

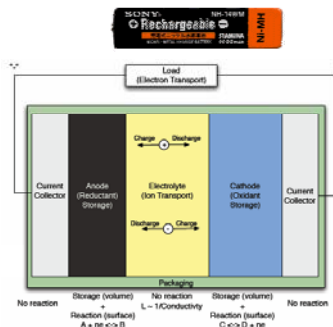
Battery

Battery Definition

Battery is an electrochemical cell that can convert chemical energy in electrical energy (redox reaction). It consists of 3 main parts:

- Electrolyte
- Anode
- Cathode

- Anode**
- Oxidation reaction takes place
 - Losing electrons
 - "Negative" terminal of a battery
- Cathode**
- Reduction reaction takes place
 - Gaining electrons
 - "Positive" terminal of a battery



Cartoon: by courtesy of Dan Steingart

Battery Definition

C rate

C rate is battery discharge rate in amperes

A rate of (nC) will discharge a battery in 1/n hours

Examples:

- a rate of C/5 will discharge a battery in 5 hours
- a rate of 5 C will discharge a battery in 0.2 hours
- for a 2 Ah battery, the C/5 rate is 400 mA

Outline

- Battery definition
- Various types of batteries
 - ✓ Alkaline battery
 - ✓ Mercury battery
 - ✓ Ni-Cd battery
 - ✓ Ni-MH battery
 - ✓ Li-ion battery
- Rechargeable Lithium Battery
 - ✓ Principle
 - ✓ Materials used for anode, cathode and electrolyte
- Performance and applications of batteries

Battery Definition

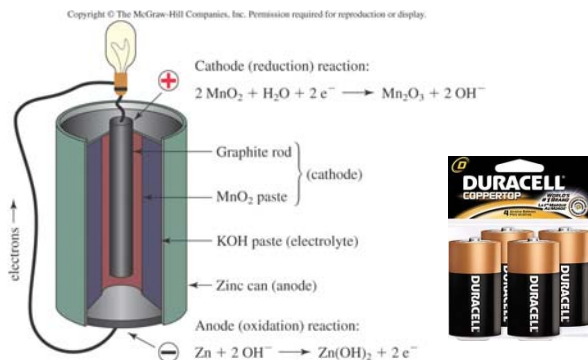
- Capacity:** The theoretical capacity of a cell or half-cell (Q_T) is calculated as: $Q_T = x(nF)$, where x is the theoretical number of moles of reaction associated with the complete discharge of the cell.
- The actual capacity Q_a is amount of capacity a battery can supply before it is fully discharged.
- Energy:** Theoretical energy can be expressed as $P_T = x(nFE_{cell})$
- The actual Energy $P_a = Q_a V_{cell}$
- Power:** The power generated by a battery can be calculated as: $P = VI$, where $V = \text{cell voltage}$ and $I = \text{cell current (or rate)}$, since $V = IR$; $P = IR$ and $P = V^2/R$.
- Specific energy (or energy density or capacity)** – Energy per cell weight or volume
- Specific power (or power density):** Power per cell mass.
- A **Regone plot** is a measure of specific power vs. specific energy.

Battery Definition

Batteries are classified into two broad categories:

- **Primary batteries:** irreversibly (within limits of practicality) transform chemical energy to electrical energy.
- **Secondary batteries:** can be recharged. The chemical reactions can be reversed by supplying electrical energy to the cell, restoring their original composition

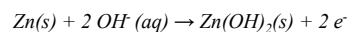
Alkaline Battery



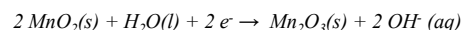
Alkaline Battery

Electrochemical reactions

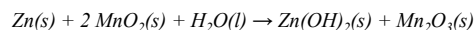
Anode (-): Oxidation



Cathode (+): Reduction

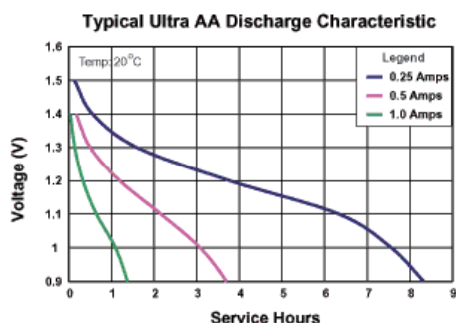


Overall



Mn₂O₃ is not sticky, and doesn't remain attached to the electrode. This battery is not rechargeable

Alkaline Battery

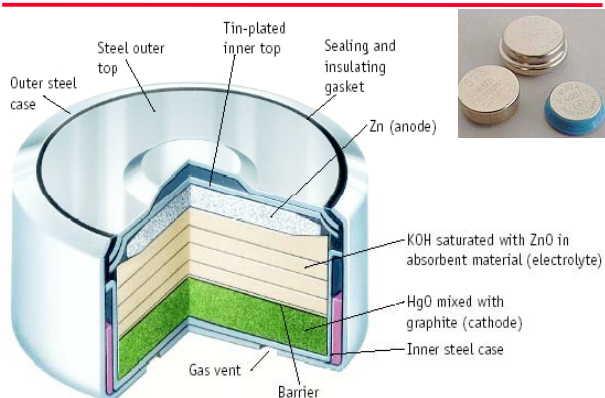


Alkaline Battery



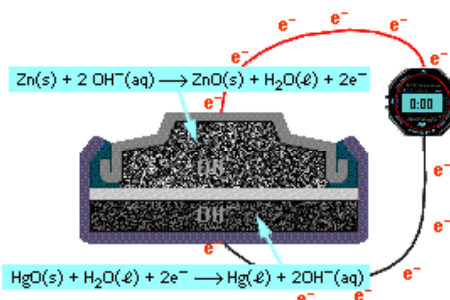
- The electrochemical reaction will not take place without connecting an external circuit. Hence they can be stored in the shelf.
- Alkaline batteries are described by size and shape – AAA to D.
- Larger batteries have more amount of mass, and thus can run longer
- But they all have the same voltage (1.5 V), because they're all based on the same electrochemical cell.
- Disposable batteries are intended to be used once and discarded.
- Alkaline batteries are not rechargeable. If you force it to be recharged, explosion may happen. The reason is that hydrogen can be built up due to the reversed electrochemical reaction.

Mercury Battery



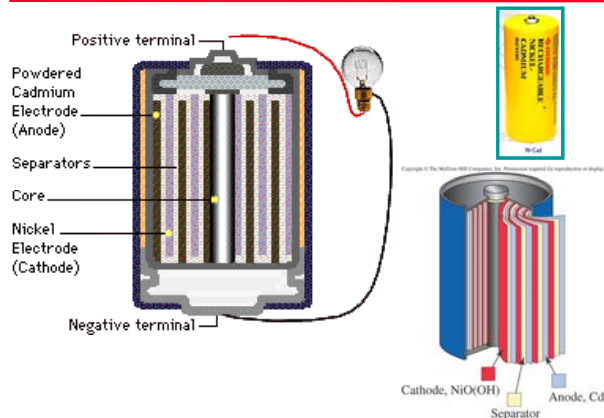
Mercury Battery

Electrochemical reactions



- Mercury batteries are small due to the high density of Hg
- They are used in watches, hearing aids and calculators, etc.
- Gradually disappeared in the market in the 80s due to the toxicity of Hg

Nickel-Cadmium Battery

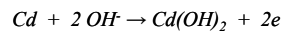


Nickel-Cadmium Battery

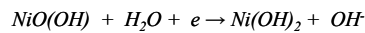
Electrochemical reactions

- The cell contains a paste of NaOH, which provides the OH⁻ ions needed for the reaction, while also providing a medium to pass charge (electrolyte)
- On the anode, solid metal is transformed into cadmium hydroxide
- On the cathode, Ni³⁺ ions in a NiO(OH) paste are transformed into nickel hydroxide.
- If current is applied, the reaction is driven backwards, and be recharged.

