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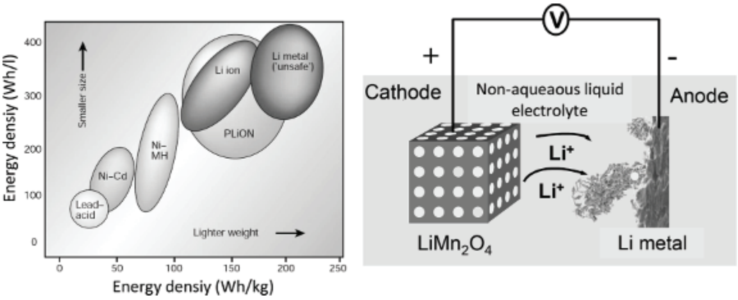
Batteries and Supercapacitors: Some Reminders

1.1. Main evolution of batteries from the 1980s to now

The concept and commercialization of a lithium-ion (Li-ion) battery dates back to 1980 and 1990, respectively. Its specificity resides in the fact that it uses: (1) a non-aqueous electrolyte and (2) positive and negative electrodes insertion compounds, which can act like lithium "sponges" [TAR 98]. A historical overview of accumulators shows us that this technology emerged through the continuous evolution of concepts that previously led to Pb, Ni-Cd, Ni-MeH, Li-metal and Li-polymer technologies. The lead–acid accumulator, which uses an aqueous electrolyte based on H_2SO_4 consumed during discharge, is based on conversion reactions. These reactions cause the breakage and formation of bonds, $PbO_2 \rightarrow Pb(SO_4)$ and $Pb \rightarrow PbSO_4$, at the positive and negative electrode, respectively. The transition to Ni-Cd accumulators has not only facilitated the transition from an electrolyte saturated in potassium that does not participate in the electrochemistry of a system, but also introduced a $Ni(OH)_2$ positive electrode, which uses the deinsertion and insertion of protons during charge and discharge, respectively. Insertion–deinsertion electrodes then made their first appearance. This concept was generalized some years later (1980) when Cd was replaced at the negative electrode of the Ni-Cd accumulator, by a $LaNi_5H_x$ intermetallic compound, capable of reversibly inserting–deinserting 5 H^+. Then the NiMeH accumulator emerged, the most efficient at the time (~80 Wh/kg, ~350Wh/l), which is nothing other than a proton accumulator.



a) b)

Figure 1.1. *Comparison of different accumulators in terms of mass energy (Wh / kg) and volumic energy a) with in b) a description of the Li-metal accumulator. The dendrites are shown*

At the same time, parallel research on solid-state chemistry revealed compounds that were capable of reversibly inserting Li^+, such as Li_xTiS_2. With Li being one of the most electropositive elements (–3.02 V vs. ENH), the thought of using Li insertion materials as the positive electrode of lithium accumulators was proposed. Therefore, due to the high reactivity of Li with H_2O, the transfer was made from an aqueous electrolyte to a non-aqueous electrolyte composed of lithium salts dissolved in an organic solvent. The Li-metal battery was introduced and marketed in 1985 by Moly-Energy. Despite their attractive performances (250 Wh/kg), the commercialization of Li-metal accumulators was short-lived due to their limited safety. In fact, some of these accumulators supplying mobile phones had to be withdrawn from the market after exploding in the ear of their users. The cause of this malfunction is associated with dendritic growth of Li caused by repetitive charging/discharging, which led to a short circuit inside the accumulator causing the explosion. This problem was known but not appreciated as it should have been due to the excitement generated by this technology with regard to the increased autonomy of mobile phones [TAR 01]. This was the end of the metallic lithium liquid technology.

To overcome the problems associated with dendritic growth, two strategies were rapidly proposed. The first strategy, proposed by M. Armand [ARM 79], involves replacing the liquid electrolyte by a conductive polymeric membrane which acts as a physical barrier between the positive and negative electrodes. All solid Li-polymer technology was initially developed by Hydro-Québec in the 1980s and was taken over by Bolloré 30 years later, which led to the first commercialization of this battery. Today, it supplies the “Blue Car” which crosses Paris as part of the urban project “Autolib”.

