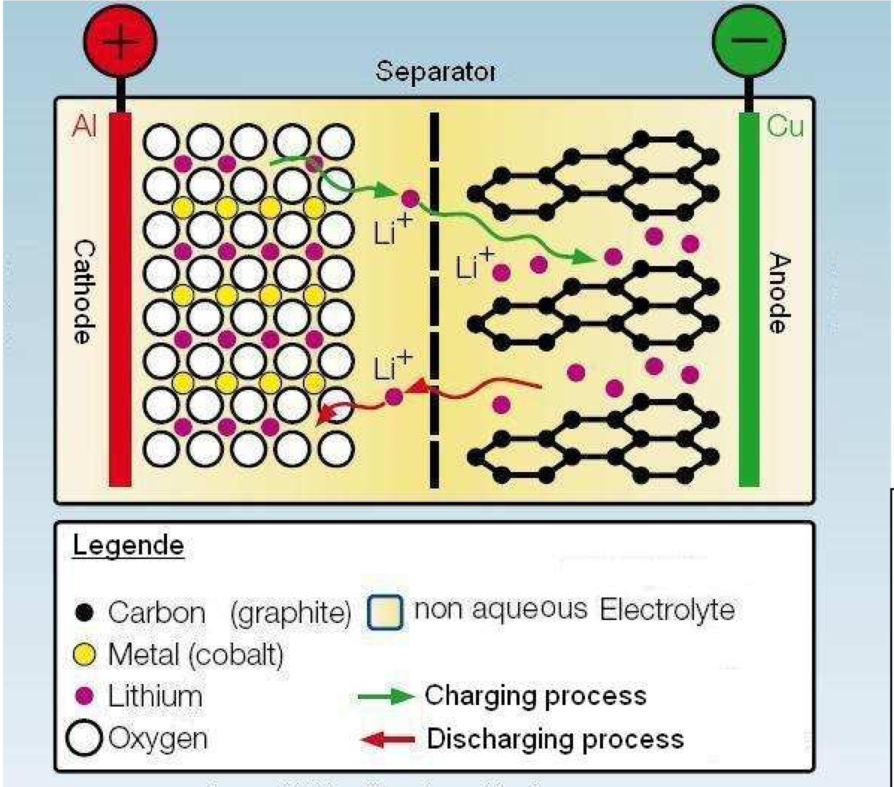
Electrochemistry of the Lithium-Ion accumulators

And notably the *LiFePO4* July 2012

SYCOMOREEN

http://sycomoreen.free.fr

Schema of working



Source Wikipedia, adapted by Sycomoreen

↲ On the left : overall structure of a Lithium-Ion accumulator (Li-ion) with $LiCoO_2$ type, but also valid for other variants :

- $LiMnO_2$
- $LiFePO_4$
- Lithium-Metaloxid

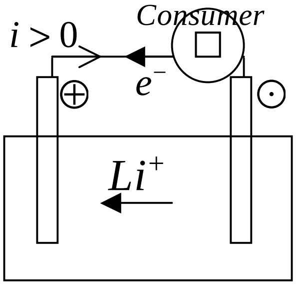
Cathode : Crystalline matrix of oxidized metal. The industrialized variants are CoO_2 (Cobalt dioxide), MnO_2 (Manganese dioxide) and **$FePO_4$** (iron phosphate, used by *CATHI*). An aluminium collector is driving the generated or absorbed electronic flux by this electrode. It is the positive pole of the battery.

Anode : Crystalline matrix of graphite. A copper collector is driving the generated or absorbed electronic flux by this electrode. It is the negative pole of the battery.

Electrolyte : organic aprotic solvent (often carbonates of alkyls) with dissolved Lithium salts (often $LiPF_6$). There is an alternative for the liquid electrolytes : the gelled polymers with polyvinyl fluorides (battery « Li-Po »). In both cases, the material is designed to ease the migration of the Lithium ions Li^+ between the cathode and the anode.

