconnecting. These thinner, lighter electronic devices can help shape the future of the way we use and think about technology. With other technological advancements being made, the possibility of even smaller, thinner and lighter electronic devices than those currently found today is not as far away as was once thought. These developments may be the step that leads to some part of the technology seen in futuristic television shows and movies, like Avatar, for example.

Chapter- 10

Lithium Iron Phosphate Battery

Lithium iron phosphate battery

specific energy	90–110 Wh/kg (320–400 J/g)
energy density	220 Wh/L (790 kJ/L)
specific power	>3 W/g
Energy/consumer-price	US$0.40–2.00/Wh (US$0.11–0.56/kJ)
Time durability	>10 years
Cycle durability	2,000 cycles
Nominal cell voltage	3.3 V

The **lithium iron phosphate ($LiFePO_4$)** battery**, also called** LFP **battery**, is a type of rechargeable battery, specifically a lithium ion battery, which uses $LiFePO_4$ as a cathode material.

History

$LiFePO_4$ was discovered by John Goodenough's research group at the University of Texas in 1996, as a cathode material for rechargeable lithium batteries. Because of its low cost, non-toxicity, the high abundance of iron, its excellent thermal stability, safety characteristics, good electrochemical performance, and high specific capacity (170 mA·h/g, or 610 C/g) it gained some market acceptance.

The key barrier to commercialization was its intrinsically low electrical conductivity. This problem, however, was then overcome partly by reducing the particle size and effectively coating the $LiFePO_4$ particles with conductive materials such as carbon, and partly by employing the doping approaches developed by Yet-Ming Chiang and his coworkers at MIT using cations of materials such as aluminum, niobium, and zirconium. It was later shown that most of the conductivity improvement was due to the presence of nanoscopic carbon originating from organic precursors. Products using the carbonized and doped nanophosphate materials developed by Chiang are now in high volume mass production and are used in industrial products by major corporations including Black and Decker's DeWalt brand, General Motors' Chevrolet Volt, Daimler, Cessna and BAE Systems.

Most lithium-ion batteries (Li-ion) used in consumer electronics products are lithium cobalt oxide batteries ($LiCoO_2$). Other varieties of lithium-ion batteries include lithium-manganese oxide ($LiMn_2O_4$) and lithium-nickel oxide ($LiNiO_2$). The batteries are named after the material used for their cathodes; the anodes are generally made of carbon and a wide variety of electrolytes are used.

Advantages and disadvantages

The $LiFePO_4$ battery uses a lithium-ion-derived chemistry and shares many of its advantages and disadvantages with other lithium ion battery chemistries.

However, one key advantage over other lithium-ion batteries is the superior thermal and chemical stability, which provides better safety characteristics than lithium-ion batteries with other cathode materials. Due to significantly stronger bonds between the oxygen atoms in the phosphate (compared to the cobalt), oxygen is not readily released, and as a result, lithium iron phosphate cells are virtually incombustable in the event of mishandling during charge or discharge, and can handle high temperatures without decomposing.

Lithium Iron Phosphate chemistry also offers a longer cycle life over standard lithium ion cells.

The use of phosphates also reduces the cost, safety and environmental concerns of Cobalt cells, particularly in regards of cobalt entering the environment through improper disposal.

One of the other major advantages for $LiFePO_4$ when compared with $LiCoO_2$ is higher current or peak-power rating.

LFP batteries have some drawbacks:

1. The energy density (energy/volume) of a new LFP battery is somewhat lower than that of a new $LiCoO_2$ battery. (14% reduction in energy density) Battery manufacturers across the world are currently working to find ways to maximize the energy storage performance and reduce size & weight.
2. Many brands of LFP's have a low discharge rate compared with lead-acid or $LiCoO_2$. Since discharge rate is a percentage of battery capacity this can be overcome by using a larger battery (more ampère-hours). However, A123Systems claims 100C pulse discharge rate.

While $LiFePO_4$ cells have lower voltage and energy density than $LiCoO_2$ Li-ion cells, this disadvantage is offset over time by the slower rate of capacity loss (aka greater calendar-life) of $LiFePO_4$ when compared with other lithium-ion battery chemistries (such as $LiCoO_2$ *cobalt* or $LiMn_2O_4$ *manganese spinel* based lithium-ion polymer batteries or lithium-ion batteries). For example:

- After one year on the shelf, a $LiFePO_4$ cell typically has approximately the same energy density as a $LiCoO_2$ Li-ion cell.
- Beyond one year on the shelf, a $LiFePO_4$ cell is likely to have *higher* energy density than a $LiCoO_2$ Li-ion cell due to the differences in their respective calendar-lives.

