Electrochemical battery managements and applications

Daniel Chatroux

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The Power Point Presentation will be available after the conference.

Abstract

This presentation situates electrochemical accumulators compared to other chemical energy storage. The performances of the different available technologies are presented and a focus is done on Lithium ion accumulator performances and management. The evolutions of some large scale applications and of the level of cost for these markets are detailed.

1. Energy storages

Energy storages are characterized by four parameters:

- Gravimetric energy density (Wh/kg)
- Volumetric energy density (Wh/l)
- Efficiency or conversion efficiency (for comparison, efficiency is used for electrochemical accumulators and conversion efficiency is used for fuels)
- Safety behavior

A Joule represents a small quantity of energy, so Wh (3600 J) and kWh (3.6 MJ) are preferred in this domain.

It's interesting to compare some energy storages and to give order of magnitudes:

Energy storage	Gravimetric energy density (Wh/kg)	Volumetric energy density (Wh/l)	Efficiency or conversion efficiency	Safety behavior and risks
Hydrogen	33 000	2.75 (gas -1bar) 2100 (liquid)	50 % (fuel cell)	Explosion
Gasoline Diesel	13 000 12 400	9 800 10 500	15 to 40 % (combustion engine efficiency curves)	Fast combustion, some explosion risks with gasoline
Wood	4 000	1600-2000	15 to 40 %	Slow combustion
Electrochemical Accumulators	40 to 200	70 to 300	80 to 95%	Fast combustion, low explosion risk, electric risk

Hydrogen has a very good gravimetric energy density but a very poor volumetric one in standard pressure and temperature condition. Pressure or liquid storages (below -253°C) are necessary for hydrogen storage.

Fuel cell provides around 50% of conversion efficiency. Efficiency has a low dependence of level of power. The efficiency is dependent of auxiliaries 'management, especially for low power requirements.

Gasoline provides high gravimetric and volumetric energy density with an easy management because it is a liquid chemical storage. Conversion efficiency may be higher than 30-35 % at high power, but is lower at low charge. Risks are related with ignition temperature point. So, risks are more important with gasoline than for diesel.

Chemical risks are linked to energy level but are very dependent of kinetic. Wood provides a high level of energy (4 kWh/kg) with low risk because his combustion with air is slow.

Electrochemical storage with accumulators provides a very good storage efficiency, near 100% for Lithium ones, but with poor gravimetric and volumetric density.

Hybrid vehicles may combine gasoline engine in high charge (high torque) at lower speed rotation mode (or stop mode) to provide higher efficiency and a battery to provides an additional power if an acceleration is required [1].

2. Electrochemical accumulators

2.1. Accumulators supplier specifications for different technologies

The document [2] indicates the level of performance specified by the suppliers for different technologies of electro-chemical accumulators.

	Lead acid	NiCd	NimH	ZEBRA	LiFePO4 Iron phosphate Li-ion	Li ion **(1)**	Li Polymer
Gravimetric energy (Wh/kg)	30-50	45-80	60-110	120	120-140	150-190	150-190
Energy density (Wh/l)	75-120	80-150	220-330	180	190-220	220-330	220-330
Power density **(2)** (W/kg)	up to 700		up to 900	200	up to 800 **(3)**	up to 1500	up to 250
Number of cycles	400-600**(1)** 1200**(2)**	2000	1500	800	>2000	500-1000	200-300
Self discharge per month	5%	20%	30% **(4)**	12 % per day **(5)**	5% **(6)**	10%	10%
Nominal voltage	2V	1,2V	1,2V	2,6 V	3,2V	3,6V	3,7V