Anode (-)



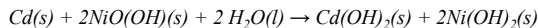
Cathode (+)



Nickel-Cadmium Battery

Recharge Electrochemical reactions

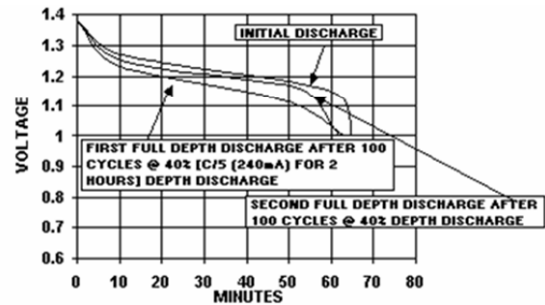
A nickel-cadmium battery can be recharged the battery by applying an electrical current from another source



Nickel-Cadmium Battery

Ni-Cd Memory Effect in Recharging

Memory effect: Ni-Cd batteries gradually lose their maximum energy capacity if they are repeatedly recharged after being only partially discharged.



By courtesy of Steve Garland & Kyle Jamieson

Nickel-Cadmium Battery

Ni-Cd Memory Effect in Recharging

True memory effect:

This long-term, repetitive cycle regime, with no provision for overcharge, resulted in a loss of capacity beyond the 25% discharge point. Hence the birth of a "memory" phenomenon, whereby nickel-cadmium batteries purportedly lose capacity if repeatedly discharged to a specific level of capacity.

True memory cannot exist if any one of the following conditions holds:

- Batteries achieve full overcharge.
- Discharge is not exactly the same each cycle, within plus or minus 3%
- Discharge is to less than 1.0 volt per cell

Source: Wikipedia

Nickel-Cadmium Battery

Ni-Cd Memory Effect in Recharging

Temporary memory effect: Voltage depression due to long-term over-charging

- A common process often ascribed to memory effect is voltage depression.. This is a common problem with high-load devices such as digital cameras.
- Voltage depression is caused by repeated over-charging of a battery, which causes the formation of small crystals of electrolyte on the plates. These can clog the plates, increasing resistance and lowering the voltage of some individual cells in the battery.
- The effect can be overcome by subjecting each cell of the battery to one or more deep charge/discharge cycles.

Permanent loss of capacity: Deep discharge

- Some rechargeable batteries can be damaged by repeated deep discharge

Permanent loss of capacity: Age and use—normal end-of-life

- All rechargeable batteries have a finite lifespan and will slowly lose storage capacity as they age due to secondary chemical reactions within the battery whether it is used or not.

Source: Wikipedia

Nickel-Cadmium Battery

Ni-Cd Battery Recharging Feature

- Over 1000 cycles (if properly maintained)
- Fast, simple charge (even after long storage)
C/3 to 4C with temperature monitoring
- Self discharge
10% in first day, then 10%/mo
Trickle charge (C/16) will maintain charge
- Memory effect
Overcome by 60% discharges to 1.1V

By courtesy of Steve Garland & Kyle Jamieson

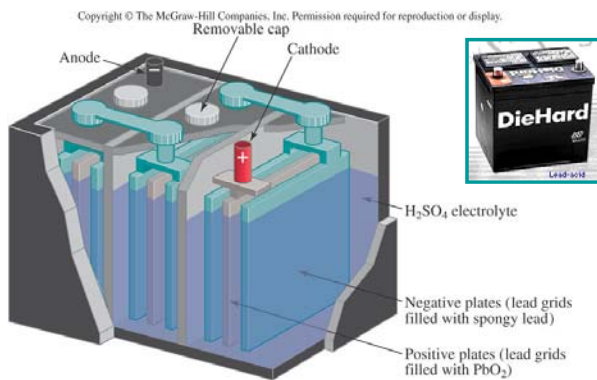
Nickel-Cadmium Battery

Features

- ✓ Good high discharge rate (for power tools)
- ✓ Rugged, long life, economical
- ✓ Relatively low energy density
- ✓ Toxic

By courtesy of Steve Garland & Kyle Jamieson

Lead-Acid Battery



Lead-Acid Battery

Electrochemical reactions

Lead-acid batteries are composed of two alternating groups of Pb plates:

Anode: pure lead (anode)

Cathode: PbO₂

Electrolyte: 40 % sulfuric acid

The lead sulfate product clings to the electrodes, so applied external voltage can reverse the reaction

During discharge

Anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cathode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

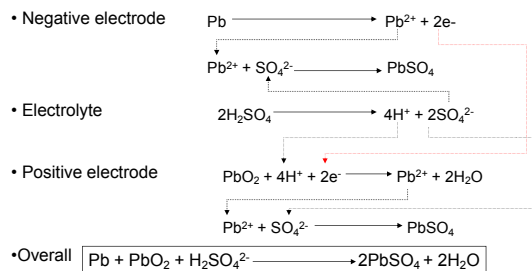
Overall: $Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$

$$E^\circ_{cell} = 2.041 V$$

- Nominally ~2 V per cell, dropping to ~1.5 over useful discharge life
- In a vehicle, 6 batteries are series connected to generate 12 V

Lead-Acid Battery

Chemical reaction (discharge)



Electrochemical reactions

by courtesy of Alexis Kwasinski,

Lead-Acid Battery

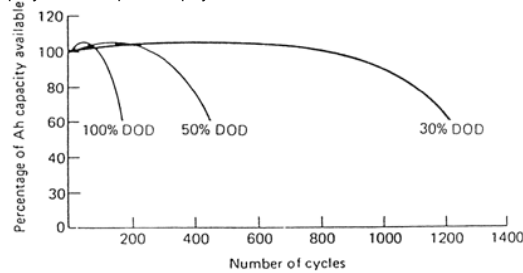
- When discharging, sulfuric acid concentration decreases. Lead sulfate is deposited on the electrode plates.
- When Charging, a small amount of lead sulfate clings to the electrode plates.
- More cycles results in the accumulation of Lead sulfate deposits on the electrode plates, reducing the reaction area and, hence, negatively affecting the battery performance.
- Electrode plates sulfation is one of the primary effect on the battery life.
- To avoid accelerating the sulfation process, batteries need to be fully charged after every discharge and they must be kept charged at a float voltage higher than the nominal voltage. For lead acid batteries and depending their technology the float voltage is between 2.08 V/Cell and 2.27 V/cell. For the same reasons, lead-acid batteries should not be discharged below 1.75 V/cell

by courtesy of Alexis Kwasinski,

Lead-Acid Battery

Lead Acid Battery Discharging

lead-acid batteries are not suitable for load-following power buffer applications because their life is significantly shortened when they are discharged very rapidly or with frequent deep cycles

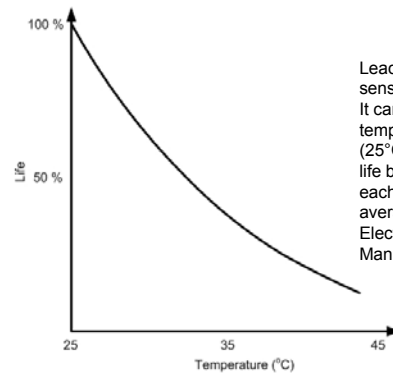


Cycle Service Life in Relation to Depth of Discharge (20°C)

<http://polarpowerinc.com/info/operation20/operation25.htm>

Lead-Acid Battery

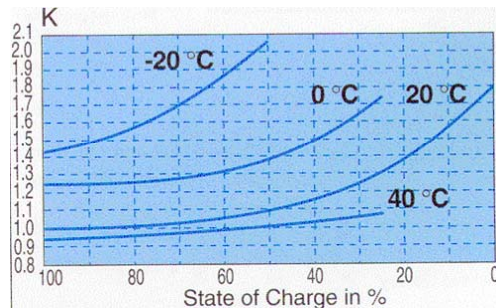
Temperature Effect on Performance



Lead-acid batteries are very sensitive to temperature effects. It can be expected that battery temperature exceeding 77°F (25°C) will decrease expected life by approximately 50% for each 18°F (10°C) increase in average temperature. [Tyco Electronics IR125 Product Manual]

Lead-Acid Battery

Temperature Effect on Performance



Lead-Acid Battery

Lead Acid Battery Recharging

- Low self-discharge
 - ✓ 40% in one year (three months for NiCd)
- No memory
- Cannot be stored when discharged
- Limited number of full discharges
- Danger of overheating during charging

Lead-Acid Battery

- Lead-acid batteries are also called "storage batteries", because the charge-discharge cycle is so reliable.
- Lead-acid batteries are extensively used in vehicles.
- The battery is discharged in order to start the engine. Once the engine is running and burning gasoline, it turns an alternator which recharges the battery.
- Lead-acid batteries typically lasts up to 5 years. After that time, lead sulfate product has been shaken off the plates that it can no longer recharge.
- Lead is an environmental concern – 97% of spent batteries are recycled in the U.S.

