

Rechargeable Battery Chemistry Faqs

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This page contains some rather technical information on Rechargeable Battery Chemistry FAQs and technology. Information is provided for battery chemistries such as Ni-Cd, NiMH and Lithium Ion.

Reading through this section should clear up some of the myths or misconceptions about some of the rechargeable battery technologies.

Regardless of the content or chemistry of the rechargeable battery, recycling should be a priority for all consumers, institutions and corporations.

{mospagebreak title=Battery Types}

Battery Types

Secondary Rechargeable Battery Chemistry

- Nickel Cadmium Cells (Ni-Cd)
- Nickel Metal Hydride Cells (NiMH)
- Lithium Ion Cells
- Rechargeable Alkaline Manganese Cells

Primary Battery Chemistry

- Alkaline
- Lithium
- Liquid cathode

- lithium cells LiSO_2
- Lithium-Sulfur Dioxide
- LiSOCl_2 Lithium Thionyl Chloride
-

Solid cathode lithium cells

- LiMnO_2 $\text{Li}(\text{CF})_n$
- Lithium polycarbon monofluoride
- Solid electrolyte lithium cells
- LiI_2 Lithium iodine cells
- Lithium-Iron cells

{mospagebreak title=Nickel Cadmium Battery}

Secondary Rechargeable Battery Chemistry

Nickel Cadmium Rechargeable Battery Chemistry

Anode : Cadmium

Cathode : Nickel oxyhydroxide $\text{Ni}(\text{OH})_2$

Electrolyte : Aqueous potassium hydroxide (KOH)

The cathode is nickel-plated, woven mesh, and the anode is a cadmium-plated net. Not to diminish any environmental issue, the cadmium is just a coating. The electrolyte, KOH, acts only as an ion conductor and does not contribute significantly to the cell's reaction. That's why not much electrolyte is needed, so this keeps the weight down. (NaOH is sometimes used as an electrolyte, which doesn't conduct as well, but also doesn't tend to leak out of the seal as much).

Cell Reaction
V vs. SHE

$\text{Cd} + 2\text{OH}^- \rightarrow \text{Cd}(\text{OH})_2 + 2\text{e}^-$
0.81

$\text{NiO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Ni}(\text{OH})_2 + 2\text{OH}^-$
0.49

$\text{Cd} + \text{NiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Cd}(\text{OH})_2 + \text{Ni}(\text{OH})_2$
1.3

Ni-Cd rechargeable batteries perform well in high-discharge and low-temperature applications. They also have long shelf and use life. Disadvantages are lower power densities. The memory effect is a temporary loss of cell capacity, which occurs when a cell is recharged without being fully discharged. This can cause cadmium hydroxide to passivate the electrode, or the battery to wear out. A few cycles of discharging and charging the cell will help correct the problem, but may shorten the lifetime of the battery. The true memory effect comes from experience with a certain style of Ni-Cd in space use, which were cycled within a few percent of discharge each time. An important note about "conditioning " a Ni-Cd battery is that the deep discharge spoken of is not a discharge to zero volts, but to about 1 volt per cell.

{mospagebreak title=Nickel Metal Hydride Cells}

Nickel Metal Hydride (NiMH) Cells

Anode : Rare-earth or nickel alloys with many metals

Cathode : Nickeloxyhydroxide

Electrolyte : Potassium hydroxide

This cell is a hybrid of the NiCd and NiH₂ cells. Hydrogen has good anodic qualities but required cell pressurization until the 1960s. The discovery that some metal alloys (hydrides such as LaNi₅ or ZrNi₂) could store hydrogen atoms solved this problem. These metals could participate irreversible chemical reactions. In modern NiMH batteries, the anode consists of many metals alloys, including V, Ti, Zr, Ni, Cr, Co, and Fe.

Except for the anode, the NiMH cell very closely resembles the NiCd cell in construction. Even the voltage is virtually identical, at 1.2 volts, making the cells interchangeable in many applications. Here are the cell reactions:

Location
Reactions
Voltage

Anode



0.83

Cathode



0.52

Overall



1.3

Anodes used in these cells are complex alloys containing many metals, such as an alloy of V, Ti, Zr, Ni, Cr, Co, Fe. The chemistry of these alloys and the reason for superior performance are not clearly understood. The compositions are determined by empirical testing methods.