Specifications

- Cell voltage = min. discharge voltage = 2.8 V. Working voltage = 3.0 V – 3.3 V. Max. charge voltage = 3.6 V.
- Volumetric energy density = 220 Wh/dm^3 (790 kJ/dm^3)
- Gravimetric energy density = >90 Wh/kg (>320 J/g)
- 100% DOD cycle life (number of cycles to 80% of original capacity) = 2,000–7,000
- Cathode composition (weight)
  - 90% C-LiFePO4, grade Phos-Dev-12
  - 5% Carbon EBN-10-10 (superior graphite)
  - 5% PVDF
- Cell Configuration
  - Carbon-coated aluminum current collector 15
  - 1.54 cm^2 cathode
  - Electrolyte: EC-DMC 1-1 $LiClO_4$ 1M
  - Anode: Metallic lithium
- Experimental conditions: ** Note the following is for Cobalt Cathode LiIon cells - should be changed for LiFePO
  - Room temperature
  - Voltage limits: 2.5 – 4.2 V
  - Charge: C/4 up to 4.2 V, then potentiostatic at 4.2 V until I < C/24

Safety

$LiFePO_4$ is an intrinsically safer cathode material than $LiCoO_2$ and manganese spinel. The Fe-P-O bond is stronger than the Co-O bond, so that when abused, (short-circuited, overheated, etc.) the oxygen atoms are much harder to remove. This stabilization of the redox energies also helps fast ion migration.

As lithium migrates out of the cathode in a $LiCoO_2$ cell, the CoO_2 undergoes non-linear expansion that affects the structural integrity of the cell. The fully lithiated and unlithiated states of $LiFePO_4$ are structurally similar which means that $LiFePO_4$ cells are more structurally stable than $LiCoO_2$ cells.

No lithium remains in the cathode of a fully charged $LiFePO_4$ cell—in a $LiCoO_2$ cell, approximately 50% remains in the cathode. $LiFePO_4$ is highly resilient during oxygen loss, which typically results in an exothermic reaction in other lithium cells.

Usage

LFP batteries were featured on the November 5, 2008 episode of *Prototype This!*. They were used as the power source for a hexapod (walking) vehicle. Lithium Technology Corp. announced in May 2007, that they had developed a new Lithium Iron Phosphate battery with cells large enough for use in hybrid cars, claiming they are "the largest cells of their kind in the world.". While they may be large enough for such uses, there remain limitations to the use of this particular Lithium battery technology which may make their use contraindicated.

This battery is used in the electric cars made by Aptera and QUICC.

This type of battery technology is used on the One Laptop per Child (OLPC) project.

Killacycle, the worlds fastest electric motorcycle, uses lithium iron phosphate batteries.

Roehr Motorcycle Company, uses a 5.8 kW·h capacity LFP battery pack to power its supersport electric motorcycle.

OLPC batteries are manufactured by BYD Company of Shenzhen, China, the world's largest producer of Li-ion batteries. BYD, also a car manufacturer, plans to use its Lithium Iron Phosphate batteries to power its PHEV, the F3DM and F6DM (Dual Mode), which will be the first commercial dual-mode electric car in the world. It plans to mass produce the cars in 2009.

LFP batteries are gaining popularity now in the world of hobby-grade R/C, due to the benefits over the ever-popular LiPo batteries. They can be recharged much faster and for more cycles, are not prone to catching fire or exploding while recharging, and are more robust than the LiPo type.

LFP batteries are used by electric vehicles manufacturer Smith Electric Vehicles to power its products.

Used by Minneapolis Electric Bike and Chicago Electric Bicycles.

Some electronic cigarette modifications also use these types of batteries.

Notable manufacturers

- A123Systems
- BYD Company
- Shandong Hipower New Energy Group.
- China Sun Group - Second largest cobalt series production line in China
- Lithium Technology Corporation
- Tenergy
- ThunderSky
- Valence Technology - makes lithium phosphate battery modules
- K2 Energy
- FULLRIVER Battery
- Zhuhai Yintong Energy

Chapter- 11

Vanadium Redox Battery

Vanadium redox battery

specific energy	10–20 Wh/kg (36–72 J/g)
energy density	15–25 Wh/L (54–65 kJ/L)
Charge/discharge efficiency	75-80%<.
Time durability	10–20 years
Cycle durability	>10,000 cycles
Nominal cell voltage	1.15–1.55 V

The **vanadium redox** (and redox flow) **battery** is a type of rechargeable flow battery that employs vanadium redox couples in both half-cells, thereby eliminating the problem of cross contamination by diffusion of ions across the membrane. The present form (with sulfuric acid electrolytes) was patented by the University of New South Wales in Australia in 1986 An earlier German Patent on a titanium chloride flow battery was registered and granted in July 1954 to Dr. Walter Kango, but most of the development of flow batteries was carried out by NASA researchers in the 1970s. Although the use of vanadium in batteries had been suggested earlier by Pissoort, by NASA researchers and by Pellegri and Spaziante in 1978, the first known successful demonstration and commercial development of the all-vanadium redox flow battery employing vanadium redox couples in a solution of sulpuric acid in both half-cells was by Maria Skyllas-Kazacos and co-workers at the University of New South Wales in the 1980s.