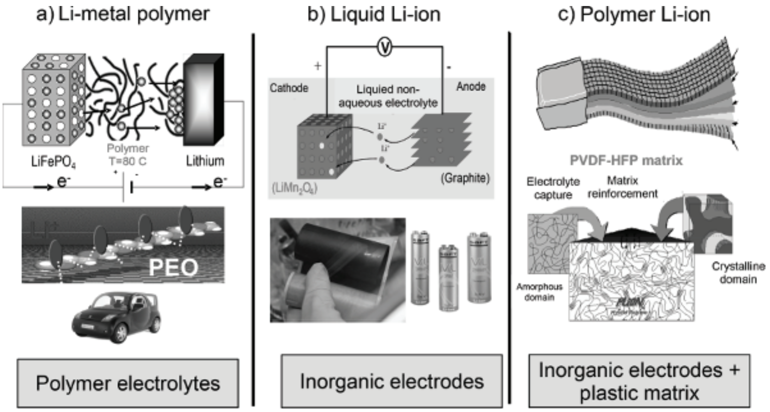


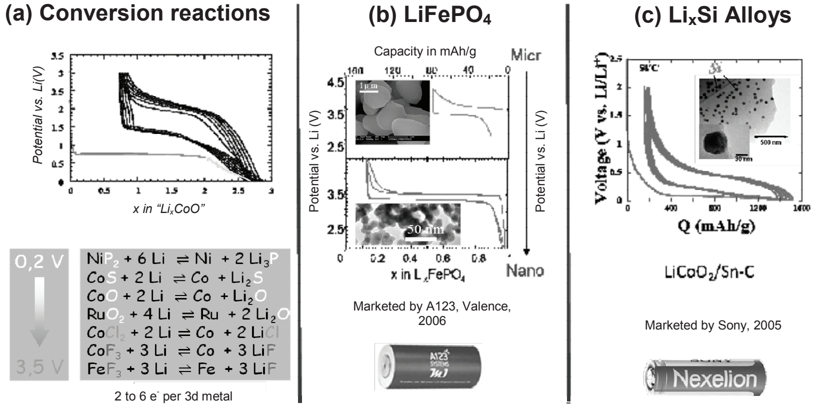
Figure 1.2. *Three currently used technologies based on Li-metal or Li^+ ions*

The second approach dates back to the 1980s and was initiated by Don Murphy [MUR 78] of “Bell Laboratories” (USA). He suggested replacing the negative Li electrode by an insertion compound that created a technology containing only Li^+ ions. This technology, devoid of Li-metal, was initially named “rocking-chair” accumulators, due to the back and forth motion of their ions between the positive and the negative electrode, and subsequently named Li-ion accumulators. Therefore, metal hydride-based systems with hygrogen ions functioning in an aqueous environment were duplicated and transferred to Li-ion systems in a non-aqueous medium. Li-ion technology was marketed in 1990 by Sony Energy [NAG 90]. Today, it is this technology which still prevails to power our mobile phones and has entered the electric vehicle market, and it is a serious candidate for grid applications (e.g. stationary storage for houses). A derivative of this technology was developed in 1995 [TAR 96] under the name Li-ion plastic technology, whose advantages resided in its flexibility and versatility with regard to its configuration, facilitating it to be adapted to the variable shapes of objects. The uniqueness of this technology is based on the use of a plastic composed of an electrolyte based on Li^+ attached to a solid polymer membrane based on poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP).

Apart from the improvements, mentioned above, to the configuration of the accumulator, the initial years of research on Li-ion technology also led to the establishment of specifications for the ideal electrode material, namely good electronic and ionic conductors of a micrometric size with an open structure. These criteria of course limit the number of candidates and only three compounds have met the criteria for 20 years: $LiCoO_2$ [MIZ 80]; $LiNiO_2$ [DAH 91] and $LiMn_2O_4$ [THA 83] with, in each case, a limitation to their usable capacity of approximately 0.5 electrons per transition metal. This means that although $LiCoO_2$ theoretically has a capacity of 290 mAh/g, in reality only half, 150 mAh/g, can be utilized, due to the collapse of the structure caused by intersheet repulsion when too many Li^+ ions are removed. To overcome this problem of structural stability, chemists successfully resorted to cationic substitution. By partial substitution of cobalt by Mn and Ni within the metal sheet, lamellar oxides with capacities of 180 mAh/g called NMC [OHZ 01] were obtained and over time gradually replaced $LiCoO_2$ in commercial batteries. Many researchers had come to believe that Li-ion had reached its limits, bringing research to a halt. Some alternatives to the conventional approach, both with regard to the material and the reaction mechanisms, were needed to remove existing technological barriers, and favor technological breakthroughs.

These criteria for the ideal insertion material were questioned at the beginning of the 2000s with the arrival of nanomaterials for which the *Laboratoire de Réactivité et Chimie des Solides* (LRCS) [POI 01] was a pioneer. Along with the structure and composition, size was the third parameter; it was possible to recover many materials previously neglected due to poor ionic and electric conductivity or to uncover new reaction mechanisms that did not require lacunar compounds. The benefits offered by nanoscale and nanostructured materials to Li-ion technology are now so numerous that we will provide only the three best examples.