Comparison of Various Types of Batteries

Discharge Rates

Type	Voltage (V)	Peak Drain	Optimal Drain
Alkaline	1.5	0.5C	< 0.2C
NiCd	1.25	20C	1C
Nickel metal	1.25	5C	< 0.5C
Lead acid	2	5C	0.2C
Lithium ion	3.6	2C	< 1C

By courtesy of Steve Garland & Kyle Jamieson

Comparison of Various Types of Batteries

Recharge

Type	Cycles (to 80%)	Charge time	Discharge per month	Cost per kWh
Alkaline	50 (50%)	3-10h	0.3%	\$95.00
NiCd	1500	1h	20%	\$7.50
NiMH	300-500	2-4h	30%	\$18.50
Li-ion	500-1000	2-4h	10%	\$24.00
Polymer	300-500	2-4h	10%	
Lead acid	200-2000	8-16h	5%	\$8.50

By courtesy of Steve Garland & Kyle Jamieson

Comparison of Various Types of Batteries

Type	Voltage	Rechargeable?	Examples of Uses
Alkaline	1.54	No	Flashlights, small appliances
Lithium-iodine	2.8	No	Camera batteries, pacemakers
Lithium ion	3.7	Yes	Laptop computers, cell phones, digital music players
Lead-acid (storage battery)	2.0	Yes	Automobiles
Nickel-cadmium (NiCd)	1.25	Yes	Consumer electronics
Nickel-metal hydride (NiMH)	1.25	Yes	Replacing NiCad for many uses; hybrid vehicles
Mercury	1.3	No	Formerly widely used in cameras, other appliances

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Battery History

1800	Voltaic pile: silver zinc
1836	Daniell cell: copper zinc
1859	Planté: rechargeable lead-acid cell
1868	Leclanché: carbon zinc wet cell
1888	Gassner: carbon zinc dry cell
1898	Commercial flashlight, D cell
1899	Junger: nickel cadmium cell
1946	Neumann: sealed Ni-Cd
1960s	Alkaline, rechargeable Ni-Cd
1970s	Sealed lead acid
1990	Nickel metal hydride (Ni-MH)
1991	Lithium ion
1999	Lithium ion polymer

Source: Steve Garland & Kyle Jamieson

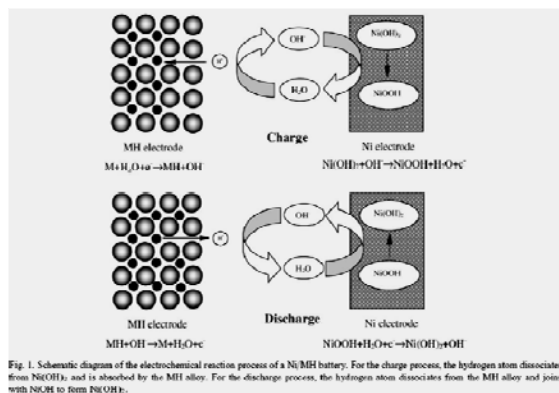
Ni-MH Battery

- Positive electrode : $\text{Ni}(\text{OH})_2 + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + e^-$
 $E^\circ = 0.4V \text{ vs SHE}$
- Negative electrode : $\text{M} + \text{H}_2\text{O} + e^- \leftrightarrow \text{MH} + \text{OH}^-$
 $E^\circ = -0.83V \text{ vs. SHE}$
- Total reaction : $\text{Ni}(\text{OH})_2 + \text{M} \leftrightarrow \text{NiOOH} + \text{MH}$
 $E_{\text{cell}} = 1.23V$

- In charging, a hydrogen atom deposits on the surface of the hydrogen storage alloy by electrolysis of water. The hydrogen atom diffuses into the metal and is stored there, i.e. the metal is reduced to a metal hydride. On the positive electrode, $\text{Ni}(\text{OH})_2$ is oxidized to an NiOOH .
- Ni-MH cells also employ nickel positive plates with NiOOH as the active material and an aqueous KOH electrolyte. The main difference is that the active material in the negative plate is hydrogen absorbed in a metal alloy.

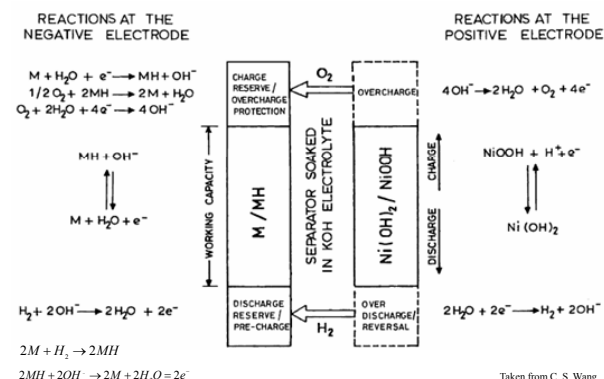
Ni-MH Battery

The mechanisms of MH electrode reactions



Ni-MH Battery

Operating principle of a sealed rechargeable Ni-MH cell



Taken from C. S. Wang

Ni-MH Battery

Metal-hydride for Ni/MH Battery

The distinct alloy families that have been largely researched as negative electrodes of Ni/MH batteries:

AB_5 (A=La, B=Ni, Co, Mn); AB_2 (A=Zr, Ti and B = V, Cr, Mn); and AB (A=Ti, B=Ni). A represents a metallic element with strong affinity for hydrogen (an early transition or rare-earth metal), whereas B is a metallic element with weak hydrogen affinity (a last transition metal).

Intermetallic compounds formed with these two elements are able to reversibly absorb hydrogen.

Taken from C. S. Wang

Ni-MH Battery

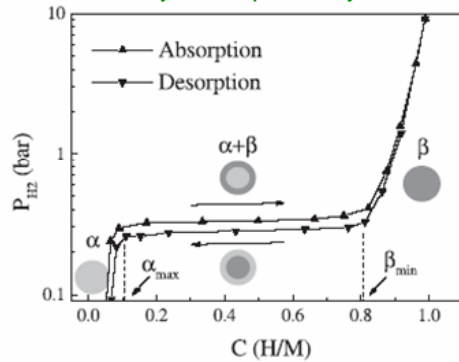
Thermodynamic Properties of Hydrides

- Hydrogen absorption in intermetallic compounds is characterized by a hydrogen capacity of about one hydrogen atom per metal atom (H/M).
- The stability of the formed hydride is determined by its hydrogen equilibrium pressure at a given temperature.
- Thus, thermodynamic properties of hydrides are usually described in pressure–composition isothermal (PCI) curves.
- A typical PCI curve for an intermetallic compound able to reversibly absorb hydrogen up to 1 H/M is represented in the figure in the next slide.