There are currently a number of suppliers and developers of these Battery Systems including Renewable Energy Dynamics (RED-T), Cellstrom GmbH, Celennium in Thailand, and Prudent Energy in China. The Vanadium Redox Battery (VRB™) is the product of over 25 years of research, development, testing and evaluation in Australia, Europe, North America and elsewhere.

The vanadium redox battery exploits the ability of vanadium to exist in solution in four different oxidation states, and uses this property to make a battery that has just one electroactive element instead of two.

The main advantages of the vanadium redox battery are that it can offer almost unlimited capacity simply by using larger and larger storage tanks, it can be left completely discharged for long periods with no ill effects, it can be recharged simply by replacing the electrolyte if no power source is available to charge it, and if the electrolytes are accidentally mixed the battery suffers no permanent damage.

The main disadvantages with vanadium redox technology are a relatively poor energy-to-volume ratio, and the system complexity in comparison with standard storage batteries.

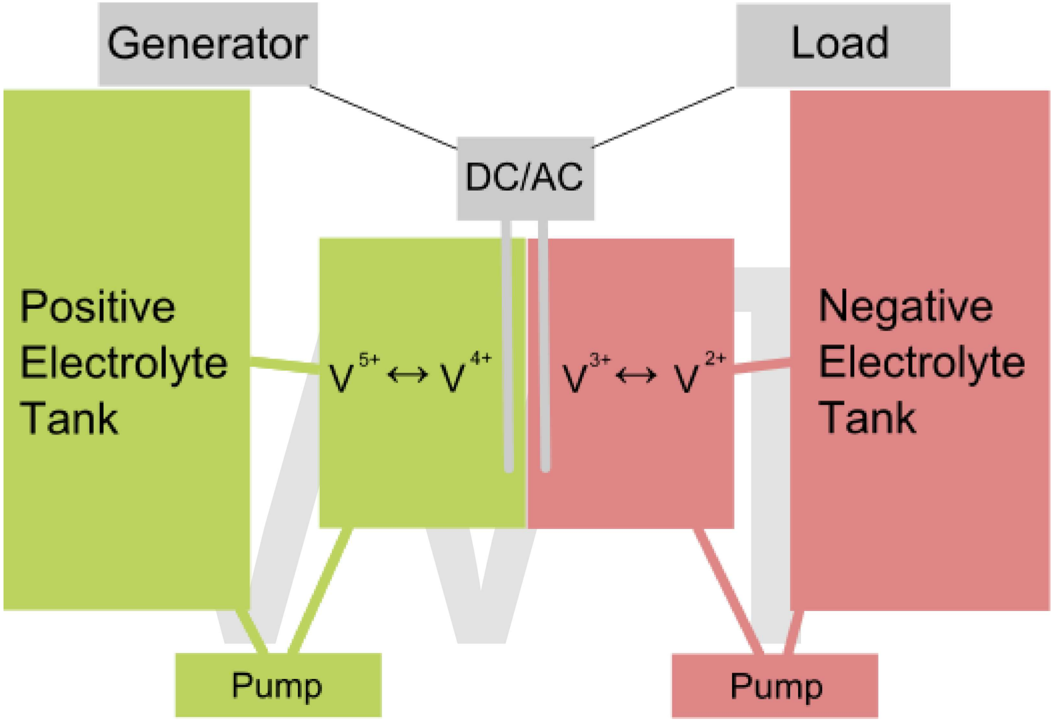


Diagram of a Vanadium Flow Battery

Operation

A vanadium redox battery consists of an assembly of power cells in which the two electrolytes are separated by a proton exchange membrane. Both electrolytes are vanadium based, the electrolyte in the positive half-cells contains VO_2^+ and VO^{2+} ions, the electrolyte in the negative half-cells, V^{3+} and V^{2+} ions. The electrolytes may be prepared by any of several processes, including electrolytically dissolving vanadium pentoxide (V_2O_5) in sulfuric acid (H_2SO_4). The solution remains strongly acidic in use.

