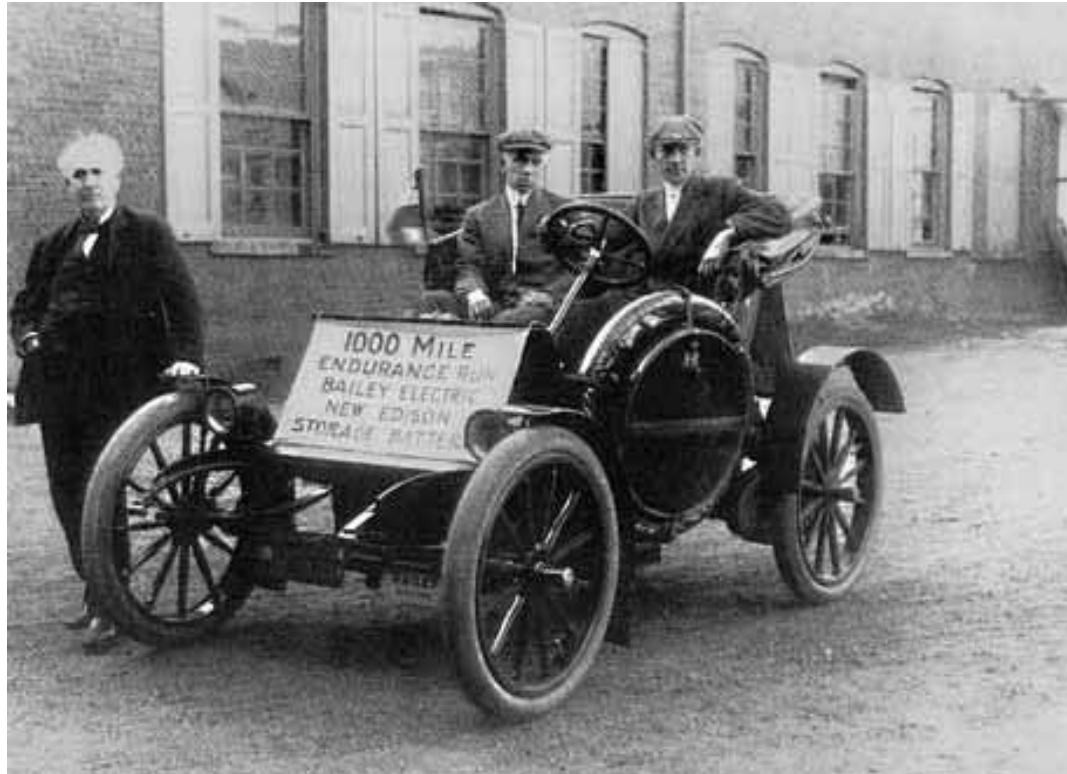# Session #6
Batteries

Edison at his West Orange lab with an electric car powered by Edison batteries, 1910

Alessandro Volta

History of Battery Development

1600 Gilbert (England) Establishment electrochemistry study

1791 Galvani (Italy) Discovery of 'animal electricity'

1800 Volta (Italy) Invention of the voltaic cell

1802 Cruickshank (England) First electric battery capable of mass production

1820 Ampère (France) Electricity through magnetism

1833 Faraday (England) Announcement of Faraday's Law

1836 Daniell (England) Invention of the Daniell cell

1859 Planté (France) Invention of the lead acid battery

1868 Leclanché (France) Invention of the Leclanché cell

1888 Gassner (USA) Completion of the dry cell

1899 Jungner (Sweden) Invention of the nickel-cadmium battery

1901 Edison (USA) Invention of the nickel-iron battery

1932 Shlecht & Ackermann (Germany) Invention of the sintered pole plate

1947 Neumann (France) Successfully sealing the nickel-cadmium battery

1960 Union Carbide (USA) Development of primary alkaline battery

1970 Development of valve regulated lead acid battery

1990 Commercialization nickel-metal hydride battery

1992 Kordesch (Canada) Commercialization reusable alkaline battery

1999 Commercialization lithium-ion polymer

Types of Primary (Disposable) Batteries

Carbon/zinc batteries — Lecianchd cells with a gelled electrolyte. First mass produced battery. They have poor low-temperature capability and low capacity. They have a discharge curve with a pronounced slope and change in voltage with time. A battery will be exhausted if it delivers less than 1 volt when on load. The ammonium chloride electrolyte is mildly corrosive and can cause damage to equipment if exhausted batteries are left in place.

Alkaline-manganese batteries — This type of cell has up to 4 times the energy content of the equivalent size of carbonlzinc. They are capable of delivering high intermittent currents and are less prone to electrolyte leakage when exhausted. The shelf life of the cell (in unused condition) is at least 3 years and the discharge curve has a much less pronounced slope than the carbon-zinc type. The electrolyte is a potassium hydroxide gel and manganese dioxide acts as the anode. Apart from its ability to deliver high currents (the cell chemistry can produce up to 2 A per cell at 2°C), the chief advantage of this type of cell is its ability to function adequately over a large range of temperature. The nominal voltage of this and the preceding type of cell is 1.55.

Mercury-zinc batteries — These are commonly referred to as 'Mallory' cells and are most commonly met with as small, button-sized cells in equipment where current drains tend to be low - such as light meters or some types of pH meter. The discharge characteristic means that a stable voltage is available for most of the cell's service life, but the discharge curve is quite steep once the cell starts to become exhausted. Mallory produce some large versions of this type of battery, such as the RMI2R in an AA (AM3, MN1500, LR6) size. This has a nominal capacity of 3.9 Ah which is more than double that of the same size alkaline-manganese type (1.6 Ah). - but costs several times as much. The voltage (1.35) of this type of cell is less than alkaline manganese or silver types and this may be a critical factor in limiting its use.

Types of Primary (Disposable) Batteries (cont'd)

Silver-zinc batteries — These are 1.5 volt types, usually buttonsized, which offer a slightly higher current density and longer service life compared with the previous type of cell. They are used where their somewhat higher voltage is an advantage compared with the 1.35 volts of similar-sized mercury types. In common with mercury batteries, the output voltage remains constant for most of the battery's life.