Some metals give off heat while others absorb heat when absorbing hydrogen. Both of these are undesirable, since hydrogen needs to move easily in and out without any energy transfer. Good alloys are all mixtures of exothermic and endothermic metals to reduce any heat transfer.

Hydrogen Storage Metal Chart :

Material

Density

H₂ Storage Capacity

LaNi₅

8.3

0.11 g/cc

FeTi

6.2

0.11

Mg₂Ni

4.1

0.15

Mg

1.74

0.13

MgNi Eutectic

2.54

0.16

Liquid H₂

0.07

0.07

Note that the density of hydrogen stored in a metal hydride is higher than that of pure liquid hydrogen. Commercial NiMH batteries are mostly of the rare earth-nickel type, such as LaNi₅. These alloys can store six hydrogen atoms per unit cell such as LaNi₅H₆. Even misch metal nickel alloys are used to save the cost of separation.

The electrolyte of commercial NiMH batteries is typically 6 M KOH. The NiMH cell cost more and has half the service life of the NiCd cell. It also has 30% more capacity and increased power density (theoretically 50% more, practically 25% more). To reduce any so called memory effect, fully discharge once every 30 or so cycles. NiCD and NiMH rechargeable batteries each has its pros and cons depending on the use.

{mospagebreak title=Lithium Ion Cells}

Lithium Ion Cells

Anode : Carbon compound, graphite

Cathode : Lithium oxide

Rechargeable batteries that use lithium metal have safety issues. This has led to a series of cell chemistry developments using lithium compounds instead of lithium metal. These are generically Lithium ion Batteries.

Cathodes consist of a layered crystal (graphite) into which the lithium is intercalated. Experimental cells have also used lithiated metal oxide such as LiCoO_2 , $\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_2$, LiNiO_2 , LiV_2O_5 , $\text{LiV}_6\text{O}_{13}$, LiMn_4O_9 , LiMn_2O_4 , $\text{LiNiO}_2\text{CoO}_2$.

Electrolytes are usually LiPF_6 , although this has a problem with aluminum corrosion, and so alternatives are being sought. One such is LiBF_4 . The electrolyte in current production batteries is liquid, and uses an organic solvent. Membranes are necessary to separate the electrons from the ions. Current batteries use microporous polyethylene membranes.

Intercalation is a long-studied process which has finally found a practical use. Small ions (lithium, sodium, and other alkali metals) can fit in the interstitial spaces in a graphite crystal. Not only that, but these metallic atoms can go farther and force the graphitic planes apart to fit two, three, or more layers of metallic atoms between the carbon sheets. A great way this is to store lithium in a battery—the graphite is conductive, dilutes the lithium for safety, is reasonably cheap, and does not allow dendrites or other unwanted crystal structures to form.

{mospagebreak title=RA Battery}

Rechargeable Alkaline Manganese Cells

Anode : Zinc

Cathode : Manganese Dioxide

Electrolyte : Potassium Hydroxide Solution

In the charging process, direct-current electrical power is used to reform the active chemicals of the battery system to their high-energy charge state. In the case of the RAM battery, this involves oxidation of manganese oxyhydroxide (MnOOH) in the discharged positive electrode to manganese dioxide (MnO_2), and of zinc oxide (ZnO) in the negative

electrode to metallic zinc.

Care must be taken not to overcharge to prevent electrolysis of the KOH solution electrolyte, or to charge at voltages higher than 1.65 V (depending on temperature) to avoid the formation of higher oxides of manganese.

{mospagebreak title=Alkaline Battery}

Primary Single Use Battery Chemistry

Alkaline Battery Chemistry

Anode : Zinc powder

Cathode : Manganese dioxide (MnO₂) powder

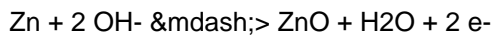
Electrolyte : Potassium hydroxide (KOH)

This cell uses an alkaline aqueous solution for the electrolytes. Alkaline battery chemistry was introduced in the early 1960s. Alkaline cell advantages over zinc-carbon includes :

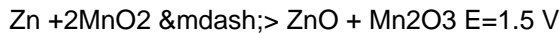
- a higher energy density;
- longer shelf life;
- superior leakage resistance;
- better performance in both continuous and intermittent duty cycles;
- and lower internal resistance, which allows high discharge rates.