Taken from C. S. Wang

Ni-MH Battery

Thermodynamic Properties of Hydrides

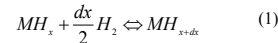


Taken from C. S. Wang

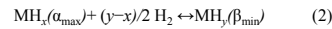
Ni-MH Battery

Thermodynamic Properties of Hydrides

Three domains can be observed. At low H content ($x < 0.1$ H/M), a solid-solution single phase domain occurs, the so-called α -phase, where hydrogen absorption/desorption can be described by the reaction



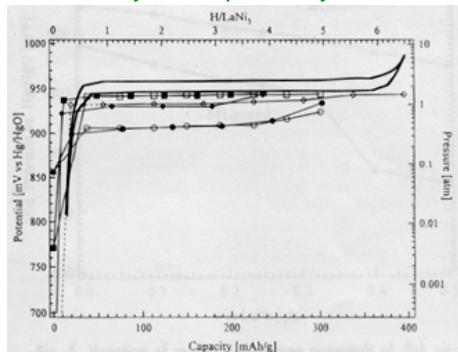
For $0.1 < x < 0.8$ H/M, there is a two-phase domain, where the saturated α -phase, with composition $x = \alpha_{\max}$, transforms into the β -phase, with composition $x = \beta_{\min}$. It corresponds to a plateau pressure that extends in the composition as long as the following equilibrium reaction takes place:



Taken from C. S. Wang

Ni-MH Battery

Thermodynamic Properties of Hydrides

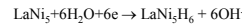


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Ni-MH Battery

Theoretical capacity calculation of metal-hydride electrode

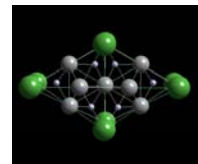
$$1) \text{ LaNi}_5\text{H}_6 \quad F=96485 \text{ C (As)}=96485 \times 1000/3600 = 26800 \text{ mAh}$$



$$Q = \frac{26800 \times 6}{\omega_{\text{LaNi}_5}} = \frac{160800}{139 + 58.7 \times 5} = 371 \text{ mAh/g}$$

Weight capacity of LaNi_5H_6

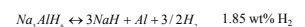
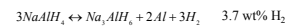
$$Q_w = \frac{W_H}{W_{\text{LaNi}_5}} = \frac{6}{139 + 58.7 \times 5} = 1.4\%$$



LaNi_5H_6

$$2) \text{ NaAlH}_4 \text{ weight capacity}$$

$$Q_w = \frac{4W_H}{W_{\text{Na}} + W_H + W_{\text{Al}}} = \frac{4}{23 + 27 + 4} = 7.4\%$$



Taken from C. S. Wang

Ni-MH Battery

Operating principle of a sealed rechargeable Ni-MH cell

- To ensure proper functioning of a sealed Ni-MH cell under a variety of conditions, it is designed in such a way that the capacity of the cell is limited by the positive electrode.
- Over-charge** O_2 evolution occurs at the positive electrode during and this diffuses to the metal-hydride electrode where it combines to form water. The negative to positive capacity ratio varies between 1.5 and 2. typically, the discharge reserve is in the range of 20% of the positive capacity.
- Reactions during cell **over-charge** are:
 Ni electrode
 $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
 M electrode:
 $M + H_2O + e^- \rightarrow MH + OH^-$
 $4MH + O_2 \rightarrow 4M + 2H_2O$

Taken from C. S. Wang

Ni-MH Battery

Features (Compared with Ni-Cd battery)

- Higher energy density (40%) than NiCd
- Nontoxic
- Reduced life, discharge rate (0.2-0.5C)
- More expensive (20%) than NiCd

By courtesy of Steve Garland & Kyle Jamieson

Ni-MH Battery

Operating principle of a sealed rechargeable Ni-MH cell

- Over-discharge conditions:
- H_2 evolution occurs at the positive electrode which is oxidized to water at the MH electrode. Thus, there are recombination mechanisms for both H_2 and O_2 gases evolved during over-discharge and over-charge, respectively, permitting sealed operation of the Ni-MH cells.
- Reactions during cell over-discharge are
 $H_2O + e^- \rightarrow 1/2H_2 + OH^-$
 and
 $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
- Since the cell reaction causes no net change in the electrolyte concentration or quantity, maintenance of electrolyte concentration results in good gas recombination, good high and low temperature operations, and good resistance to cycle life limitations caused by corrosion and swelling.

Taken from C. S. Wang

Ni-MH Battery

Recharge Characteristics (Compared with Ni-Cd battery)

- Less prone to memory than NiCd
- Shallow discharge better than deep
 Degrades after 200-300 deep cycles
 Need regular full discharge to avoid crystals
- Self discharge 1.5-2.0 more than NiCd
- Longer charge time than for NiCd
 To avoid overheating

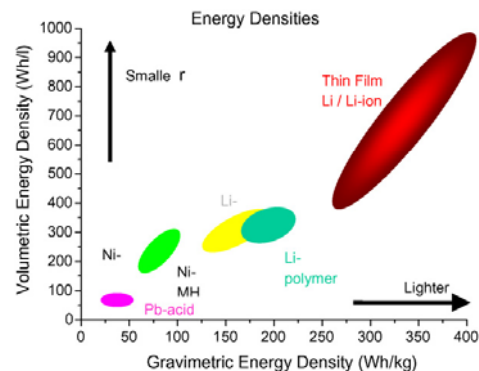
By courtesy of Steve Garland & Kyle Jamieson

Spotlight of research on

Lithium Ion Battery

Rechargeable Li-ion Battery

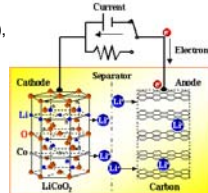
Comparison of the volumetric and gravimetric energy density



Rechargeable Li-ion Battery

Operating Principle of Li-ion Battery

- Anode:** Carbon
Lithium reacts with graphite to form LiC_6
- Cathode:** Oxide
Three type of materials: a layered oxide (such as lithium cobalt oxide), a polyanion (such as lithium iron phosphate), or a spinel (such as lithium manganese oxide)
- Electrolyte:** A mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions.
lithium hexafluorophosphate (LiPF_6),
lithium hexafluoroarsenate monohydrate (LiAsF_6),
lithium perchlorate (LiClO_4),
lithium tetrafluoroborate (LiBF_4),
lithium triflate (LiCF_3SO_3).

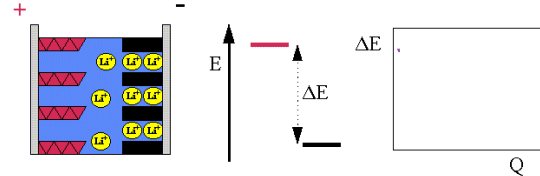


Rechargeable Li-ion Battery

Operating Principle of Li-ion Battery

Discharging: Lithium ions (yellow) spontaneously shuttle from the negative insertion electrode (black) into the electrolyte (blue) and from the electrolyte into the positive insertion electrode (red). The electrolyte allows the diffusion of ions but prevents electrons flow. At the same time electrons spontaneously flow through the only way we let them free from the negative to the positive electrode: through the load.

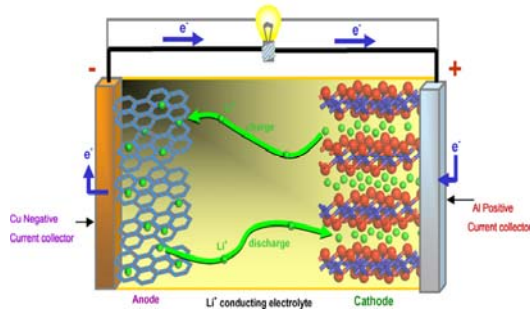
Charging: Lithium ions are forced out of the positive into the electrolyte and into the negative electrode. Electrons are injected into the negative and taken from the positive electrode



<http://www.cienciaeca.com/stalibat.html>

Rechargeable Li-ion Battery

Operating Principle of Li-ion Battery



Li-ion batteries are conventionally called 'rocking-chair' batteries because they operate primarily due to the movement of Li ions into and out of host lattices, alternatively, during charge-discharge cycles.