Lithium batteries — Recent developments in battery technology have lead to the availability of primary cells with outputs in excess of 3 volts and extended temperature tolerance. The lithium thionyl chloride type has a very high energy density and 'is usually employed for low to medium current drain applications, such as memory or clock backup in data loggers. These batteries have a shelf life in excess of 10 years and are rated for operation over a similar period at low levels of discharge current (< 0.5 mA). At higher discharge currents, the capacity appears to be slightly superior to a physically similar-sized alkaline-manganese type. The output voltage is stable over a wide range of moderate to low discharge currents and the capacity of the AA size is approximately 1.6 Ah.
The lithium CFX type is intended for low current drain applications, such as memory or clock backup in microprocessor-controlled equipment. They are often referred to as 'coin' cells because of their appearance and they have similar storage characteristics to the previous type. The discharge characteristic is remarkably level for most of the service life of the cell and the voltage is stable over a wide range of moderate to low discharge currents. The capacity of this type of cell is approximately 0.17 - 0.25 Ah.
(Self Discharge: 5% loss in first 24hrs, 5-10%/month afterwards)

Types of Secondary (Rechargeable) Batteries

Nickel Cadmium (NiCd) — mature and well understood but relatively low in energy density. The NiCd is used where long life, high discharge rate and economical price are important. Main applications are two-way radios, biomedical equipment, professional video cameras and power tools. The NiCd contains toxic metals and is not environmentally friendly. (1.2V/cell) (Self Discharge: 10% loss in first 24hrs, 10%/month afterwards)

Nickel-Metal Hydride (NiMH) — has a higher energy density compared to the NiCd at the expense of reduced cycle life. NiMH contains no toxic metals. Applications include mobile phones and laptop computers. (1.2V/cell) (Self Discharge: 15% loss in first 24hrs, 20-30%/month afterwards)

Lead Acid — most economical for larger power applications where weight is of little concern. The lead acid battery is the preferred choice for hospital equipment, wheelchairs, emergency lighting and UPS systems. (2.2V/cell) (Self Discharge: 5%/month)
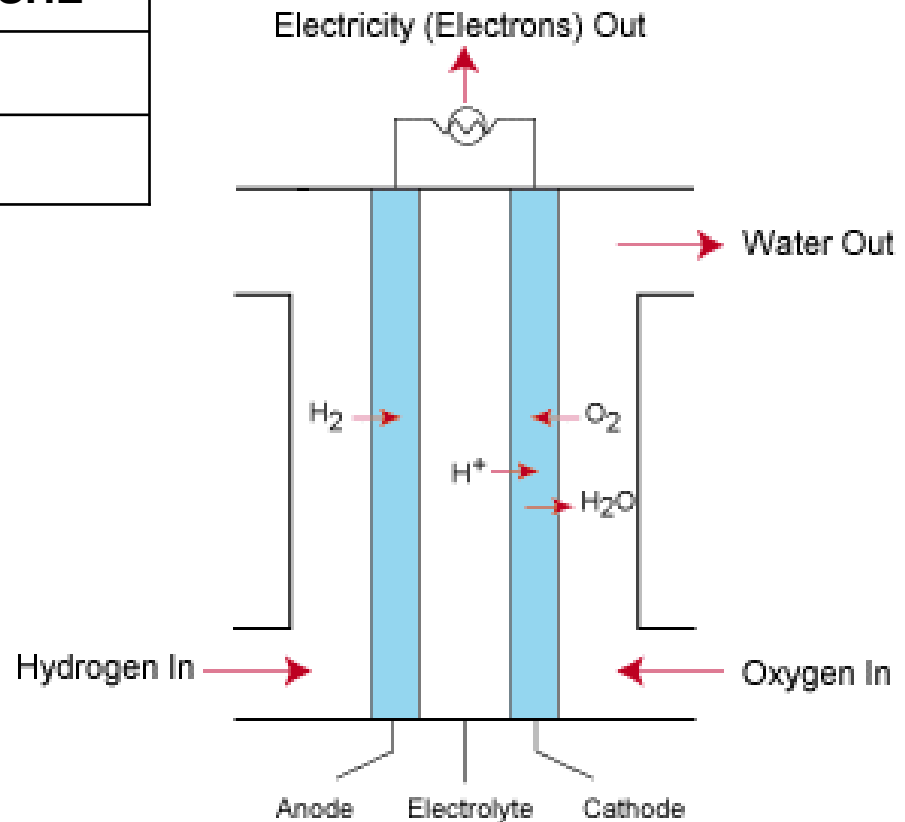
Lithium Ion (Li-ion) — fastest growing battery system. Li-ion is used where high-energy density and light weight is of prime importance. The Li-ion is more expensive than other systems and must follow strict guidelines to assure safety. Applications include notebook computers and cellular phones. (3.6V/cell) (Self Discharge: 5% loss in first 24hrs, 2-5%/month afterwards)

Lithium Ion Polymer (Li-ion polymer) — a potentially lower cost version of the Li-ion. This chemistry is similar to the Li-ion in terms of energy density. It enables very slim geometry and allows simplified packaging. Main applications are mobile phones. (3.6V/cell)

Reusable Alkaline — replaces disposable household batteries; suitable for low-power applications. Its limited cycle life is compensated by low self-discharge, making this battery ideal for portable entertainment devices and flashlights. (1.5V/cell)

Fuel Cells: A battery where reactants are supplied to the cell from an external source. An example is the H2 / O2 fuel cell, in which these gases react (in separate half-reactions at separate electrodes) to form protons and hydroxide, which are combined to form water.

half-reaction	V vs SHE
$H_2 = 2\ H^+ + 2\ e^-$	0
$H^+ + 1/2\ O_2 + 2\ e^- = OH^-$	1.2

Electricity (Electrons) Out

Water Out

H_2 O_2

H^+

H_2O

Hydrogen In

Oxygen In

Anode   Electrolyte   Cathode

Battery Lifecycle Cost

	AAA Cell 1.5V	AA Cell 1.5V	C Cell 1.5V	D Cell 1.5V	9 Volt	BA-5590 for military
Capacity	1.1 Ah Alkaline	2.5 Ah Alkaline	7.1 Ah Alkaline	14.3 Ah Alkaline	0.6 Ah Alkaline	7AhLithium sulfur dioxide
Energy	1.4 Wh per cell	3Wh per cell	9Wh per cell	18 Wh per cell	4.2 Wh per pack	168Wh per pack
Battery Cost (estimated US$)	$1.25	$1.00	$1.60	$1.60	$3.10	$60.00
Cost per kWh	$890	$330	$180	$90	$730	$357

Figure 1: Cost of energy obtained by primary batteries. Compared to other energy sources, the energy cost from primary batteries is very high. The cost increases with smaller battery sizes.

	NiCdAA Cell	NiMHAA Cell	Lead Acid (plastic)	Li-ion 18650 Cell	BB-390 for military
Energy per discharge	4.5Wh	7.5Wh	24Wh	8.6Wh	130Wh
Cycle life (best cases)	1500	500	250	500	250
Cost per battery (ref. only)	$50	$70	$50	$100	$260
Cost per kWh ($US)	$7.50	$18.50	$8.50	$24.00	$8.00

Figure 2: Energy and cost comparison using rechargeable cells. Older battery technologies offer lower energy costs compared to new systems. Larger cells are more cost-effective than smaller packages. The prices of the battery packs are estimated.