	Lead acid	NiCd	NimH	ZEBRA	LiFePO4	Li ion **(1)**	Li Polymer
Temperature range	-20°C +60° C	-40°C +60° C	-20°C +60° C	-40°C +50° C	0°C +45°C (charge) -20°C +60°C (discharge)	-20°C +60°C **(7)**	0°C +60°C
Advantages	Cost	Reliability, low tempe rature	Good energy density (Wh/l)	Good energy density (Wh/l), number of cycles	Good energy density (Wh/l), safety, cost, number of cycles	Excellent energy and power	Thin batteries are possible
Disadvantag es	Poor energy instantaneous death	Low energy, toxicity	Raw material cost **(8)**, temperature behavior	Power limitation, energy losses	Low temp erature charge **(7)**	Security for b ig accumulator cost **(7)**	Low temperature performance cost **(7)**
Cost estimation **(9)** (€/kWh)	200 to 250 (a) 200 (b)	600	1500 to 2000	800 to 900	1000 to 1800	2000	1500 to 2000

(a) sealed (b) tubular

This synthesis is a good overview with a lot of information.
The table can be completed with new results or some precisions:

(1) Li ion has several main families with different behaviors; this will be presented in this document

(2) For all accumulators, there are energy versions optimized for energy with less power, and power versions with less energy density,

(3) The A123Systems company designed LiFePO4 cells for electric tools at 2 600 W/kg (for 10 s discharge) and Saft VL10VFe cell have 5 kW/kg continuous dis-charge,

(4) For high quality NimH, the initial self-discharge is high (30% for example) but decrease a lot in a second phase. We measure that a NimH battery of a Vectrix scooter from GP is only half discharged after more than one year of storage

(5) ZEBRA is a high temperature accumulator with high temperature conditioning. Resistors are used to maintain the temperature in storage. Per year, the electricity needed to warm the accumulators in storage increases significantly the electricity bill

(6) For example, a 26650 A123Systems cell have low discharge after more than three years of storage.

(7) As for LiFePO4, most of Lithium ion technologies are adapted for discharge at negative temperatures, but for charge the minimum temperature is around 0°C. The charge below 0°C is critical. The recommendations of the supplier have to be followed. In real use, it is possible to charge at negative temperatures but with lower current. The low temperature charge has a great impact on the number of cycles. Specific tests on this point may be necessary according the applications requirements.

(8) Lanthanum, a rare earth, is used in non-plugin Hydrid cars

(9) Since 2005, the battery costs have decreased. Cost is very dependent of market. In 2015, an example of good quality LiFePO4 Lithium ion module is 1000€/kWh. Accumulators (cells) for computers cost is around 200-300€/kWh.

2.2. Aqueous batteries

The three main aqueous technologies (lead acid, NiCd and NimH) have a lot of parasitic electrochemical reactions in parallel with the main one. These parasitic reactions have different electrochemical potentials, and so have different chemical kinetics depending of the accumulator voltage.

One first impact of these parasitic reactions is self-discharge phenomenon.

At nominal voltage, these parasitic reactions are still active. It is a consumption of energy with a discharge rate of some weeks or months. This is a disadvantage of aqueous electrochemical accumulators.

The second impact is intrinsic voltage clamping at the end of the charge.

For example, at the end of the charge for a lead acid battery, the main electrochemical reaction is finished, so the voltage drops up to the water dissociation voltage. If the charge goes on, the current generates heat and gas from the water dissociation but the voltage stay the same: it is the voltage clamping behavior of the accumulator cell which can be simulated by a “zener diode”, as in the figure 1.

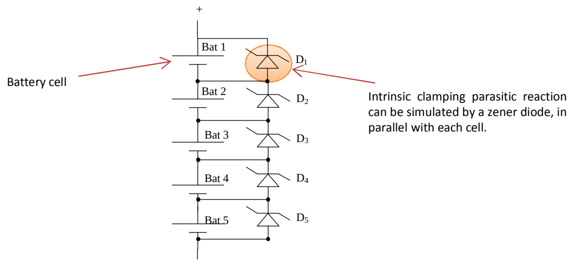

Figure 1: parasitic reactions simulation in aqueous batteries technologies

This parasitic reaction is an advantage when charging multiple cells connected in series (a battery of electrochemical accumulators). As all cells are not identical, or not in the same state of charge, a cell will end its charge first. As other cells are not fully charged, the current is maintained to charge these cells. The first cell stays fully charged and produce heat and water dissociation: it’s a natural balancing that allows the end of charge for other cells.