Taken from C. S. Wang

Rechargeable Li-ion Battery

Operating Principle of Li-ion Battery

Positive electrode (Cathode): $\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$

Negative electrode (Anode): $x\text{Li}^+ + xe^- + 6\text{C} \rightleftharpoons \text{Li}_x\text{C}_6$

Overdischarge: $\text{Li}^+ + \text{LiCoO}_2 \rightarrow \text{Li}_2\text{O} + \text{CoO}$

Overcharge up to 5.2 V: $\text{LiCoO}_2 \rightarrow \text{Li}^+ + \text{CoO}_2$

In a lithium-ion battery, the lithium ions are transported to and from the cathode or anode. Co in LiCoO_2 is oxidized from Co^{3+} to Co^{4+} during charging, and reduced from Co^{4+} to Co^{3+} during discharge.

Source: Wikipedia

Anode of Rechargeable Li-ion Battery

Requirements of Materials for Li-ion Battery

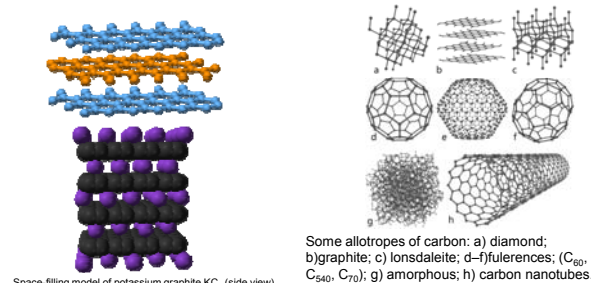
Anode

- High capacity
- Low irreversible capacity
- Low Li insertion potential (>70 -100 mv)
- Long cycle life
- High rate capability
- Electrochemical stability
- High mixed conductivity

Anode of Rechargeable Li-ion Battery

Carbon Anode

- Natural graphite materials and synthetic graphite materials
- Alternate host lattices. Typically, a variety of carbon materials with different levels of graphitization can be obtained from any starting material depending essentially on the processing parameters, especially on the HTT.

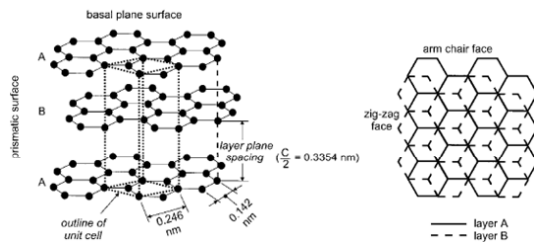


Some allotropes of carbon: a) diamond; b) graphite; c) lonsdaleite; d-f) fullerenes; (C_{60} , C_{540} , C_{70}); g) amorphous; h) carbon nanotubes.

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Graphite Anode

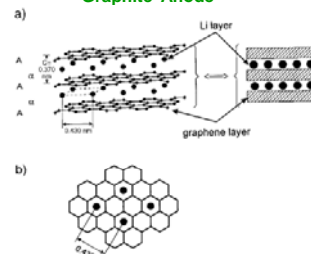


From a crystallographic point of view the term "graphite" is only applicable to carbons having a layered lattice structure with a perfect stacking order of graphene layers, either the prevalent AB (hexagonal graphite) or the less common ABC rhombohedral graphite).

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Graphite Anode



During intercalation into graphite the stacking order of the carbon layers (named graphene layers) shifts to AA. Thus, two neighboring graphene layers in LiC_6 directly face each other (Fig. a). Owing to lithium intercalation the interlayer distance between the graphene layers increases moderately (10.3% has been calculated for LiC_6). The stacking order of the lithium interlayers is aa (a Li-C6-Li-C6-Li chain exists along the c-axis). In LiC_6 the lithium is distributed in-plane in such a manner that it avoids the occupation of the nearest neighbor sites (Fig. b).

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Graphite Anode

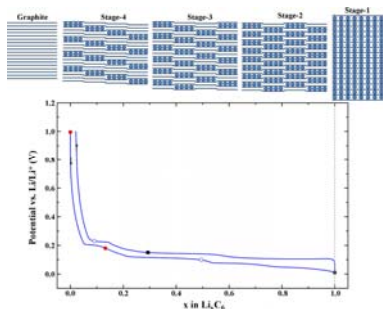
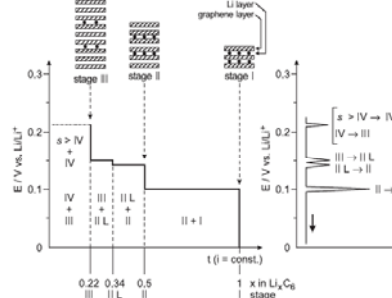


Fig. 1. Charge-discharge profile of a MAG-10 electrode at $\text{C}/25$ rate shown vs. composition along with the upper- and lower-potential limits (shown as symbols) for the three different cycling protocols: 1.0 and 0.18 V vs. Li/Li^+ (●), 0.099 and 0.23 V vs. Li/Li^+ (○) and 0.005 and 0.15 V vs. Li/Li^+ (■). Schematic representation of the staging phenomena is shown above the charge-discharge curve.

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Graphite Anode



Apart from the stage $s = 1$, four other binary phases, corresponding to the stages $s = \text{IV}$, III , II L, and II (which can also be obtained by chemical synthesis), were identified from electrochemical curves and confirmed by X-ray diffraction and Raman spectroscopy. The splitting of the second stage into two, $s = \text{II}$ ($x = 0.5$ in Li_xC_6) and $s = \text{II L}$ ($x = 0.33$ in Li_xC_6), is due to different lithium packing densities.

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Graphite Anode

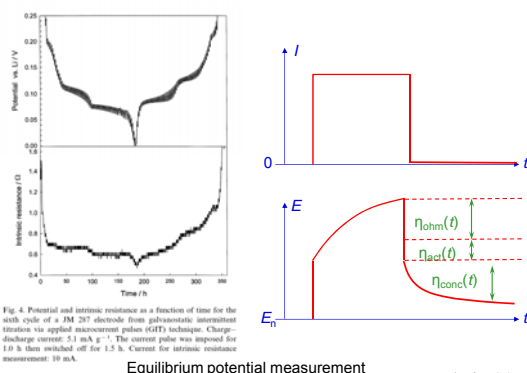


Fig. 4. Potential and intrinsic resistance as a function of time for the sixth cycle of a JM 287 electrode from galvanostatic intermittent titration via applied microcurrent pulsed (GIMP) technique. Charge-discharge current: 5.1 mA g^{-1} . The current pulse was imposed for 1.0 h then switched off for 1.5 h. Current for intrinsic resistance measurement: 10 mA.

Equilibrium potential measurement

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Graphite Anode

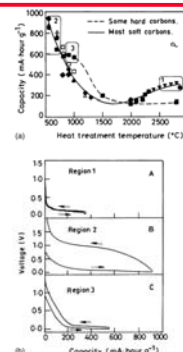
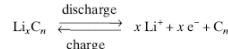


Fig. 2. (a) Plot of reversible capacity for lithium vs. heat treatment temperature (HTT) for a variety of carbon samples (type symbols, hard carbon: solid symbols, soft carbon: open symbols). (b) Voltage vs. capacity for regions A: synthetic carbon (region B) preheated peak heat-treated at 700 °C (region C) needle resin heat-treated at 1800 °C. These data are for second cycle of Li-carbon test cell [39].



Graphite materials obtained with heat-treatment at 2800 °C generally have a reversible capacity of 372 mAh g^{-1} (LiC_6 composition). The charge-discharge process does not exhibit significant hysteresis as shown by plot A in Fig. 2(b).

Soft carbon materials are generally heat-treated beyond 700 °C. These carbonaceous materials contain considerable hydrogen as C-H bonding and can take large quantities of Li ions and, hence, possess very high capacity (plot B, Fig. 2(b)). During discharge, however, the materials exhibit considerable overvoltage or voltage loss and, hence, are not suitable for battery applications.

Hard carbon materials obtained in the HTT range 800–1200 °C generally contain much less hydrogen. They essentially consist of non-graphitized carbon platelets. These materials generally possess high irreversible capacity during the first cycle and also higher reversible capacity in subsequent cycles (plot C, Fig. 2(b)).