Battery Lifecycle Cost

Prices in $US	Investment Cost of equipment to generate 1kW	Lifespan of equipment before major overhaul or replacement	Cost of fuel to generate 1 kWh	Total Cost per kWh, incl. fuel maintenance and equipment replacement
Primary battery AA alkaline cells	$4.004 AA cells	10h one time use	N/A	$330
Secondary battery pack for portable use	$7,000, based on 7.2V, 1000mAh at $50/pack	1500h based on 1C discharge	$0.15 for electricity	$7.50
Combustion Engine for mobile use	$30 based on purchase price of $3,000/100kW (134hp)	4000 h	$0.25	$0.30
Fuel Cell - for portable use - for mobile use - for stationary use	$3,000 - 7,500	2000 h 4000 h 40,000 h	estimated $0.35 $0.10 $0.03	$1.85 - 4.10 $1.30 - 0.60 $0.10 - 0.20
Electricity from electric grid	All inclusive	All inclusive	$0.03	$0.10typical

Figure 3: Cost of generating 1kW of energy. This takes into account the initial investment, fuel consumption where applicable, maintenance and eventual replacement of the equipment. The cheapest power source is the utility; the most expensive is primary batteries.
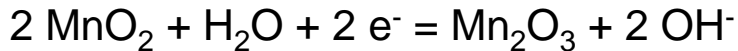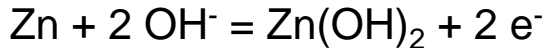
Battery Chemistry

Anode (negative terminal) Oxidation reaction
Cathode (positive terminal) Reduction reaction

Alkaline cells:

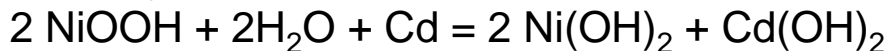These batteries use a high-surface-area Zn powder anode, a high grade MnO_2 cathode and a KOH aqueous electrolyte.

$Zn + 2\ OH^- = Zn(OH)_2 + 2\ e^-$

$2\ MnO_2 + H_2O + 2\ e^- = Mn_2O_3 + 2\ OH^-$

Pb/acid

First commercialized over a century ago by Plante, they are primarily used as car batteries. The cells are constructed from a PbO_2 cathode, Pb anode, and sulfuric acid electrolyte. The half-cell reactions are:
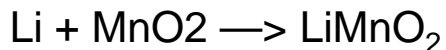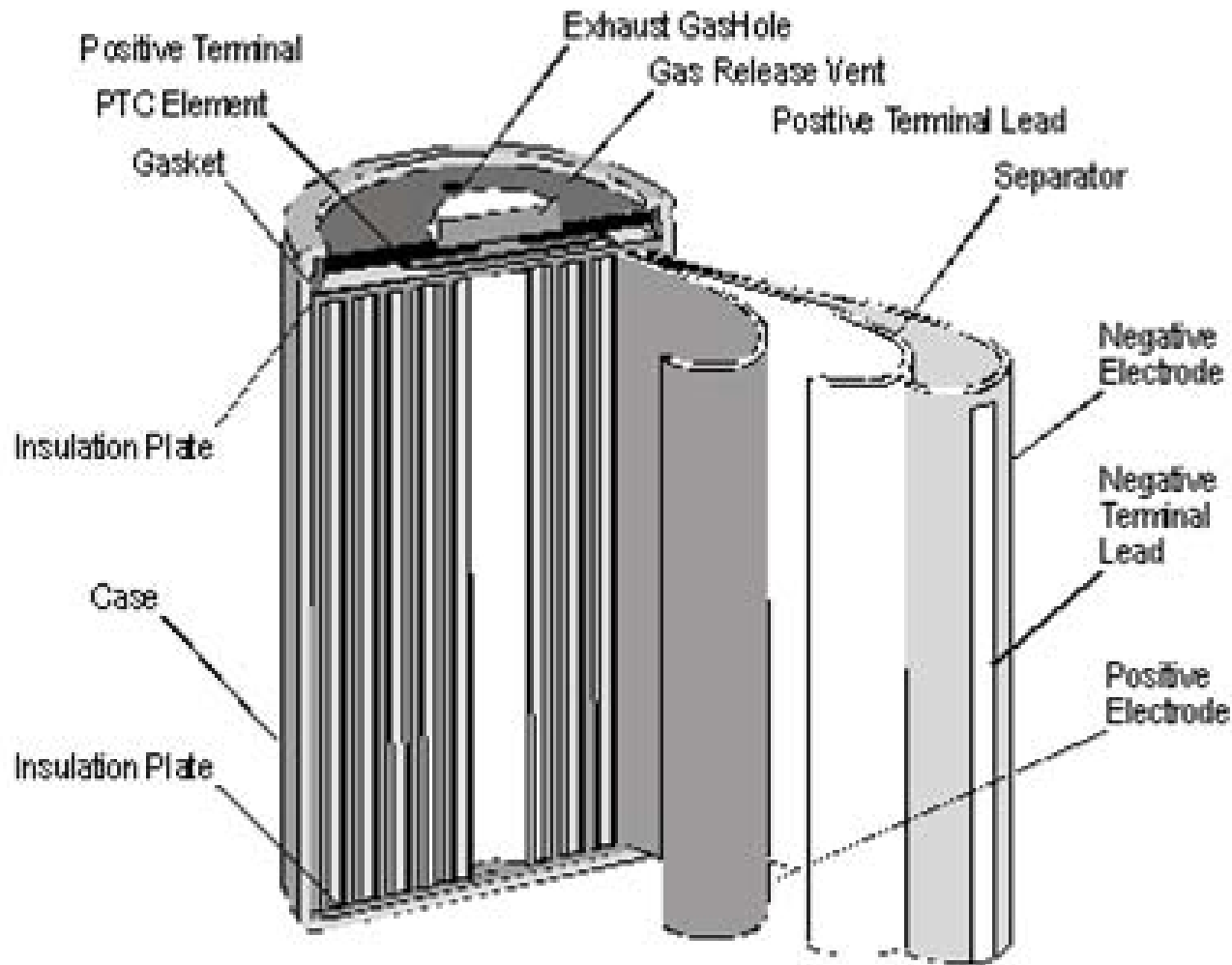
$Pb + SO_4^{2-} = PbSO_4^{2-}$ (sol) + 2 e-