In vanadium flow batteries, both half-cells are additionally connected to storage tanks and pumps so that very large volumes of the electrolytes can be circulated through the cell. This circulation of liquid electrolytes is somewhat cumbersome and does restrict the use of vanadium flow batteries in mobile applications, effectively confining them to large fixed installations, although one company has focused on electric vehicle applications, using rapid replacement of electrolyte to refuel the battery.

When the vanadium battery is charged, the VO^{2+} ions in the positive half-cell are converted to VO_2^+ ions when electrons are removed from the positive terminal of the battery. Similarly in the negative half-cell, electrons are introduced converting the V^{3+} ions into V^{2+}. During discharge this process is reversed and results in a typical open-circuit voltage of 1.41 V at 25 °C.

Other useful properties of vanadium flow batteries are their very fast response to changing loads and their extremely large overload capacities. Studies by the University of New South Wales have shown that they can achieve a response time of under half a millisecond for a 100% load change, and allowed overloads of as much as 400% for 10 seconds. The response time is mostly limited by the electrical equipment. Round trip efficiency in practical applications is around 65-75%.

Generation 2 vanadium redox batteries (vanadium/Polyhalide) may approximately double the energy density and increase the temperature range in which the battery can operate.

Energy density

Current production vanadium redox batteries achieve an energy density of about 25 Wh/kg of electrolyte. More recent research at UNSW indicates that the use of precipitation inhibitors can increase the density to about 35 Wh/kg, with even higher densities made possible by controlling the electrolyte temperature. This energy density is quite low as compared to other rechargeable battery types (e.g., lead-acid, 30–40 Wh/kg; and lithium ion, 80–200 Wh/kg).

Researchers at the Fraunhofer Institute for Chemical Technology claim to have built a prototype for a cell which is capable of energy densities "with a four or fivefold improvement, improving on lead acid to approximately that of lithium-ion batteries".

Applications

The extremely large capacities possible from vanadium redox batteries make them well suited to use in large power storage applications such as helping to average out the production of highly variable generation sources such as wind or solar power, or to help generators cope with large surges in demand.

The limited self-discharge characteristics of vanadium redox batteries make them useful in applications where the batteries must be stored for long periods of time with little maintenance while maintaining a ready state. This has led to their adoption in some military electronics, such as the sensor components of the GATOR mine system.

Their extremely rapid response times also make them superbly well suited to UPS type applications, where they can be used to replace lead-acid batteries and even diesel generators.

Installations

Currently installed vanadium batteries include:

- A 1.5 MW UPS system in a semiconductor fabrication plant in Japan.
- A 275 kW output balancer in use on a wind power project in the Tomari Wind Hills of Hokkaido.
- A 200 kW, 800 kW·h (2.9 GJ) output leveler in use at the Huxley Hill Wind Farm on King Island, Tasmania.
- A 250 kW, 2 MW·h (7.2 GJ) load leveler in use at Castle Valley, Utah.
- Two 5-kW units installed at Safaricom GSM site in Katangi and Njabini, Winafrique Technologies, Kenya.
- Two 5-kW units installed in St. Petersburg, Florida, under the auspices of USF's Power Center for Utility Explorations.

Chapter- 12

Other Rechargeable Batteries

Rechargeable alkaline battery

Rechargeable Alkaline AA battery

Rechargeable alkaline battery (also known as Alkaline Rechargeable or Rechargeable Alkaline Manganese (RAM)) is a type of alkaline battery that is rechargeable. The first generation rechargeable alkaline technology was developed by Battery Technologies Inc in Canada and licensed to Pure Energy, EnviroCell, Rayovac, and Grandcell. Subsequent patent and advancements in technology have been introduced. The shapes include AAA, AA, C, D, and snap-on 9-volt batteries. Rechargeable alkaline batteries have the ability to carry their charge for years, unlike most NiCd and NiMH batteries which self-discharge in 90 days. However, new low self-discharge NiMH cells, such as Sanyo "Eneloop", claim to retain 85% charge after 1 year. If produced properly, rechargeable alkaline batteries can have a charge/recharge efficiency of as much as 99.9% and be an environmentally-friendly form of energy storage.

Chemical composition

The main difference in composition between rechargeable and regular alkaline is that the blend of materials and formula used to make the batteries has been altered to allow for the batteries to recharge. Without this modification in chemical composition, the batteries would not hold multiple charges. The batteries are also designed to resist leakage, which is sometimes a problem when traditional alkaline batteries are recharged or discharged too far.

Proper use and durability

Although these batteries can be used in any device that supports a standard size (AA, AAA, C, D, etc.), they are formulated to last longest in periodical use items. This type of battery is best suited for use in low-drain devices such as remote controls or for devices that are used periodically such as flashlights, television remotes, portable radios, etc.