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Solid Electrolyte Interface (SEI) Film

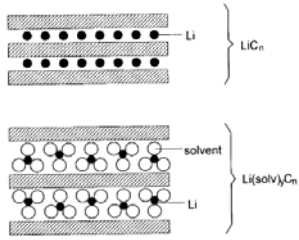


Fig. 9. Schematic drawing of binary (LiC_6) and ternary (Li(soln)C_6) lithium-graphite intercalation compounds. Modified and redrawn from [6].

Intercalation of Li^+ and other alkali metal ions from organic donor solvent electrolytes into fairly crystalline graphitic carbons quite often leads to solvated (ternary) graphite intercalation compounds, Li(soln)C_6 .

The so-called "solvated intercalation" is associated with extreme expansion of the graphite matrix (typically ~150 %), frequently leading to deterioration (exfoliation) of the graphite and as a result to a drastically decreased charge storage capability.

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Solid Electrolyte Interface (SEI) Film

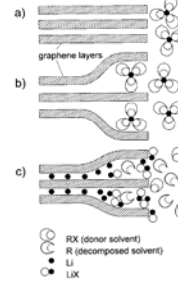


Fig. 10. Schematic model of the film-forming mechanism on the graphite. (a) Before reaction, (b) Formation of ternary solvated lithium-graphite intercalation compounds Li(soln)C_6 , (c) Film formation due to decomposition of Li(soln)C_6 . Modified and redrawn from [7].

The solvated intercalation compounds are thermodynamically favored over the corresponding binary compounds, that is, the potentials of their electrochemical formation are more positive than those for the formation of the corresponding binary graphite intercalation compounds (GICs).

The solvated GICs are thermodynamically unstable with respect to the reduction of the co-intercalated solvent molecules. This kinetically controlled reduction contributes considerably to the self-discharge of LiC_6 electrodes.

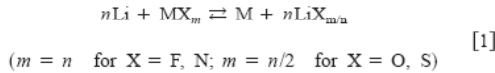
Taken from C. S. Wang

Electrode of Rechargeable Li-ion Battery

Alternative Anode Materials

Thermodynamic Considerations

The overall Li uptake and Li extraction from a binary metal compound MX_m under investigation ($X = \text{F}, \text{O}, \text{S}, \text{N}$) can be written as



For such a reaction, the values of the cell voltage [electromotive force (emf)] can be calculated using the Nernst equation

$$\Delta G = n\Delta G_f^\circ(\text{LiX}_{m/n}) - \Delta G_f^\circ(\text{MX}_m) = -nEF \quad [2]$$

Taken from C. S. Wang

Electrode of Rechargeable Li-ion Battery

Voltage versus capacity for positive- and negative-electrode materials

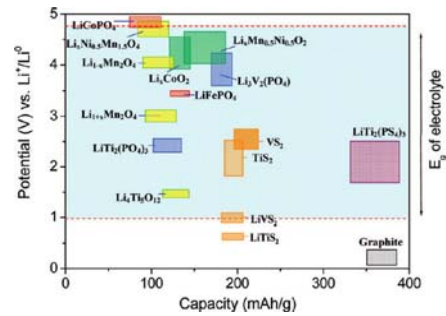
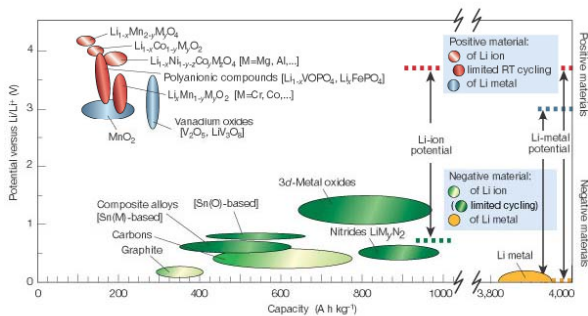


Figure 5. Voltage versus capacity of several electrode materials relative to the window of the electrolyte 1 M LiPF_6 in EC/DEC (1:1).

Taken from C. S. Wang

Rechargeable Li-ion Battery

Voltage versus capacity for positive- and negative-electrode materials

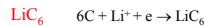


Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Theoretical capacities of anodes for Li-ion battery

$$F = 96485 \text{ C (A} \cdot \text{s)} = 26800 \text{ mAh}$$



$$Q = \frac{1F}{Wc} = \frac{26800 \times 1}{6 \times 12} = 372 \text{ mAh/g}$$

$$Q = \frac{1F}{W_{\text{LiC}_6}} = \frac{26800}{12 \times 6 + 7} = 339 \text{ mAh/g}$$



$$Q_{(\text{mAh/g})} = \frac{4.4F}{W_{\text{Sn}}} = \frac{4.4 \times 26800}{118.7} = 993 \text{ mAh/g}$$

$$Q_{(\text{mAh/g})} = \frac{4.4F}{W_{\text{SnLi}_{4.4}}} = \frac{4.4 \times 26800}{118.7 + 4.4 \times 7} = 788.7 \text{ mAh/g}$$

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Theoretical capacities of anodes for Li-ion battery

SiLi₄

$$Q_{(mAh/g)} = \frac{4.4F}{W_{Si}} = \frac{4.4 \times 26800}{28} = 421 \text{ mAh/g}$$

$$Q_{(mAh/g)} = \frac{4.4F}{W_{SiLi_4}} = \frac{4.4 \times 26800}{28 + 4.4 \times 7} = 2005.4 \text{ mAh/g}$$

Li metal

$$Q_{Li} = \frac{1F}{W_{Li}} = \frac{26800}{6.94} = 3861 \text{ mAh/g}$$

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Alternative Anode Materials

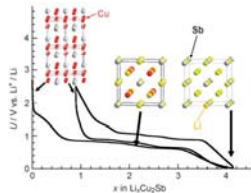
Electrode material	Average potential difference	Specific capacity	Specific energy
Graphite (LiC ₆)	0.1-0.2 V	372 mA·h/g	0.0372-0.0744 kW·h/kg
Hard Carbon (LiC ₆)	? V	? mA·h/g	? kW·h/kg
Titanate (Li ₄ Ti ₅ O ₁₂)	1-2 V	160 mA·h/g	0.16-0.32 kW·h/kg
Si (Li _{4.4} Si)	0.5-1 V	4212 mA·h/g	2.106-4.212 kW·h/kg
Ge (Li _{4.4} Ge)	0.7-1.2 V	1624 mA·h/g	1.137-1.949 kW·h/kg

Source: Wikipedia

Anode of Rechargeable Li-ion Battery

Alternative Anode Materials

- Alloys, Li_{4.4}Sn, Li_{4.4}Si
- Displacement Reactions (such as Cu₆Sn₅, InSb, and Cu₃Sb)
 - The concept of displacing one metal A from a binary intermetallic AB by lithium reduction, with the end result being the formation of a composite containing the displaced metal A together with the alloy Li₄B



The voltage composition curve for Li/Cu₂Sb, with the structural evolution upon cycling so as to emphasize both the copper extrusion/reinjection upon cycling together with the maintenance of the antimony array.

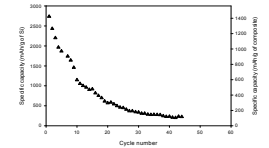
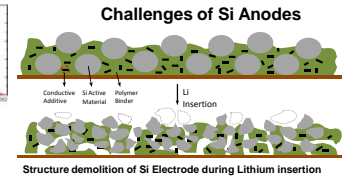
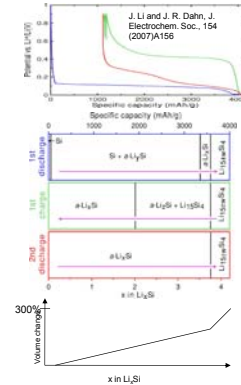
- Conversion Reactions (MO+2Li+2e⁻ ↔ Li₂O+M)
- Mixed reaction (SnO)

Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery

Alternative Anode Materials

Challenges of Si Anodes



Cycling stability of carboxymethyl cellulose binder-5.2 wt% bulk Si (1 μm) electrodes. Cut off potential: 0.0-1.5V

Anode of Rechargeable Li-ion Battery

Alternative Anode Materials

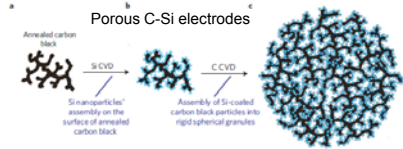
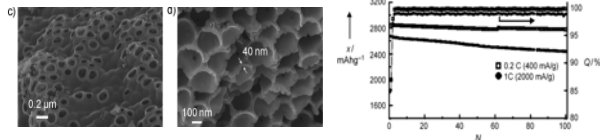


Figure 1 | Schematic of Si-C nanocomposite granule formation through hierarchical bottom-up assembly. (a) Annealed carbon-black dendritic particles (b) are coated by Si nanoparticles (b) and then assembled into rigid spheres with open interconnected internal channels during C deposition (c).