$PbO^2 + 4\ H+ + 2\ e^- + SO_4^{2-} = PbSO_4^{2-}$ (sol)
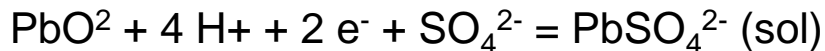
NiCd

These batteries contain a $Ni(OH)_2$ cathode, Cd anode and aqueous KOH electrolyte. The overall cell reaction is:

$2\ NiOOH + 2H_2O + Cd = 2\ Ni(OH)_2 + Cd(OH)_2$

Lithium

Li + MnO2 —> $LiMnO_2$

Cross-section of a classic NiCd cell labels: Positive Terminal, PTC Element, Gasket, Insulation Plate, Case, Insulation Plate, Exhaust GasHole, Gas Release Vent, Positive Terminal Lead, Separator, Negative Electrode, Negative Terminal Lead, Positive Electrode
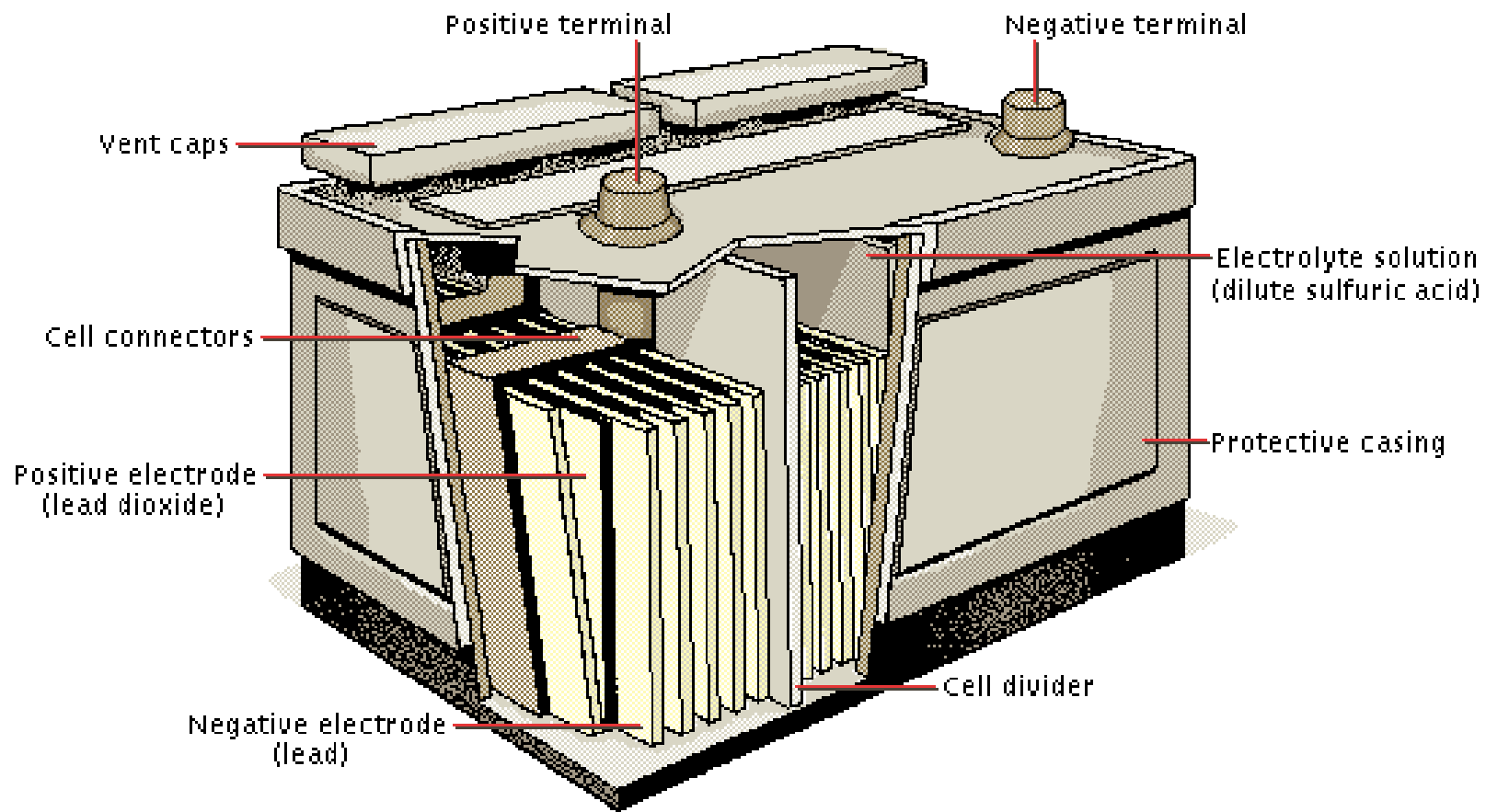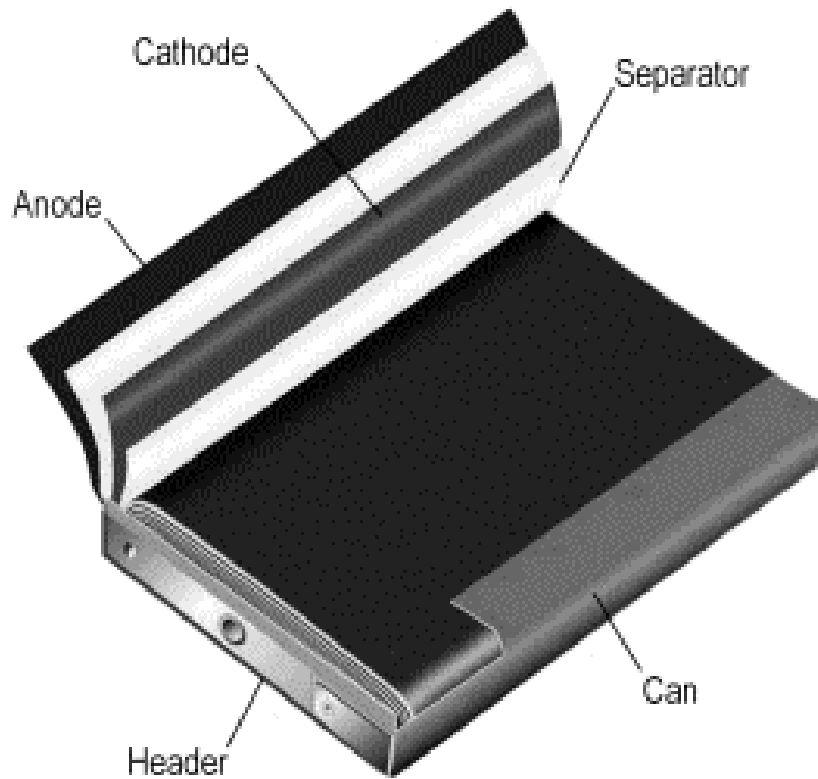
Cross-section of a classic NiCd cell.