Zinc in a powdered form increases the surface area of the anode, allowing more particle interaction. This lowers the internal resistance and increases the power density. The cathode, MnO₂, is synthetically produced because of its superiority to naturally occurring MnO₂. This increases the energy density. Just as in the zinc carbon cell, graphite is added to the cathode to increase conductivity. The electrolyte, KOH, allows high ionic conductivity. Zinc oxide is often added to slow down corrosion of the zinc anode. A cellulose derivative is thrown in as well as a gelling agent. These materials make the alkaline cell more expensive than the zinc-carbon, but its improved performance makes it more cost effective, especially in high drain situations where the alkaline cell's energy density is much higher.

The half-reactions are :



The overall reaction is :



Other alkaline cell designs include mercury oxide, silver oxide, and zinc air cells. Mercury and silver give even higher energy densities, but carry a higher cost. They have or are being phased out by pollution regulations because of their high toxicity and heavy metals.

{mospagebreak title=Lithium Cells}

Lithium Cells

Lithium battery chemistry consists of a number of cell designs that use lithium as the anode. Lithium is gaining a lot of

popularity as an anode for a number of reasons.

Comparison of anode materials :

Anode

Atomic mass (g)

Standard potential (V)

Density g/cm³

Melting point C

Electrochemical Equivalence (Ah/g)

Li

6.94

3.05

0.54

180

3.86

Na

23.0

2.7

0.97

97.8

1.16

Mg

24.3

2.4

1.74

650

2.20

Al

26.9

1.7

2.7

659

2.98

Ca

40.1

2.87

1.54

851

1.34

Fe

55.8

0.44

7.85

1528

0.96

Zn

65.4

0.76

7.1

419

0.82

Cd

112

0.40

8.65

321

0.48

Pb

207

0.13

11.3

327

0.26

Lithium, the lightest of the metals, also has the highest standard potential of all the metals, at over 3 V. Some of the lithium cell designs have a voltage of nearly 4 V. This means that lithium has the highest energy density. Many different lithium cells exist because of its stability and low reactivity with a number of cathodes and non-aqueous electrolytes. The most common electrolytes are organic liquids with the notable exceptions of SOCl_2 (Thionyl chloride) and SO_2Cl_2 (sulfur chloride). Solutes are added to the electrolytes to increase conductivity.

Lithium cells have only recently become commercially viable because lithium reacts violently with water, as well as nitrogen in air. This requires sealed cells. High-rate lithium cells can build up pressure if they short circuit and cause the temperature and pressure to rise. The cell design needs to include weak points, or safety vents, which rupture at a certain pressure to prevent explosion.

Lithium cells can be grouped into three general categories: liquid cathode, solid cathode, and solid electrolyte.

{mospagebreak title=Liquid Cathode Lithium Cells}

Liquid Cathode Lithium Cells

These cells tend to offer higher discharge rates because the reactions occur at the cathode surface. In a solid cathode, the reactions take longer because the lithium ions must enter into the cathode for discharge to occur. The direct contact between the liquid cathode and the lithium forms a film over the lithium, called the solid electrolyte interface (SEI). This prevents further chemical reaction when not in use, thus preserving the cell's shelf life. One drawback, though, is that if the film is too thick, it causes an initial voltage delay. Usually, water contamination is the reason for the thicker film, so quality control is important.

LiSO₂ Lithium–Sulfur Dioxide

This cell performs very well in high current applications as well as in low temperatures. It has an open voltage of almost 3 V and a typical energy density of 240–280 Wh/kg. It uses a cathode of porous carbon with sulfur dioxide taking part in the reaction at the cathode. The electrolyte consists of an acetonitrile solvent and a lithium bromide solute. Polypropylene acts as a separator. Lithium and sulfur dioxide combine to form lithium dithionite:



These cells are mainly used in military applications for communication because of high cost and safety concerns in high-discharge situations, i.e., pressure build up and overheating.

LiSOCl₂ Lithium Thionyl Chloride

This cell consists of a high-surface area carbon cathode, a non-woven glass separator, and Thionyl chloride, which doubles as the electrolyte solvent and the active cathode material. Lithium aluminum chloride (LiAlCl₄) acts as the electrolyte salt.

Location
Reaction

Anode

$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$

Cathode

$4\text{Li}^+ + 4\text{e}^- + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S}$

Overall

$4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S}$

During discharge the anode gives off lithium ions. On the carbon surface, the thionyl chloride reduces to chloride ions, sulfur dioxide, and sulfur. The lithium and chloride ions then form lithium chloride. Once the lithium chloride has deposited at a site on the carbon surface, that site is rendered inactive. The sulfur and sulfur dioxide dissolve in the electrolyte, but at higher-rate discharges SO_2 will increase the cell pressure.