Nano-porous Si-C

Controversy in cycling stability

Pristinely rigid silicon framework cannot sustain the volume c...

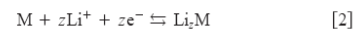
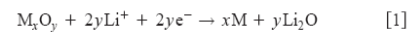


J. Cho et al, Angew. Chem. Int. Ed. 47(2008)10151

Anode of Rechargeable Li-ion Battery

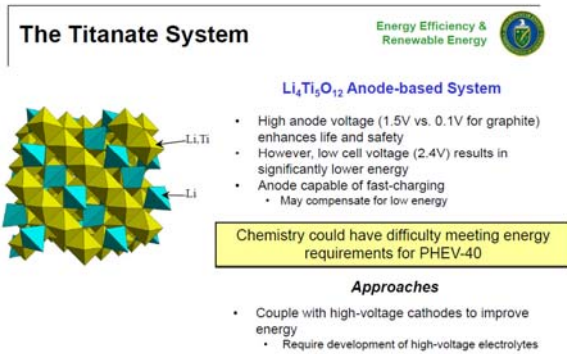
Glasses and crystalline tin oxides: SnO and SnO₂

Tin dioxide, SnO₂, was found to react with lithium to generate nanodomains of metallic Sn dispersed in a lithia matrix, Li₂O (Eq. 1). The nanodomains of Sn subsequently alloy with lithium (Eq. 2), thereby providing the reversible capacity of the electrode. Li₂O remains inert, providing mechanical stability to the composite electrode, which in turn results in good capacity retention



Taken from C. S. Wang

Anode of Rechargeable Li-ion Battery



Rechargeable Li-ion Battery

Requirements of Materials for Cathode

- (1) Contain a readily reducible/oxidizable ion, for example a transition metal.
- (2) React with lithium in a reversible manner.
- (3) React with lithium with a high free energy of reaction, leading to a high-energy storage.
 - High capacity, preferably at least one lithium per transition metal.
 - High voltage, preferably around 4 V (as limited by stability of electrolyte).
- (4) React with lithium very rapidly both on insertion and removal, leading to high power density, which is needed to replace the Ni/Cd battery or for batteries that can be recharged using HEV regenerative braking.
- (5) The material be a good electronic conductor, preferably a metal.
 - allows for the easy addition or removal of electrons during the electrochemical reaction.
 - allows for reaction at all contact points between the cathode active material and the electrolyte rather than at ternary contact points between the cathode active material, the electrolyte, and the electronic conductor (such as carbon black).
 - minimizes the need for inactive conductive diluents, which take away from the overall energy density.
- (6) stable, i.e., not change structure to overdischarge and overcharge.
- (7) Low cost.
- (8) Environmentally benign.

Taken from C. S. Wang

Cathode of Rechargeable Li-ion Battery

Voltage versus capacity for positive- and negative-electrode materials

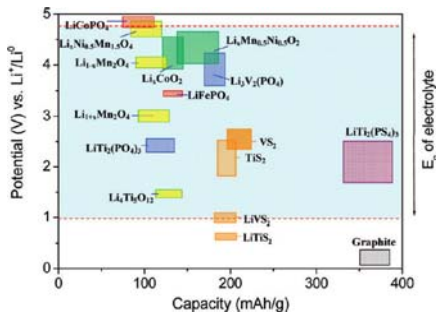
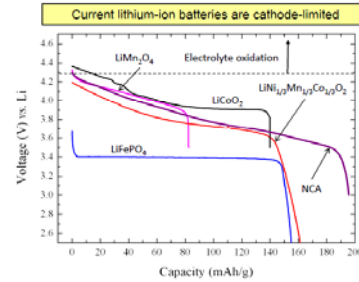


Figure 5. Voltage versus capacity of several electrode materials relative to the window of the electrolyte 1 M LiPF_6 in EC/DEC (1:1).

Taken from C. S. Wang

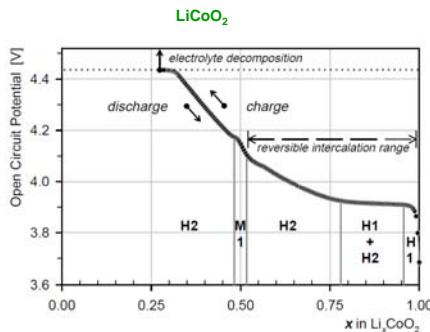
Cathode of Rechargeable Li-ion Battery

Equilibrium Potentials for Commercially Available Cathodes



Dr. Tien Duong, Energy Storage R&D for Vehicles: Status and Research Directions, invited talk at UMD

Cathode of Rechargeable Li-ion Battery



The Open Circuit Potential (OCP) of a commercial LiCoO_2 electrode recorded against metallic lithium as a function of the degree of lithium intercalation (25°C). The reported LiCoO_2 phase structures are indicated (H: hexagonal, M: monoclinic).

Taken from C. S. Wang

Cathode of Rechargeable Li-ion Battery

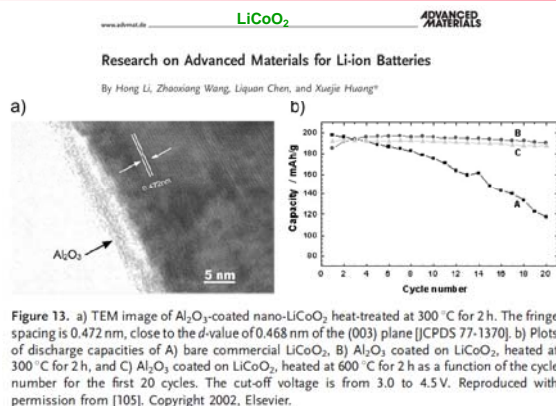
LiCoO_2

- LiCoO_2 cathode materials are typically cycled between the fully lithiated discharge state LiCoO_2 (3.0 V vs Li/Li^+) and a roughly half-delithiated charge state Li_xCoO_2 ($x=0.5-0.6$, 4.2 V vs Li/Li^+) to yield a useable specific capacity below 150mAh/g.
- When the Li/LiCoO_2 cell is cycled within a limited composition range of $0 < x < 0.5$, it shows excellent cycling performance. However, its capacity fades rapidly when more Li is deintercalated from the lattice due to cathode degradation and electrolyte decomposition at high voltage.
- A high concentration of Co^{4+} will damage the cathode crystallinity and result in a significant decrease of the c-axis dimension caused by a phase transition
- The performance degradation of LiCoO_2 is related to the dissolution of its Co^{3+} ions in the electrolyte solution

Solution: coating the LiCoO_2 surface with inert oxides such as SnO_2 , Al_2O_3 , and MgO , ZrO_2 .

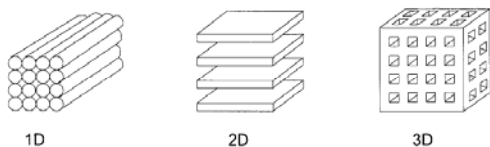
Taken from C. S. Wang

Cathode of Rechargeable Li-ion Battery



Cathode of Rechargeable Li-ion Battery

One-, Two-, and Three-Dimensional Transition-Metal oxides



Schematic representation of void spaces in one-, two-, and three-dimensional transition-metal oxides.