The negative and positive plates are rolled together in a metal cylinder. The positive plate is sintered and filled with nickel hydroxide. The negative plate is coated with cadmium active material. A separator moistened with electrolyte isolates the two plates.
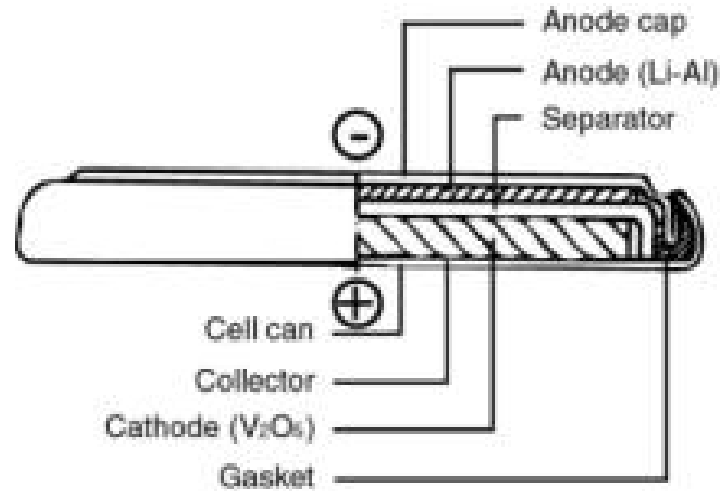
Lead-Acid Battery

Cross-section of a prismatic cell.

The prismatic cell improves space utilization and allows more flexibility in pack design. This cell construction is less cost effective than the cylindrical equivalent and provides a slightly lower energy density.

Diagram labels:
- Anode cap
- Anode (Li-Al)
- Separator
- Cell can
- Collector
- Cathode (V_2O_5)
- Gasket

The button cell.

The button cell offers small size and ease of stacking but does not allow fast charging. Coin cells, which are similar in appearance, are normally lithium-based and are non-rechargeable.

Figure 2-1: Characteristics of commonly used rechargeable batteries.

	NiCd	NiMH	Lead Acid	Li-ion	Li-ion polymer	Reusable Alkaline
Gravimetric Energy Density (Wh/kg)	45-80	60-120	30-50	110-160	100-130	80 (initial)
Internal Resistance (includes peripheral circuits) in mW	100 to 200[1] 6V pack	200 to 300[1] 6V pack	<100[1] 12V pack	150 to 250[1] 7.2V pack	200 to 300[1] 7.2V pack	200 to 2000[1] 6V pack
Cycle Life (to 80% of initial capacity)	1500[2]	300 to 500[2,3]	200 to 300[2]	500 to 1000[3]	300 to 500	50[3] (to 50%)
Fast Charge Time	1h typical	2-4h	8-16h	2-4h	2-4h	2-3h
Overcharge Tolerance	moderate	low	high	very low	low	moderate
Self-discharge / Month (room temperature)	20%[4]	30%[4]	5%	10%[5]	~10%[5]	0.3%
Cell Voltage (nominal)	1.25V[6]	1.25V[6]	2V	3.6V	3.6V	1.5V
Load Current - peak - best result	20C 1C	5C 0.5C or lower	5C[7] 0.2C	>2C 1C or lower	>2C 1C or lower	0.5C 0.2C or lower
Operating Temperature (discharge only)	-40 to 60°C	-20 to 60°C	-20 to 60°C	-20 to 60°C	0 to 60°C	0 to 65°C
Maintenance Requirement	30 to 60 days	60 to 90 days	3 to 6 months[9]	not req.	not req.	not req.
Typical Battery Cost (US$, reference only)	$50 (7.2V)	$60 (7.2V)	$25 (6V)	$100 (7.2V)	$100 (7.2V)	$5 (9V)
Cost per Cycle (US$)[11]	$0.04	$0.12	$0.10	$0.14	$0.29	$0.10-0.50
Commercial use since	1950	1990	1970	1991	1999	1992