The first example is the transformation of $LiFePO_4$, by the nanoscale morphology/coating coupled approach [RAV 99], (an insulating material once abandoned) into one of the most sought electrode materials by battery manufacturers due to its abundance and low cost. It is ironic that this material (once insulating) is today the most efficient for power applications. The benefit of the nano/coating approach can be explained as follows: on the one hand, the nanoscale character of the particle reduces the travel time of an ion from the center to the surface of the material by a factor of 100 when the radius is divided by 10; on the other hand, the coating of a uniform layer of carbon on the electrode provides electron percolation for access to the whole active material. The two effects combined improve the kinetics of the electrode. Thus, today's Li-ion $LiFePO_4$/C batteries, marketed since 2006 by A123, are still the preferred technology for electric vehicles and grid applications.



Marketed by A123, Valence, 2006

Marketed by Sony, 2005

Figure 1.3. *The use of nanomaterials to transform $LiFePO_4$ insulators into attractive insertion materials a), to make the insertion of Li into Si possible b) and finally to develop new reaction mechanisms such as conversion reactions c)*

The second example shows how the transition from the nanometric scale helped solve the 20 year old problem regarding negative silicon or tin electrodes with lithium (Li_xSi_y) alloy reactions that caused significant changes in volume and consequently a loss of electronic percolation within the electrode [ANA 87]. Nanoparticles are in fact more resistant to fractures since the elastic energy that they store during deformation is not sufficient to initiate-propagate a fracture. In other words, for a nanoparticle, the volumetric strain relief required to initiate a fracture is not sufficient to counteract the surface energy associated with its propagation. Therefore, due to the strain relief provided by the nanoparticulate state, Si and Sn electrodes, combining nanometric character and carbon coating, were created [WIN 99]. They were marketed in 2005 (NEXELION technology with Sn) and in 2011 (Si technology by PANASONIC).

Finally, we recall that the transition to the nanometric scale also allows us to go beyond some well-established typical Li-ion insertion/deinsertion processes, by the discovery of a new mechanism reaction called “conversion reaction” [POI 01] which causes the breakage of bonds. According to this new mechanism, the electrochemical reduction of a binary oxide (CoO) by lithium forms a composite electrode formed from nanoparticles of metallic Co inserted into a Li_2O matrix which, due to its nanometric character, can be reduced during recharging. The reversible change from Co^{2+} to Co is associated with the absorption/desorption of two Li by 3D metal (instead of a maximum of one for insertion reactions) facilitating access to high capacity electrode materials. This surprising reactivity, previously unknown, proved universal, taking place regardless of the nature of the 3D metal or anion (F, O, S, N, P, etc.) with the possibility of adjusting: (1) the capacity of the electrode material which can reach up to 6 Li with 3D metals $(NiP_2 + 6Li^+ + 6e^- \rightarrow 2Li_3P + Ni)$ or even (2) the redox potential which can vary from 0.4 V to 3 V by increasing the ionicity of the MX bond. Thus, FeF_2 phases were studied as positive electrodes. Despite these improved capacities and good cyclability, it should be noted that unlike the previous technologies based on $LiFePO_4$ or Si, Li-ion systems with a conversion electrode are still under development due to the difficulties found with their energetic efficiency, which does not exceed 70%.

All the developments described above form the Li-ion technology of today, which, due to its assembly flexibility and performance, (~210 Wh/kg and ~800 Wh/L) which has doubled in 20 years, have conquered several markets. However, with regard to the evolution of this technology, we must ensure that it is also a success for electronic vehicles, hence the need to identify the critical points for this application.

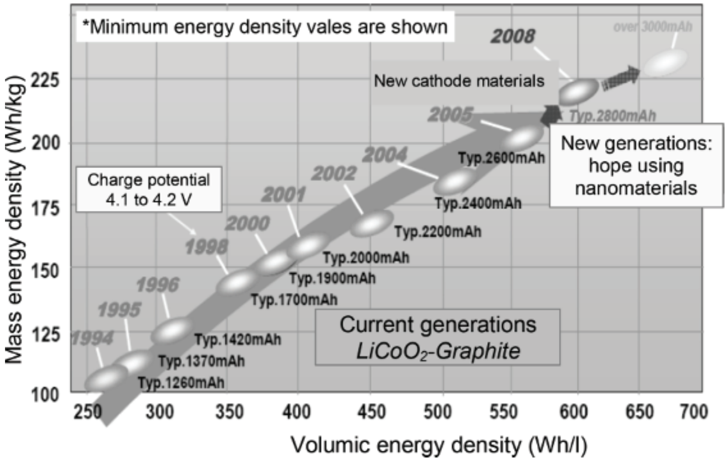


Figure 1.4. *Evolution of Li-ion technology since it was launched on the market*

1.2. Supercapacitors: recent developments

As for supercapacitors, as previously mentioned, they can deliver or recover large power peaks. However, they do have an energy density much lower than that of batteries [SIM 08]. The main challenge in this field is to increase the energy density of these systems, while maintaining the exceptional power performances. The energy E (J) given by the relation $E=1/2\ C.V^2$ where C is the capacity (F) and V is the voltage, there are several possible strategies to increase the energy density.