Thanks to the parasitic reaction, there is an intrinsic voltage clamping with the possibility to balance the different accumulators in series only by the prolongation of the charging phase without any additional electronic circuit.

However, balancing phase duration has to be minimized because of its great impact on battery life time and charge efficiency.

2.3. Lithium ions batteries

The composition of Lithium ion accumulator is for standard design: a copper foil with graphite layers (the two faces) for the negative electrode, a separator with electrolyte impregnation, a positive electrode with aluminum foil and layers of a positive active material. The electrochemical reaction is based on Lithium ion insertion (intercalation) in graphite or in positive active material for charge and discharge. The reaction mechanism of lithium-ion batteries is presented in the Figure 2. The positive and negative materials usually have a layered structure to facilitate lithium ions insertion. The main effect of the charge and discharge reaction is the back and forth movement of lithium ions between the electrodes, matched by a corresponding flow of electrons in the external circuit.

This electrochemical process is sometimes called a “rocking-chair” mechanism.

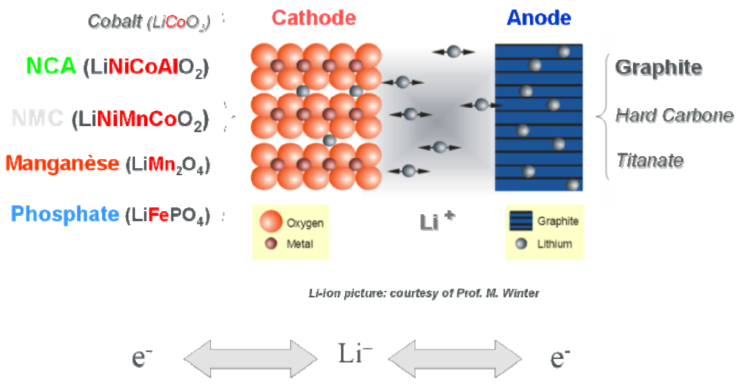

Figure 2: Lithium ion technologies

The Lithium ion electrochemistry is a dry one.

Because water is a pollutant in this chemistry, the accumulators are built in dry room. The need of dry room has an important impact on accumulator process cost.

Except long term ageing, there is no parasitic reaction, so:

- No discharge current
  - **Good quality Lithium ion accumulator stores energy for years**. It’s a great advantage in the application to get the battery charged. For example, a portative electric tool may operate after some months of storage.
- No intrinsic voltage clamping reaction
  - There is no natural balancing, **minimum and maximum voltage detections are required to cut the charge or discharge current and an external electronic balancing circuit is necessary** when accumulators are connected in series

2.4. Lithium ion battery management specificity

For safety reason and to provide a high lifetime, the voltage of each accumulator is monitored. Charge has to be stopped when one accumulator reach the maximum voltage specified. Discharge has to be stopped when the first accumulator reach the minimum specified voltage.

For balancing, good quality Lithium ion accumulators are nearly perfect. Leakage currents are very low, so unbalancing is a very slow mechanism. It’s not necessary to balance after each charge. For example, after a fast charge the unbalancing may be 0.4%. It’s only 400m for a 100 km range. But it’s a cumulative phenomenon so a balancing circuit is necessary. A standard dissipative circuit is adapted low cost solution. At the end of the charge, the accumulators with higher voltages are discharges at the same level as lower ones, before a cycle of charge. After some cycles balance of all the accumulators is provided.

Specific circuits are designed for balancing. Other designs used linked microcontrollers for each level of accumulators in series.

Balancing circuit is necessary because of very small differences of leakage currents or faradic efficiencies between accumulators in series.

The goal of balancing circuit is not to manage the dispersion of accumulators in series. The capacity of a series of accumulator is the capacity of the lower. So an additional circuit to manage the dispersion of accumulators in series seems to be interesting. For this function power electronic is necessary. Because of low voltage, high efficiency is difficult. And at the end, the cost of the function is too high, and production improvements allow to limits the dispersion when high volume occurs.