Disadvantages from other rechargeable batteries

Recharging issues

Though rechargeable alkaline batteries are relatively cheap and contain a high charge-capacity, their rechargeable capacity will vary by how much they are discharged:

- If they are discharged by less than 25%, they can be recharged for hundreds of cycles to about 1.42V.
- If they are discharged by less than 50%, they can be almost-fully recharged for a few dozen cycles, to about 1.32V.
- After a "Deep Discharge", they can be brought to their original high-capacity charge only after a few charge-discharge cycles.

Environmental issues

Some types of cells contain mercury or cadmium and thus are a serious environment hazard unless special care is taken for their disposal. As of August 2007, a number of companies make batteries that are non-toxic and free from heavy metals. According to the websites of EnviroCell and PureEnergy and according to old Rayovac packaging, these manufacturers' rechargeable alkaline batteries have no mercury or cadmium.

Environmental benefits

Recent advancements in technology and chemical composition has resulted in the modern rechargeable alkaline battery emerging as a leader in the industry-wide push towards more environmentally responsible batteries.

EnviroCell

According to its advertising, a company called EnviroCell makes rechargeable alkaline batteries that use a patented technology. EnviroCell claims that their batteries can be recharged safely up to 60 times with no memory effect and also that they contain no toxic metals and can be safely disposed.

Production and supply issues

- Rayovac produced a variety of these rechargeable batteries called Renewal. Rayovac discontinued these products, possibly due to poor market acceptance and cell leakage problems, or due to corporate strategy and superior profit from single-use batteries. Similar rechargeable alkaline batteries are still available from other vendors. More recently, Rayovac has released a new line of rechargeable NiMH batteries, but from the information listed on their website, they no longer produce an alkaline rechargeable battery.
- Another Rechargeable Alkaline battery brand is "PureEnergy". PureEnergy's website states: "Rechargeable Alkaline is the only rechargeable battery that can be used in any application that uses disposable alkaline batteries. It also offers several performance and cost saving advantages over other rechargeable batteries."

- Some say that certain types of battery chargers are able to recharge alkaline batteries as well as NiCd and NiMH, provided that the charger only has one type in it at any one time. PureEnergy currently sells a NiMH and alkaline dual chemistry charger that does work well for both battery types. Some claim that it is indeed possible to recharge a regular non-rechargeable alkaline battery under the right conditions and using the right type of current; however, this is still dangerous. There are chargers available which are specially designed to recharge ordinary alkaline batteries, in addition to NiCd and NiMH. Under ideal conditions, it is supposed to recharge regular alkalines up to 10 or 15 times; although in practice, five recharges is more common (after which, they start to leak). It is also possible to recharge primary alkaline batteries in a rechargeable alkaline charger or even some NiMH/NiCd chargers, but the manufacturers recommend against doing so.

Nickel-iron battery

Nickel-iron battery

specific energy	30 -50 Wh/kg
energy density	30 Wh/l
specific power	100 W/kg
Charge/discharge efficiency	65%-80%
Energy/consumer-price	1.5 – 6.6 Wh/US$
Self-discharge rate	20% – 30%/month
Time durability	30 – 50 years
Cycle durability	Repeated deep discharge does not reduce life significantly.
Nominal cell voltage	1.2 V
Charge temperature interval	min.-40 °C – max.46 °C

The **nickel-iron battery** (NiFe battery) is a storage battery having a nickel(III) oxide-hydroxide cathode and an iron anode, with an electrolyte of potassium hydroxide. The active materials are held in nickel-plated steel tubes or perforated pockets. It is a very robust battery which is tolerant of abuse, (overcharge, overdischarge, and short-circuiting) and can have very long life even if so treated. It is often used in backup situations where it can be continuously charged and can last for more than 20 years. Due to low specific energy, poor charge retention, and its high cost of manufacture, other types of rechargeable batteries have displaced the nickel-iron battery in most applications. They are currently gaining popularity for off-the-grid applications where daily charging makes them an appropriate technology.

Durability

The ability of these batteries to survive frequent cycling is due to the low solubility of the reactants in the electrolyte. The formation of metallic iron during charge is slow because of the low solubility of the ferrous hydroxide. While the slow formation of iron crystals preserves the electrodes, it also limits the high rate performance: these cells charge slowly, and are only able to discharge slowly. Nickel-iron cells should not be charged from a constant voltage supply since they can be damaged by thermal runaway; the cell internal voltage drops as gassing begins, raising temperature, which increases current drawn and so further increases gassing and temperature.

Nickel-iron batteries have long been used in European mining operations because of their ability to withstand vibrations, high temperatures and other physical stress. They are being examined again for use in wind and solar power systems and for modern electric vehicles, especially boats, where the weight of the batteries is not an issue.