This system has a very high energy density (about 500 Wh/kg) and an operating voltage of 3.3 – 3.5 V. The cell is generally a low-pressure system.

In high-rate discharge, the voltage delay is more pronounced and the pressure increases as mentioned before. Low-rate cells are used commercially for small electronics and memory backup. High-rate cells are used mainly for military applications.

{mospagebreak title= Solid Cathode Li Battery}

Solid Cathode Lithium Battery Chemistry

These cells cannot be used in high-drain applications and don't perform as well as the liquid cathode cells in low

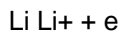
temperatures. However, they don't have the same voltage delay and the cells don't require pressurization.

They are used generally for memory backup, watches, portable electronic devices, etc.

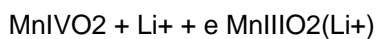
LiMnO₂

These account for about 80% of all primary lithium cells, one reason being their low cost. The cathode used is a heat-treated MnO₂ and the electrolyte a mixture of propylene carbonate and 1,2-dimethoxyethane. The half reactions are :

Anode



Cathode



Overall

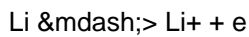


At lower temperatures and in high-rate discharge, the LiSO₂ cell performs much better than the LiMnO₂ cell. At low-rate discharge and higher temperatures, the two cells perform equally well, but LiMnO₂ cell has the advantage because it doesn't require pressurization.

Li(CF)_n Lithium Polycarbon Monofluoride

The cathode in this cell is carbon monofluoride, a compound formed through high-temperature intercalation. This is the process where foreign atoms (in this case fluorine gas) incorporate themselves into some crystal lattice (graphite powder), with the crystal lattice atoms retaining their positions relative to one another. A typical electrolyte is lithium tetrafluorobate (LiBF₄) salt in a solution of propylene carbonate (PC) and dimethoxyethane (DME).

Anode



Cathode



Overall



These cells also have a high voltage (about 3.0 V open voltage) and a high energy density (around 250 Wh/kg). All this and a 7-year shelf life makes them very suitable for low- to moderate-drain use, e.g., watches, calculators, and memory applications.

{mospagebreak title=Solid Electrolyte Li Battery}

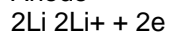
Solid electrolyte lithium Battery Chemistry

All commercially manufactured cells that use a solid electrolyte have a lithium anode. They perform best in low-current applications and have a very long service life. For this reason, they are used in pacemakers

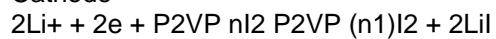
Lil—Lithium Iodine Cells

Lil—Lithium iodine cells use solid Lil as their electrolyte and also produce Lil as the cell discharges. The cathode is poly-2-vinylpyridine (P2VP) with the following reactions:

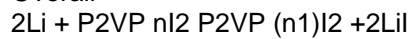
Anode



Cathode



Overall



Lil is formed in situ by direct reaction of the electrodes.

Lithium-Iron Cells

The Lithium-Iron chemistry deserves a separate section because it is one of a handful of lithium metal systems that have a 1.5 volt output (others are lithium/lead bismuthate, lithium/bismuth trioxide, lithium/copper oxide, and lithium/copper sulfide).

Recently consumer cells that use the Li/Fe have reached the market, including the Energizer. These have the advantage of having the same voltage as alkaline batteries with much more energy storage capacity, so they are called "voltage compatible" lithiums. They are not rechargeable. They have about 2.5 times the capacity of an alkaline battery of the same size, but only under high current discharge conditions (digital cameras, flashlights, motor driven toys, etc.). For small currents they don't have any advantage. Another advantage is the low self-discharge rate—10 years storage is quoted by the manufacturer. The discharge reactions are:

Type
Reaction
Nominal Voltage
Range

FeS₂ Version
 $2 \text{FeS}_2 + 4 \text{Li Fe} + 2\text{Li}_2\text{S}$
1.6 Volts
1.6-1.4v

FeS Version
 $\text{FeS} + 2\text{Li Fe} + \text{Li}_2\text{S}$
1.5 Volts
1.5-1.2v

Both Iron sulfide and Iron disulfide are used, the FeS₂ is used in the Energizer. Electrolytes are organic materials such as propylene carbonate, dioxolane and dimethoxyelthane.