In our realization, balancing current is 250 mA with a 1W resistor. In automotive batteries, the balancing current may be as low as 10 mA for cost reason. A single PCB manages around hundred stages of accumulators in series. With 10 mA an external MOSFET is not necessary. The power may be dissipated on a single cart.

Because of low power, it is not possible to balance the battery after production, if the accumulators are not at the same state of charge. With 10 mA circuit, an unbalance of 1Ah needs 100 hours to be corrected! Accumulators with the same state of charge may be assembled. It’s not a problem, because when accumulators are processed, it’s necessary to form the accumulators with some charge and discharge cycles. So capacity is measured and the last charge may be finished exactly at the same state of charge; without over costs.

Another important specificity of Lithium ion batteries is short circuit current level.

Because of low internal resistance, Lithium ion batteries are adapted for fast charge and discharge but the disadvantage is the level of short circuit current for example three or five times more important than other technologies. A small LiFePO4 cell for electric tool with a capacitance of 2.5 Ah has a short circuit current of 350A!

With these cells a 40Ah pack has a 5.6 kA short circuit current.

Short circuit current levels are higher with Lithium ion batteries.

This parameter is important for fuse choice.

2.5. Differences between aqueous and lithium ion technologies

The faradic efficiency is the ratio between the charge extracted from the battery in discharge compared and the charge injected.

For aqueous battery, the faradic efficiency is about 90% because of the loss of electrons in parasitic reaction and in the overcharge during the balancing phase.

For Lithium accumulator, the Faradic efficiency is near 100%.

The energy efficiency takes into account the faradic efficiency and the energy losses in the serial resistance: it’s the reason why the energy efficiency is directly linked with the levels of charge and discharge currents.
For lithium accumulator, energy efficiency is higher than 90-95%, typically 10 to 20% higher than aqueous ones.

End of charge detection is very interesting for the applications, especially for electric vehicle one.

NiCd and NimH end of charge detections are well known for room temperature and around one hour charge. At the end of the charge, the voltage rise first and decrease, and the temperature rises. Chargers used a combination of negative dV/dt and temperature rise detections. At higher temperature, after a ride when the battery is hot, this mechanism disappeared. Voltage charging curve is nearly flat, and it's difficult to discriminate the end of charge with the only temperature evolution. An existing solution is cooling the battery in a first phase, before starting the charge but it may a loss of time. Another solution is charge counter to inject an amount of charge correlated to the discharge. This solution is not perfect because faradic efficiency is not 100% and the battery managing systems has to estimate the charge losses.

Compared to the aqueous technologies, lithium ion end of charge may be perfectly detected by the voltage of the accumulators.

The advantages and disadvantages of accumulator technologies are the following:

Parameter	Aqueous technologies	Lithium ion
Balancing	☺	☹
End of charge detection	☹	☺
Self-discharge	☹	☺☺
Energy	☹	☺☺
Safety	☺	☹ or ☹☹
Hydrogen risk	☹	☺
Temperature range	☺	☹
Cost	Constant	Decrease

2.6. Different Lithium ion technologies

There are different Lithium-ion technologies with different energy and safety performances.

The main differences are due to positive material:

Cobalt oxide is the oldest material. It's a very reactive one. In case of failure or abusive conditions, dissociation occurs at a low level of temperature and oxygen reacts with combustible materials of the accumulator. Cobalt has a high cost.

NCA (Nickel Cobalt Aluminum oxide) is reactive. It provides a level of energy as high as 200 Wh/kg. Calendar aging is good. TESLA used PANASONIC accumulators of this technology.

Manganese oxide is a low cost material but a poor calendar aging. Energy is high. Number of charge discharge cycles is low.

NMC (Nickel Manganese Cobalt oxide) performances depend on the percentage of Co and Ni. Energy is high. Safety behavior and cost depend of Cobalt percentage. Now most accumulators for laptops, electric tools and vehicles are NMC ones.