Electrochemistry

The half-cell reaction at the cathode:

$$2\ \mathrm{NiOOH} + 2\ \mathrm{H_2O} + 2\ e^- \leftrightarrow 2\ \mathrm{Ni(OH)_2} + 2\ \mathrm{OH^-}$$

and at the anode:

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

(Discharging is read left to right, charging is from right to left.)

The open-circuit voltage is 1.4 volts, dropping to 1.2 volts during discharge. The electrolyte mixture of potassium hydroxide and lithium hydroxide is not consumed in charging or discharging, so unlike a lead-acid battery the electrolyte specific gravity does not indicate state of charge. Lithium hydroxide improves the performance of the cell. the voltage required to charge the cells is between 1.45 and 1.65 volts. The equalization charge voltage is 1.65 volts.

History

Swedish inventor Waldemar Jungner(1869–1924) had invented the nickel-cadmium battery in 1899. Jungner experimented with substituting iron for the cadmium in varying proportions, including 100% iron. Jungner had already discovered that the main advantage over the nickel-cadmium chemistry was cost, but due to the poorer efficiency of the charging reaction and more pronounced formation of hydrogen (gassing), the nickel-iron technology was wanting and was abandoned. Jungner had several patents for the iron version of his battery (Swedesh pat.Nos 8.558/1897, 10.177/1899, 11.132/1899, 11.487/1899 and German Patent No.110.210 /1899. Moreover he had one patent for NiCd-battery: Swed.pat No. 15.567/1899.

The battery was developed by Thomas Edison in 1901, and used as the energy source for electric vehicles, such as the Detroit Electric and Baker Electric. Edison claimed the nickel-iron design to be, "far superior to batteries using lead plates and acid" (lead-acid battery). Edison had also several patents: US.Pat No.678.722/1901, 692.507/1902 and German patent No 157.290/1901.

Jungner's work was largely unknown in the US until the 1940s, when nickel-cadmium batteries went into production there. A 50 volt nickel-iron battery was the main power supply in the World War II German V2 rocket (together with two 16 volt accumulators which powered the four gyroscopes), with a smaller version used in the V1 flying bomb. (viz. 1946 Operation Backfire blueprints.)

Manufacture

Edison's batteries were made from about 1903 to 1972 by the Edison Battery Storage Company located in East Orange, NJ. They were quite profitable for the company. In 1972 the battery company was sold to the Exide Battery Corporation, which discontinued making the battery in 1975.

Edison was disappointed that his battery was not adopted for starting internal combustion engines and that electric vehicles went out of production only a few years after his battery was introduced. He actually developed the battery to be the battery of choice for electric vehicles which were the preferred transportation mode in the early 1900s (followed by gasoline and steam). Edison's batteries had a significantly higher energy density than the lead acid batteries in use at the time, and could be charged in half the time, however they performed poorly at low ambient temperatures and were more expensive. The battery enjoyed wide use for railroad signaling, fork lift, and standby power applications.

Nickel-iron cells were made with capacities from 5 Ah to 1250 Ah. Many of the original manufacturers no longer make nickel iron cells. Currently they are being manufactured in China and Russia.

Environmental impact

Nickel-iron batteries do not have the lead or cadmium of the lead-acid and nickel-cadmium batteries, which makes them a lesser burden on human and ecological health.

Nickel-zinc battery

Nickel-zinc battery	
specific energy	100 W·h/kg
energy density	280 W·h/L
specific power	> 900 W/kg
Energy/consumer-price	2-3Wh/US$
Cycle durability	400-1000
Nominal cell voltage	1.65 V

The **nickel-zinc battery** (sometimes abbreviated **NiZn**) is a type of rechargeable battery that may be used in cordless power tools, cordless telephone, digital cameras, battery operated lawn and garden tools, professional photography, electric bike, and light electric vehicle sectors.

Nickel-zinc battery systems have been known for over 100 years. Since 2000, development of a stabilized zinc electrode system made this technology viable and competitive with other commercially available rechargeable battery systems.

History

Thomas Edison was awarded U.S. Patent 684,204 for a rechargeable nickel-zinc battery system in 1901.

The battery was later developed by an Irish chemist, Dr. James J. Drumm (1897–1974) and installed in four 2-car Drumm Railcar sets between 1932 and 1948 for use on the Dublin-Bray line. Although successful they were then withdrawn when the batteries wore out. Early nickel-zinc batteries were plagued by limited number of discharge cycles. In the 1960s nickel-zinc batteries were investigated as an alternative to silver-zinc batteries for military applications, and in the 1970s were again of interest for electric vechicles. A company called *Evercel Inc.* formerly developed and patented several improvements in nickel-zinc batteries but withdrew from that area in 2004.