The figures are based on average ratings of batteries available commercially at the time of publication; experimental batteries with above average ratings are not included.
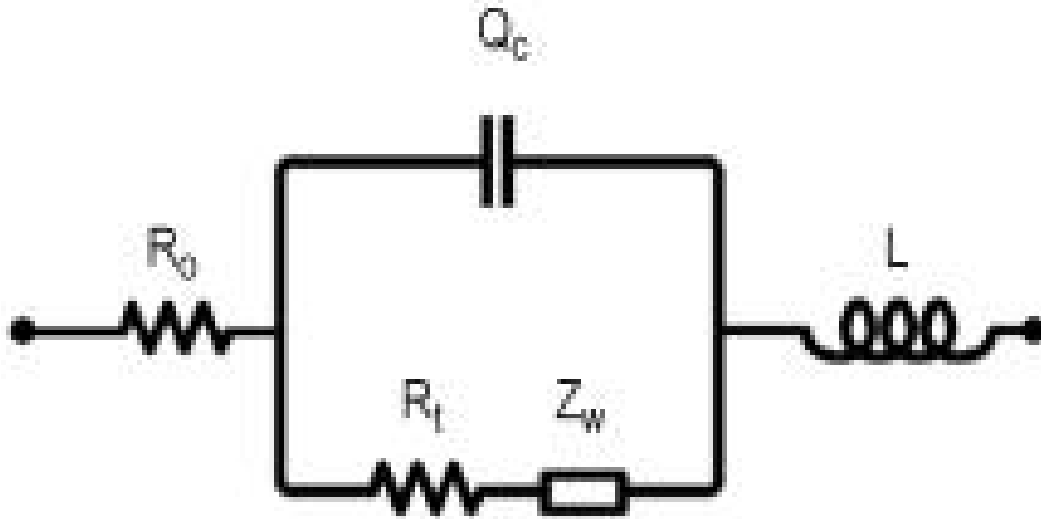
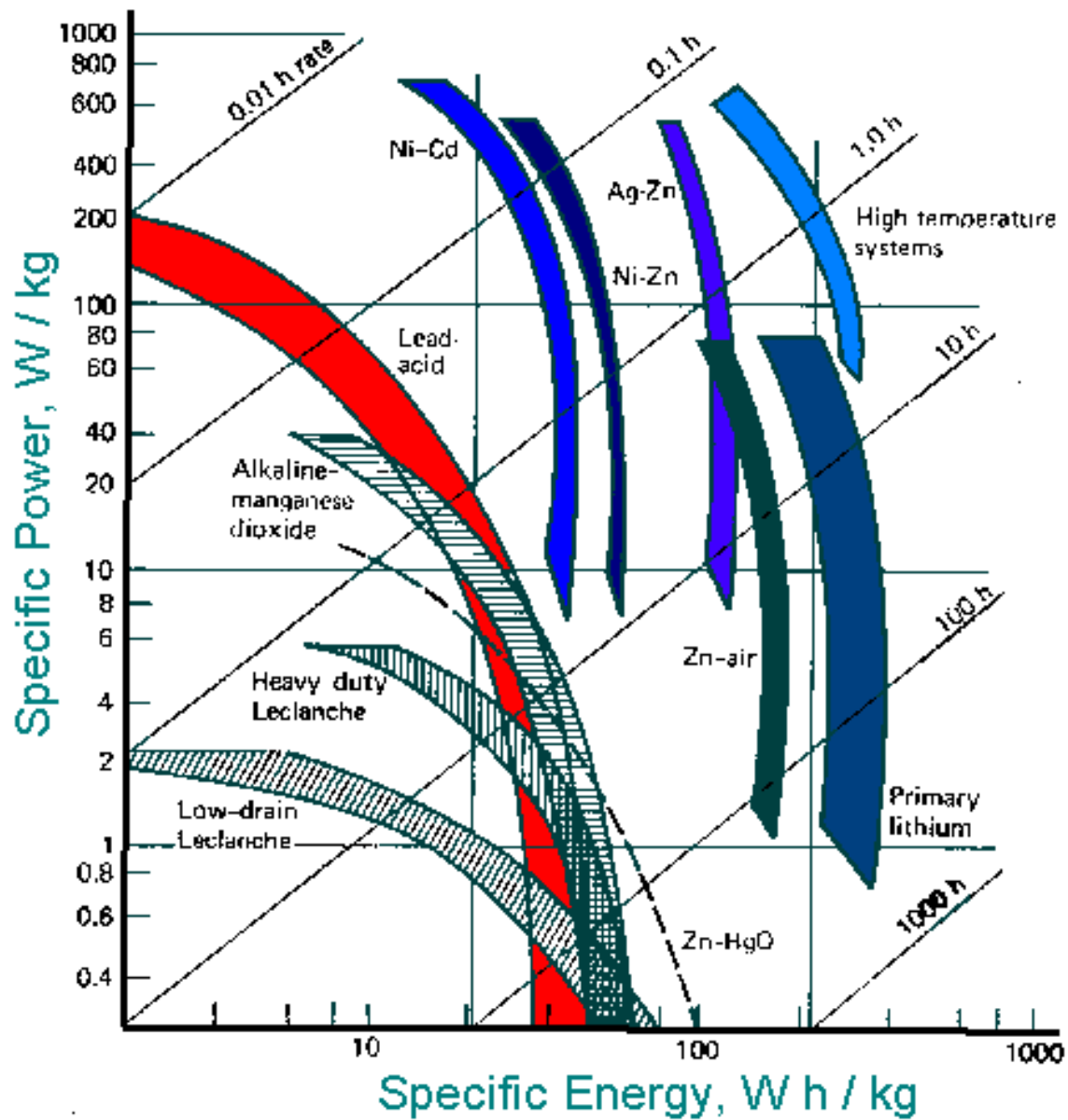Ohmic, inductive and capacitive resistance in batteries.