Iron Phosphate is the safest material, because dissociation is not possible. The energy is lower because voltage and capacity are lower. The voltage curve is near flat at 3.3V. The end of charge is 3.6V. The end of discharge is 2V, but there is a very low energy between 2V and 3V. So this accumulator technology can provide a stable voltage with only +/-10% variation. It's an advantage for power electronic dimensioning. Iron phosphate has good calendar life and provides a high number of cycles. Iron phosphate high volume accumulators are designed in China for automotive or buses applications.

Positive and negative material performances are:

Material		Charge (mAh/g)	Nominal voltage (V vs. Li)	Energy density (Wh/kg)	Advantages	Drawbacks
$LiCoO_2$	LCO	150	3.9	585	High energy	Cost - unstable
$LiNiMnCoO_2$	NMC	160-180	3.85	615-695	High energy - stable	Cost
$LiNiCoAlO_2$	NCA	190-200	3.75	710-750	The highest energy	unstable
$LiFePO_4$	LFP	150-160	3.45	515-550	Low cost- safe	Lowest energy
$LiMn_2O_4$	LMO	105-120	4.1	430-490	Very low cost- safe	Low energy – low calendar life at high temperature
Graphite	G	330-360	0.15	NA	Low cost – high energy	Charge at low temperature
$Li_4Ti_5O_{12}$	LTO	150-165	1.55	NA	High power, calendar life, safe	Low energy
Silicium	Si/C - Si	500-2000	0.4	NA	Energy density	Very low number of cycle
Hard carbon	HC	200-300	0.4	NA	High power	Low energy

2.7. Security

The security of a battery pack is a system problem with a lot of parameters:

- Chemistry (thermal stability of positive material and negative material)
- Solvent (combustible in most cases)

- Separator (separator fusion can stop ion diffusion in case of over-temperature (if the voltage applied is not too high)
- Internal fuse or CTP (Polyswitch®) or pressure mechanical switch in the cell can open the circuit (if the voltage applied is not too high).
- Cells (accumulator) design
- Module design for example distance between the cells to avoid thermal runaway propagation
- Pack design (fire resistant enclosure, impact absorption, cooling to avoid thermal runaway propagation, fire resistant polymer, exhaust pipe for gases)
- Electronic of battery management system to keep the cells in the voltage and temperature limitations, MOSFET to open the circuit for low voltage packs
- Electromechanical architecture (vacuum or gas contactor to open the circuit, DC current breaker, fuses able to cut the very high level or short circuit current

The security of a battery pack is a combination of all these aspects, with a lot of different solutions and choices.

In laboratory, the standard solution to extinguish a battery fire is neutral gas injection to inert the volume. For car fires, the firefighters uses water pulverization and inert the battery pack with water. The water is very efficient for cooling and stopping the thermal runaway.

3. Application and associated costs in the different markets

3.1. Main applications for lead-acid, NiCd, NimH

A first market for lead-acid battery is the thermal engine start, with the evolution to stop and start applications. In this application, the thermal range of lead acid battery is an advantage.

Another market is energy storage for UPS (uninterruptible power supply) or telecom centrals.

NiCd batteries are used in aircraft to start the engines and for safety power supply. The other important market is railway application. Now there are batteries in the locomotives and nearly each cars. NiCd has a large temperature range and a good lifetime in these applications, but with maintenance needs (water adding).

Nimh batteries are generally used in non-plug-in hybrid cars, and it is a small size designed for high power (1.2 kWh, 20 kW, for Toyota Prius). In this application, the battery is used mainly in micro-cycle mode (5%) in a small allowed window of charge (20%) [1]. Millions of batteries were manufactured.

3.2. Batteries technologies for electric or plug-in hybrid vehicles

Electric vehicles of the 90's-00's were designed with the batteries technologies of that time. With aqueous solutions (lead acid, NiCd, NimH) the energy storage provide less than one hour of continuous driving, and these technologies are not adapted for these rates of discharge, for a discharge in one hour or less.