Applications

Nickel-zinc batteries have a charge/discharge curve similar to 1.2V NiCd or NiMH cells—but with a higher 1.6V nominal voltage.

Presently this battery technology has limited consumer availability, with only AA cells offered for the digital camera market in some camera stores. Both D-cells and sub-C cells are currently used in commercial applications.

Nickel-zinc batteries perform well in high drain applications, and may have the potential to replace lead-acid batteries because of their higher-energy-to-mass ratio and higher-power-to-mass ratio (up to 75% lighter for the same power), and are cheap compared to nickel-cadmium batteries (expected to be priced somewhere in between NiCd and lead-acids). NiZn may be used as a substitute for nickel-cadmium. The European Parliament has supported bans on cadmium-based batteries; nickel-zinc offers the European power tool industry an alternative.

Electrochemistry

Charge Reaction: $2Ni(OH)_2(s) + Zn(OH)_2(s) \leftrightarrow 2Ni(OH)_3(s) + Zn(s)$

Note that the stoichiometry above is different than below, but the reactions are identical. Water is consumed and generated on the charge and discharge cycles.

Discharge Reaction: $H_2O + Zn + 2NiOOH \leftrightarrow ZnO + 2Ni(OH)_2$

Electrochemical open circuit voltage potential: ~1.73V

Battery Life

The tendency of the zinc electrode to dissolve into solution and not fully migrate back to the cathode during charging has, in the past, presented challenges to the commercial viability of the NiZn battery. The zinc's reluctance to fully return to the same location of the solid electrode adversely manifests itself as shape change and dendrites or whiskers, which may reduce the cell discharging performance or eventually short out the cell, resulting in low cycle life.

Recent advancements have enabled manufacturers to prevent this problem. These advancements include improved electrode separator materials, zinc material stabilizers, and electrolyte improvements. One manufacturer (PowerGenix) claims battery cycle life comparable to NiCd batteries.

Battery cycle life is most commonly specified at a discharge depth of 80 percent of rated capacity and assuming a one hour discharge current rate. If the discharge current rate is reduced or if the depth of discharge is reduced then the number of charge/discharge cyles for a battery increases.

When comparing NiZn to other battery technologies it is important to note that cycle life specifications may vary with other battery technologies depending on the discharge rate and depth of discharge that were used.

Advantages

Nickel-zinc cells have an open circuit voltage of 1.8 volts when fully charged and a nominal voltage of 1.65V. This makes NiZn an excellent replacement for electronic products that were designed to use alkaline primary cells (1.5V). NiCd and NiMH both have nominal cell voltages of 1.2V, which may cause some electronic equipment to shut off prior to a complete discharge of the battery because the minimal operating voltage is not provided.

Due to their higher voltage, fewer cells are required (compared to NiCd and NiMH)to achieve a given battery pack voltage, reducing pack weight, size and improving pack reliability. They also have low internal impedance (typ. 5 milliohms) which allows for high battery discharge rates.

NiZn batteries do not use mercury, lead or cadmium, or metal hydrides (rare earth metals) that are difficult to recycle. Both nickel and zinc are commonly occurring elements in nature. Zinc and nickel can be fully recycled.

NiZn cells use no flammable active material or organic electrolyte.

Properly designed NiZn cells can have very high power density and low temperature discharging performance.

Disadvantages

Currently, only Sub C and AA NiZn cells are available. Compared with other secondary systems, nickel-zinc cells have lower volumetric energy density.. Nickel is also more costly than the lead used in lead acid batteries.

Charging

NiZn technology is well suited for fast recharge cycling as optimum charge rates of C or C/2 are preferred .

Known charging regimes include constant current of C or C/2 to cell voltage = 1.9V. Maximum charge time is 2½ hours. Trickle charging is not recommended as recombination is not provided for and excess hydrogen will eventually vent adversely affecting battery cycle life. Charge is reinitiated after cell voltage has fallen below 1.6V.

Lithium sulfur battery

Lithium sulfur battery	
specific energy	350 Wh/kg demonstrated 500-600 Wh/kg achievable
energy density	350 Wh/l
Charge/discharge efficiency	C/5 nominal; up to 2C
Cycle durability	disputed
Nominal cell voltage	cell voltage varies nonlinearly in the range 2.5-1.7 during discharge; batteries often packaged for 3V

The **lithium sulfur battery** (Li-S battery) is a rechargeable galvanic cell with a very high energy density. By virtue of the low atomic weight of lithium and moderate weight of sulfur, Li-S batteries are relatively light; about the density of water. They were demonstrated on the longest and highest-altitude solar-powered airplane flight in August, 2008. Lithium Sulfur batteries may succeed lithium-ion cells because of their higher energy density and the low cost of sulfur. There is much interest in using them for electric vehicles.