R_o = ohmic resistance
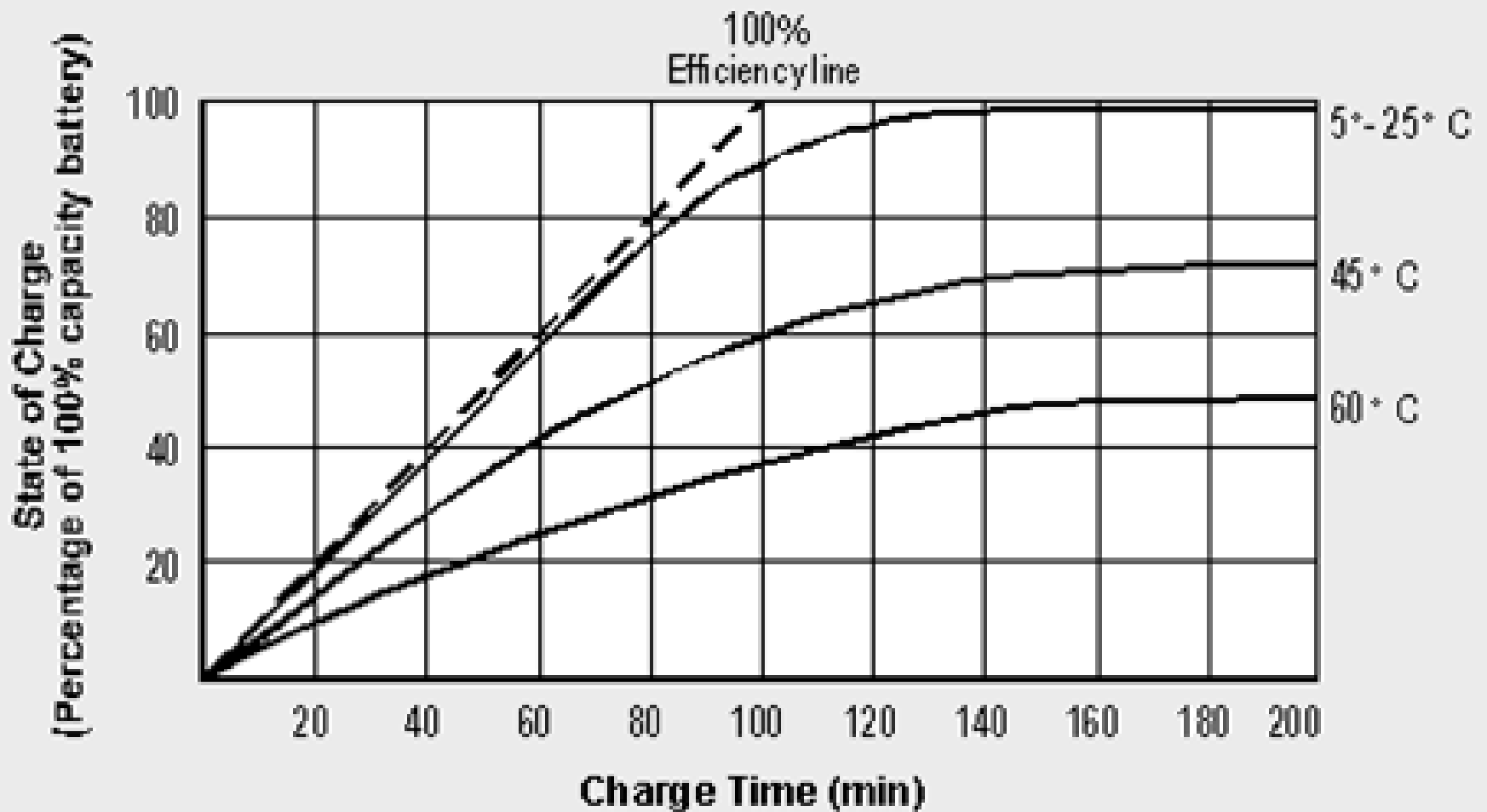Q_c = constant phase loop (type of capacitance)
L =   inductor
Z_w = Warburg impedance (particle movement within the electrolyte)
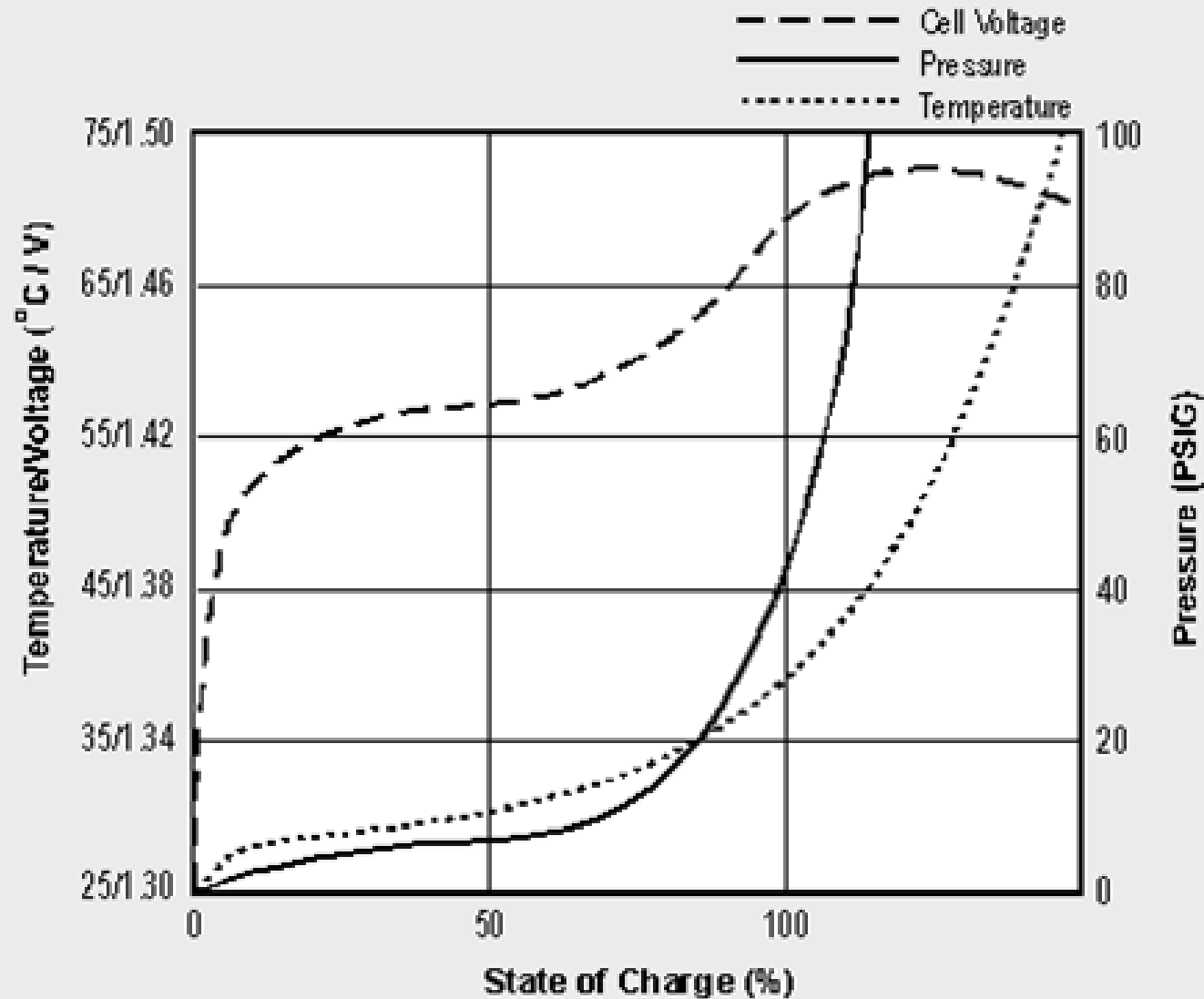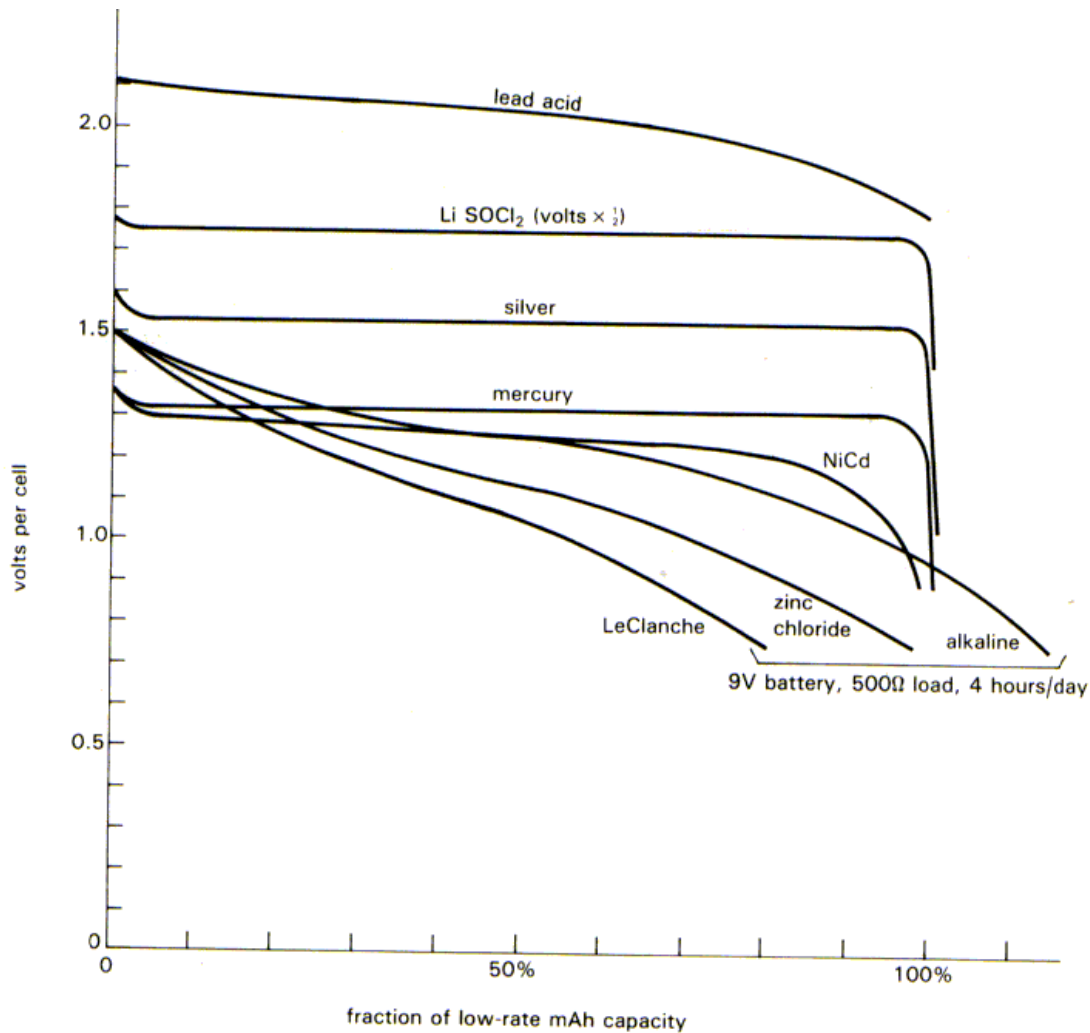R_t = transfer resistance