One line of research widely developed in the literature involves taking advantage of the different existing structural forms of carbon (Figure 1.5) to increase the capacity of supercapacitors by developing porous carbon structures whose pore size is best suited to electrolyte ions thus optimizing the capacity.

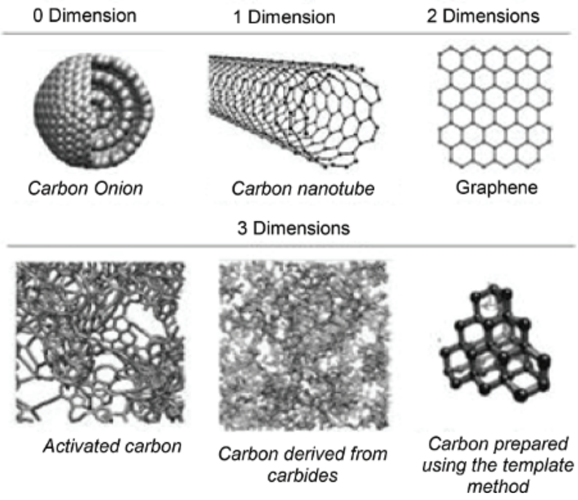


Figure 1.5. *The different carbon forms used in supercapacitors, from 1 to 3 dimensions [SIM 13] (source: Account for Chemical Research)*

Another strategy is to prepare pseudocapacitive materials by carbon replacement to improve capacity through redox surface reactions [SIM 08]. This can also be achieved by adding electroactive redox functional groups to the carbon surface [POG 12]. Here the challenge is to preserve the lifespan and find materials that function in an organic environment. Increasing the operating voltage also improves power and energy. Its aim, common with batteries, is to develop electrolytes with the highest possible electrochemical stability while maintaining sufficient ionic conductivity.

A final approach involves developing hybrid systems, which combine a battery electrode with a positive supercapacitor electrode. This idea is attractive as it increases both the capacity and voltage by carefully choosing materials for electrode. In practice, we come across several challenges including balancing of electrodes, limited lifespan of electrodes in batteries or even power limitations of these electrodes.

Figure 1.6 summarizes the evolution of the energy density of ultracapacitors over time according to the active materials used. We can see that the increase in the system's energy density requires the use of organic electrolytes. Hybrid systems are also of great interest but we must not forget that in the latter case, the increasing performance is usually done at the expense of power and cyclability, which are limited by the faradaic electrode.

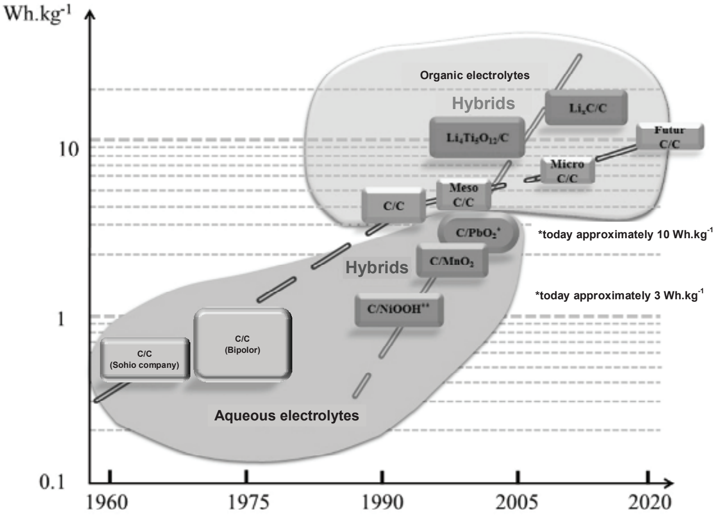


Figure 1.6. *Evolution of energy density of superapacitors over time, according to the different active materials used (source: l'Actualité Chimique)*

After having reviewed the state of the art and established the platform of knowledge required to appreciate the scientific challenges of this domain, we can now explain the logic, ambition and innovative nature of the RS2E's scientific program and reveal to the reader what we mean by research areas such as "Advanced Li-ion", "Eco-compatible storage", "New chemistries", "Smart materials" and "Capacitive storage".