Taken from C. S. Wang

Rechargeable Li-ion Battery

Requirements of Materials for Electrolyte

1. A large electrolyte window E_g ,
2. Retention of the electrode/electrolyte interface during cycling when the electrode particles are changing their volume.
3. A Li⁺-ion conductivity $\sigma_{Li^+} > 10^{-4}$ S/cm over the temperature range of battery operation.
4. An electronic conductivity $\sigma_e < 10^{-10}$ S/cm.
5. A transference number $\sigma_{Li^+}/\sigma_{total} \approx 1$, where σ_{total} includes conductivities by other ions in the electrolyte as well as $\sigma_{Li^+} + \sigma_e$.
6. Chemical stability over ambient temperature ranges and temperatures in the battery under high power.
7. Chemical stability with respect to the electrodes, including the ability to form rapidly a passivating solid/electrolyte-interface (SEI) layer where kinetic stability is required because the electrode potential lies outside the electrolyte window.
8. Safe materials, i.e., preferably nonflammable and nonexplosive if short-circuited.
9. Low toxicity and low cost.

Taken from C. S. Wang

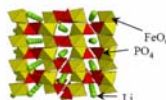
Cathode of Rechargeable Li-ion Battery

The Iron Phosphate System

Energy Efficiency & Renewable Energy



LiFePO₄ / Carbon-based



- Best chemistry in terms of safety characteristics
- Excellent power capability due to nanosize
- Low energy due to low operating voltage (3.4V)
- Cycle life unknown due to limited data
 - Life appears to be related to impurities formed during material synthesis, which could be prevented.
- Flat voltage leads to cell balancing and SOC determination problems

Low energy could impede use in PHEV-40



Approaches

- Move to prismatic designs to increase specific energy and energy density
- Tailor size of nanoparticles to increase tap-density
- Move to alternative phosphate systems that have higher energy, while maintaining safety

Cathode of Rechargeable Li-ion Battery

Alternative Cathode Materials

Electrode material	Average potential difference	Specific capacity	Specific energy
LiCoO ₂	3.7 V	140 mA·h/g	0.518 kW·h/kg
LiMn ₂ O ₄	4.0 V	100 mA·h/g	0.400 kW·h/kg
LiNiO ₂	3.5 V	180 mA·h/g	0.630 kW·h/kg
LiFePO ₄	3.3 V	150 mA·h/g	0.495 kW·h/kg
Li ₂ FePO ₄ F	3.6 V	115 mA·h/g	0.414 kW·h/kg
LiCo _{1/3} Ni _{1/3} Mn _{1/3} O ₂	3.6 V	160 mA·h/g	0.576 kW·h/kg
Li(Li _{0.5} Ni _{0.5} Mn _{0.5} Co _{0.5})O ₂	4.2 V	220 mA·h/g	0.920 kW·h/kg

Source: Wikipedia

Electrolyte of Rechargeable Li-ion Battery

Physical constants of organic solvents

Solvent	Dielectric Constant	Density [g·cm ⁻³]	MP [°C]	BP [°C]	Viscosity [cP]
Ethylene Carbonate (EC)	89.6 (40°C)	1.3218 (39°C)	39-40	248	1.85 (40°C)
Propylene Carbonate (PC)	64.4	1.19	18.55	241	2.53
Diethyl Carbonate (DEC)	2.82	0.9693	-43	127	0.748
Dimethyl Carbonate (DMC)	3.12	-	3	90	0.585

Taken from C. S. Wang

Electrolyte of Rechargeable Li-ion Battery

Electrolyte conductivity of carbonate-based solutions (1M at 25°C)

Electrolyte salt (1.0 M)	Solvent (1:1 by volume) conductivity $\times 10^{-3}$ [S.cm ⁻¹]		
	EC + DMC	EC + DEC	PC + DMC
LiPF ₆	11.2	7.8	10.0
LiClO ₄	10.1	6.4	6.8
LiCF ₃ SO ₃	3.1	2.1	2.2

Taken from C. S. Wang

Electrolyte of Rechargeable Li-ion Battery

Challenges of carbonate based electrolyte

1. Carbonate- based solvents are highly flammable with flash points below 30 °C.
2. LiPF₆ can undergo an autocatalytic decomposition into LiF and PF₅; the PF₅ reacts irreversibly with any water present (PF₅+ H₂O=PF₃O + 2HF) and, above 60 °C, with a carbonate electrolyte.
3. These reactions degrade the battery and lead to safety hazards

Taken from C. S. Wang

Electrolyte of Rechargeable Li-ion Battery

Ionic Liquid electrolyte

Advantages over carbonate-based electrolytes:

- High oxidation potential (~5.3 V vs Li⁺/Li⁰)
- Non-flammability,
- low vapor pressure,
- Better thermal stability,
- low toxicity, high boiling points,
- high Li-salt solubility.
- higher viscosity
- Low Li⁺ -ion conductivity.

Electrolyte of Rechargeable Li-ion Battery

Polymer Electrolytes

- (i) Dry solid polymer electrolyte
 - a) Polymer host itself is used as a solid solvent along with lithium salt and does not contain any organic liquids
 - b) these dry polymer electrolyte systems (PEOeLiX) offer very low ionic conductivity of the order of 10⁻⁶ S/cm at ambient temperature
- (ii) Gel polymer electrolytes
Poly(vinylidene fluoride-hexa fluoropropylene) (PVdF-HFP) (88:12)
This copolymer comprising an amorphous phase of HFP which helps to entrap large amount of liquid electrolytes and the PVdF crystalline phase acts as a mechanical support for the polymer matrix
- (iii) Composite polymer electrolytes

Electrolyte of Rechargeable Li-ion Battery

Dry polymer electrolyte

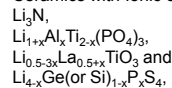
1. Poly(ethylene oxide) (PEO); Ionic conductivity is too low (10⁻⁶ S/cm)
2. Poly(acrylonitrile) (PAN); ionic conductivity of the order of 10⁻³ S/cm, severe passivation upon contact with lithium metal anode
3. Poly(methyl methacrylate) (PMMA); mechanical strength of plasticized PMMA is poor; adding PVC can enhance the mechanical property.

Taken from C. S. Wang

Electrolyte of Rechargeable Li-ion Battery

Fast Ceramic Li-ion electrolytes

Ceramics with Ionic conductivity of order of 10⁻³ S cm⁻¹



Advantage: A single Li ionic conductor (lithium ionic transference number near to 1). PEO-Li salt: lithium ionic transference number is only around of 0.3

Low activation energy (0.2-0.3 eV)

Disadvantage: **Poor mechanical properties (too brittle)**
Low chemical stability to reduction (some ceramics)
unstable at potential below 1.5V for $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$
and $\text{Li}_{0.5-3x}\text{La}_{0.5+x}\text{TiO}_3$

Taken from C. S. Wang

Rechargeable Li-ion Battery

Advantages of Li-ion Battery as Compared to Other Counterparts

- best energy density
- no memory effect
- slow loss of charge when not in use

Comparison of Various Types of Batteries

	Lead-Acid	Ni-Cd	Ni-MH	Li-ion
Cell voltage (V)	2	1.2	1.2	3.6
Specific energy (Wh/kg)	1-60	20-55	1-80	3-100
Specific power (W/kg)	< 300	150 – 300	< 200	100 – 1000
Energy density (kWh/m ³)	25-60	25	70-100	80-200
Power density (MW/m ³)	< 0.6	0.125	1.5 – 4	0.4 – 2
Maximum cycles	200-700	500-1000	600-1000	3000
Discharge time range	> 1 min	1 min-8 hr	> 1 min	10 s-1 h
Cost (\$/kWh)	125	600	540	600
Cost (\$/kW)	200	600	1000	1100
Efficiency (%)	75 - 90	75	81	99