Effects of temperature on NiCd charge acceptance.
Charge acceptance is much reduced at higher temperatures. NiMH cells follow a similar pattern.

Charge characteristics of a NiCd cell.
These cell voltage, pressure and temperature characteristics are similar in a NiMH cell

The charge and discharge current of a battery is measured in C-rate. Most portable batteries, with the exception of the lead acid, are rated at 1C. A discharge of 1C draws a current equal to the rated capacity. For example, a battery rated at 1000mAh provides 1000mA for one hour if discharged at 1C rate. The same battery discharged at 0.5C provides 500mA for two hours. At 2C, the same battery delivers 2000mA for 30 minutes. 1C is often referred to as a one-hour discharge; a 0.5C would be a two-hour, and a 0.1C a 10 hour discharge

Reliability

Battery makers (and common sense) tell us that most of the problems with rechargeable batteries can be traced to misuse:

NI-CD and NI-MH: HOW CELLS ARE DAMAGED

Sustained high-current overcharge and cell polarity reversal (during discharge) are the main killers of Ni-Cd and Ni-MH batteries: If a high charge rate is used, it is essential to terminate charge when the cell is full. If this is not done, the temperature and pressure within the cell will rise quickly as the charging current is dissipated as heat. Both Ni-Cd and Ni-MH cells have internal vents which will open to allow gas to escape
and prevent explosion of the cell. In the case of Ni-Cd, the gas released is oxygen, while a Ni-MH cell will vent hydrogen. The gas that is lost can never be replaced, which means that the lost cell capacity which results from a severe overcharge is not recoverable.
It is never wise to rely on the cell's vent as a failsafe, because they often corrode over time and can not be assumed to be absolutely reliable. Avoiding abusive high-current overcharge can only be ensured with a well-designed charging system that responds to the signal the battery gives when fully charged. Cell polarity reversal is a potential problem with any series-connected string of cells: as the battery is discharged, the cell that goes down to zero volts first will continue to have current forced through it by the other cells. When this occurs, the voltage across the fully-discharged cell is reversed. A cell that has current forced through it with a reverse voltage across it will heat up very quickly and vent gas in a similar mode to that described for the sustained overcharge, with the same resultant damage.

AGE-RELATED FAILURE MODES
Ni-Cd: After a period of time, the insulator within a Ni-Cd battery often develops holes which allow the cell to grow crystalline "shorts" that provide a conduction path between the positive and negative electrodes of the cell (which basically shorts out the cell).
If this happens, you may have to blow open this short with a high current pulse before the cell will again accept charge (a process sometimes referred to as "zapping").
A leaky Ni-Cd cell will always have a high self-discharge rate and will re-grow internal shorts if left on the shelf without some kind of trickle charge. The annoyance factor of batteries that go dead quickly often prompts users to throw away leaky Ni-Cd batteries, even though they may still be able to give nearly full A-hr capacity during discharge.
Ni-MH: The Ni-MH cell (according to the manufacturers) is not supposed to be prone to developing internal shorts like a Ni-Cd battery. User feedback (so far) on Ni-MH has been good, with no major problems reported.
Li-Ion: The Li-Ion battery got off to a weak start, as there were many failures in the first batteries shipped. However, the addition of the internal protection circuitry inside the battery (and increased knowledge about the failure modes) has improved this.
At present, there are no known problems which appear significant enough to prevent Li-Ion from successfully penetrating the high-end consumer market.
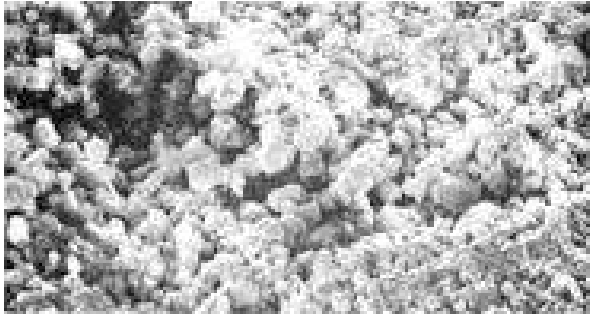
New NiCd cell.
The anode is in fresh condition (capacity of 8.1Ah). Hexagonal cadmium hydroxide crystals are about 1 micron in cross section, exposing large surface area to the liquid electrolyte for maximum performance.

Cell with crystalline formation.
Crystals have grown to an enormous 50 to 100 microns in cross section, concealing large portions of the active material from the electrolyte (capacity of 6.5Ah). Jagged edges and sharp corners may pierce the separator, which can lead to increased self-discharge or electrical short.

Restored cell.
After pulsed charge, the crystals are reduced to 3 to 5 microns, an almost 100% restoration (capacity of 8.0A). Exercise or recondition are needed if the pulse charge alone is not effective.

Crystalline formation on NiCd cell.