Chemistry

The chemical processes in the Li-S cell include lithium dissolution from the anode surface (and incorporation into polysulfides) during discharge, and reverse lithium plating to the nominal anode while charging. This contrasts with conventional lithium-ion cells, where the lithium ions are intercalated in the anode and cathodes, and consequently Li-S allows for a much higher lithium storage density. Polysulfides are reduced on the anode surface in sequence while the cell is discharging:

$$S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_3$$

Across a porous diffusion separator, sulfur polymers form at the nominal cathode as the cell charges:

$$Li_2S \rightarrow Li_2S_2 \rightarrow Li_2S_3 \rightarrow Li_2S_4 \rightarrow Li_2S_6 \rightarrow Li_2S_8 \rightarrow S_8$$

These reactions are analogous to those in the sodium-sulfur battery.

For experimental purposes most batteries are constructed with a carbon and sulfur cathode and a lithium anode. Sulfur as a raw material has the advantage for mass production that it is very cheap, but it lacks electroconductivity. Sulfur alone being at $5*10^{-30}$ S cm^{-1} at 25°C. The carbon coating on the sulfur then provides the electroconductivity missing from pure sulfur. The solution to this problem is carbon nanofibers. The carbon materials provide an effective electron conduction path and structural integrity. The downside of carbon nanofibres is the high cost.

Each sulfur atom can host two lithium ions. Typically, in lithium-ion batteries, for every host atom, only 0.5 to 0.7 lithium ions can be accommodated.

Degradation

One of the primary shortfalls of most Li-S cells is intermediary reactions with the electrolytes. While S and Li_2S are relatively insoluble in most electrolytes, many of the intermediary polysulfides are not. The dissolving of LiS_n into electrolytes causes irreversible loss of active sulfur material. The majority of research on Lithium-sulfur batteries in 2010 is to improve the choice of electrolytes to minimize this side reaction.

Safety

Because of the high potential energy density and the nonlinear discharge and charging response of the cell, a microcontroller and other safety circuitry is sometimes used along with voltage regulators to control cell operation and prevent rapid discharge.

Recent advances

Research conducted at the University of Waterloo has produced Li-S cells with 84% of the theoretical maximum energy density for Li-S that suffer minimal degradation during charge cycling, and thus potentially offering four times the gravimetric energy density of lithium-ion. The team accomplished this through use of a mesoporous carbon cathode, full of deep pits. Sulfur and carbon were milled and heated together, causing the low surface tension sulfur to seep into the pits, with just enough room to expand. The composite was then heated to bake off residual sulfur from the surface. To further trap the polysulfides in the cathode, the surface was functionalized and coated with polyethylene glycol to repel the hydrophobic polysulfides and keep them trapped in the pits. In a "worst case scenario" test using a glyme solvent known for its affinity for dissolving polysulfides, a traditional LiS cathode lost 96% of its sulfur over 30 cycles, while the new cathode lost only 25%.

Lithium-titanate battery

The **Lithium-titanate battery** is a type of rechargeable battery, which has the advantage of being faster to charge than other lithium-ion batteries. Some analysts speculate that lithium-titanate batteries will power electric cars of the future.

A lithium-titanate battery is a modified lithium-ion battery that uses lithium-titanate nanocrystals on the surface of its anode instead of carbon. This gives the anode a surface area of about 100 square meters per gram, compared with 3 square meters per gram for carbon, allowing electrons to enter and leave the anode quickly. This makes fast recharging possible and provides high currents when needed. The disadvantage is that lithium-titanate batteries have a lower voltage and capacity than conventional lithium-ion battery technologies.

Brands and uses

Altairnano

Altairnano produce lithium-titanate batteries under the "Nanosafe" line, mainly for battery electric vehicles. Some vehicle manufacturers which announced plans to use Altairnano batteries includes Lightning Car Company, which plan to use them for Lightning GT, an all-electric sports car, Phoenix Motorcars, in its electric sport-utility vehicles, and Proterra, in its all-electric EcoRide BE35 vehicle, a lightweight 35-foot bus.

Altairnano has also deployed their lithium-titanate energy storage systems for electric grid ancillary services and in various military applications.

Toshiba

An example of a SCiB cell

Toshiba released a lithium-titanate battery, dubbed Super Charge Ion Battery (SCiB). The battery is designed to offer 90% charge capacity in just 10 minutes.

SCiB batteries are used in the Schwinn Tailwind electric bike. Toshiba has also demonstrated its use as a laptop battery. Toshiba announced plans to bring the SCiB battery to electric vehicles.