Voltage : about 3,3V for the LiFePO4 or 3,6V for the LiCoO2 or 3,8V for the LiMnO2

Chemical reactions while discharging (on the example of LiFePO4)



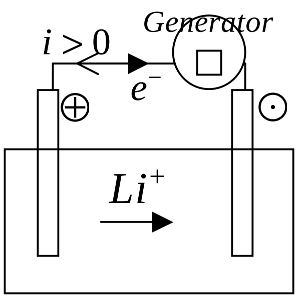
Cathodic reduction : $Li_{1-x} + FePO_4 + xLi^+ + xe^- \rightarrow LiFePO_4$

Anodic Oxidization : $Li_xC_n \rightarrow nC + xLi^+ + xe^-$ with n an integer and $0<x<1$

Net reaction : $Li_{1-x} + Li_xC_n + FePO_4 \rightarrow LiFePO_4 + nC$

Commentaries : the discharging entails *a LiFePO4 formation at the cathode* while the *Lithium graphite is dividing into carbon and Li^+ cation at the anode*. The crystalline shapes which are combination between Lithium, metal oxides and carbon are still not well known : they appear as an *intercalation process of* the Lithium elements, as well ionic as atomic. For the *numbers of oxidization*, the Lithium is reduced at the cathode by passing from +I to 0, in the same time, it is oxidized at the anode while passing from 0 to +I. Thus the migration of *x* Lithium cations generates *the transfer of x electrons from the anode towards the cathode.*

Chemical reactions while charging (on the example of LiFePO4)



Cathodic oxidization : $LiFePO_4 \rightarrow Li_{1-x} + FePO_4 + xLi^+ + xe^-$

Anodic reduction : $nC + xLi^+ + xe^- \rightarrow Li_xC_n$ with n an integer and $0<x<1$

Net reaction : $LiFePO_4 + nC \rightarrow Li_{1-x} + Li_xC_n + FePO_4$

Commentaries : the charging shows *the destruction of LiFePO4 at the cathode* while the *Lithium graphite is appearing at the anode*. The *process of intercalation* of the Lithium elements, as well ionic as atomic, takes place in the reverse way in comparison with the discharging time. Regarding the *numbers of oxidization*, the Lithium is reduced at the anode by going from +I to 0, while it is oxidized at the cathode by coming from 0 to +I. Thus, the migration of *x* Lithium cations generates *the transfer of x electrons from the cathode towards the anode.*

Notices and perspectives about the Lithium batteries

Regarding the LiFePO4 : This version has a little lower voltage (~3,3 V) but is staying more reliable, less toxic and less expensive. (the cobalt, nickel, or manganese are costly). Moreover, the iron can be easily recycled. For the chemical aspect, this cathode is very stable and doesn't leave dioxygen which can start Lithium fires inside the $LiCoO_2$ / $LiMnO_2$ batteries.

A very large range of accumulators : the Lithium-Ion accumulators are not linked with a specific electrochemical couple. Any material which is able to store Lithium ion or atoms by intercalation can be used for Lithium-ion technology. Thus the Li-ion batteries are declining themselves with :

- *The material at their cathode* (very numerous choices of metal oxides)
- *The material at their anode* : often graphite/graphene, but research is active for this matter (amorphous Silicon, Lithium titanate $Li_5T_4O_{12}$, tin dioxide SnO2, several experimental nanocrystals …)
- *The electrolyte or the polymer of migration* for the Li^+ cations
- Moreover, some transverse technologies are adding like the LMP battery (Lithium metal polymer) which uses microsheets of Lithium metal, of insulator, of electrolyte (the *Batscap* battery developed for the *Bolloré Blue Car*).

It explains the big variety of batteries with ionic Lithium, whereas before, the Lead/Acid or Nickel batteries knew only few evolutions and/or variants (for example the electrolytic evolutions with the Pb gel and absorbent Glass ; the Nickel Metal Hydride (NiMH) to replace the Cadmium; more original, the ZEBRA battery with its melted salts of Sodium and Nickel Chloride).

What hyphens ? *What distinguishes all the Lithium batteries nevertheless, it is the strong mass energy or density, but also their big weakness* to any overvoltage, under-voltage or current too strong. Indeed, *it damages in* ***an irreversible manner*** *either the cathode, either the anode, either the polymer/ electrolyte* Therefore, an effective controlling electronics and permanent balancing of the batteries are absolutely necessary (called BMS: Batteries' Managing System); **it penalizes the Lithium in the automotive domain** since its applications require very strong currents for the acceleration and the regenerative the braking, and full charges and discharges to increase the autonomy.

A good autonomy ? In spite of everything, *the densities of energies really remain too weak in comparison with the hydrocarbons*. For example, to get the mechanical energy provided by the combustion of one kg of gas (about 3 mechanical kWh), it is necessary to carry about 30 kg of Lithium batteries. In other words, **a tank of 50 L of gas is equivalent to 1 500 kg of ionic Lithium batteries.**

Thus Sycomoreen recommends the triple hybridization NiCad / LiFePO4 / Hydrocarbons.

Car **A**ctuated by **T**riple **H**ybrid **I**ntegration Sycomoreen CATHI