The impacts measured one vehicle are:

- a smaller energy storage than expected,
- a decreasing of lifetime,
- a kilometric cost tree times more important than gasoline engine ones [3]

The gravimetric energy measured on vehicles is typically half than expected [4]:

	Lead acid	**NiCd**	**NimH**	**ZEBRA**	**LiFePO4** Iron phosphate Li-ion	**Li ion**	**Li Polymer**
Specified gravimetric energy (Wh/kg	30-50	45-80	60-110	120	120-140	150-190	150-190
Measured pack gravimetric energy (Wh/kg)	20	30	40	?	70-80	100 ?	?

Aqueous electrochemical technologies (lead acid, NiCd, NimH) are not adapted for electric or plug-in hybrid vehicles.

NimH is used on millions of hybrid vehicle (non-plug-in ones), because for this application battery is only used for micro-cycles [1]

Lithium batteries are adapted for electric vehicles or plug-in hybrid ones:

- With the same weight, twice or three times more energy is provided
- Charge and discharge may be less than an hour without important loss of energy
- The battery has a good efficiency between 95 and 90%, depending of discharge rate
- End of charge detection is very easy and reliable

3.3. Lithium ion big markets

The first market for Lithium-ion accumulators is laptop. The standard accumulator size is 18650: a cylinder of 18mm of diameter and 65 mm long. The main parameter for this market is laptop autonomy so Cobalt oxide has been used first and now the chemistry are the most energetic ones (NCA, NMC). To provide security, the quality level of accumulator must be high. There may be internal protection in the accumulator (CTP, mechanical switch). A polymer closed enclosure protects the accumulators and local electronic. This electronic manage the battery and is able to open the circuit in case of short circuit at the output of the battery, or in case of risk of overcharge. In this application the charge is for example one hour and the discharge is a three hours.

The laptop battery of Figure 3 store 60 Wh for 388 g. The energy densities are 154 Wh/kg and 310 Wh/l. The final price for battery replacement is 30€. So, the level of price for the customer is 500€/kWh

Figure 3: laptop battery

Figure 4: different tools with the same battery

The second market for Lithium-ion accumulators is electric tools. Due to Lithium ion technologies, electric tool is in fast mutation. Five years ago, NimH and NiCd were used on standard electric tools. Lithium-ion, for example LiFePO4 was used for professional applications. Now, electric tools are Lithium ion ones from low cost to professional ones. The manufacturer standardizes a pack design for different tools of his range. Most accumulators are NMC ones. There are two standard formats 18650 (as laptop) and 26650: a cylinder of 26 mm of diameter and 65 mm long. In this application, the charge and discharge may be done in less than one hour. For example, the charge duration may be 20 mn.

Figure 5: standard format for electric tools

3.4. Application of Lithium ion for electric cars market

The last and new market is car and other vehicles applications. It is an emerging market with first interesting vehicles and different approaches. There is not any accumulator dedicated for electric car manufactured by quantity. There is not standard dimension for accumulators for this market.

Tesla approach is to design a high acceleration and speed car with a large range with thousands of laptop standard accumulators. Because of high volume production, the cost is low, for example 200€/kWh, the energy density and the level of quality are high. The energy in each accumulator is limited by the small volume, so it is possible to limit thermal runaway propagation in the pack by specific designs: air space between accumulators or water cooling pipe between the accumulators. Battery pack is very thin and is a part of the vehicle mechanical structure [5]. As said before, the 500 km range is possible but with limited speed around 90 km/h.

Figure 6: TESLA model S battery concept

Figure 7: BMW i3 battery

Figure 8: accumulator and module

Renault Zoé, BMW i3 are designed with specific design of accumulators with a specific size of accumulator. These cars provide a good level of customer services. The ranges are now limited to 150 km (with room temperature and 1/3 less in winter) but the second generations are announced twice the initial range.

Electric car panorama grows quickly and constantly [6]:

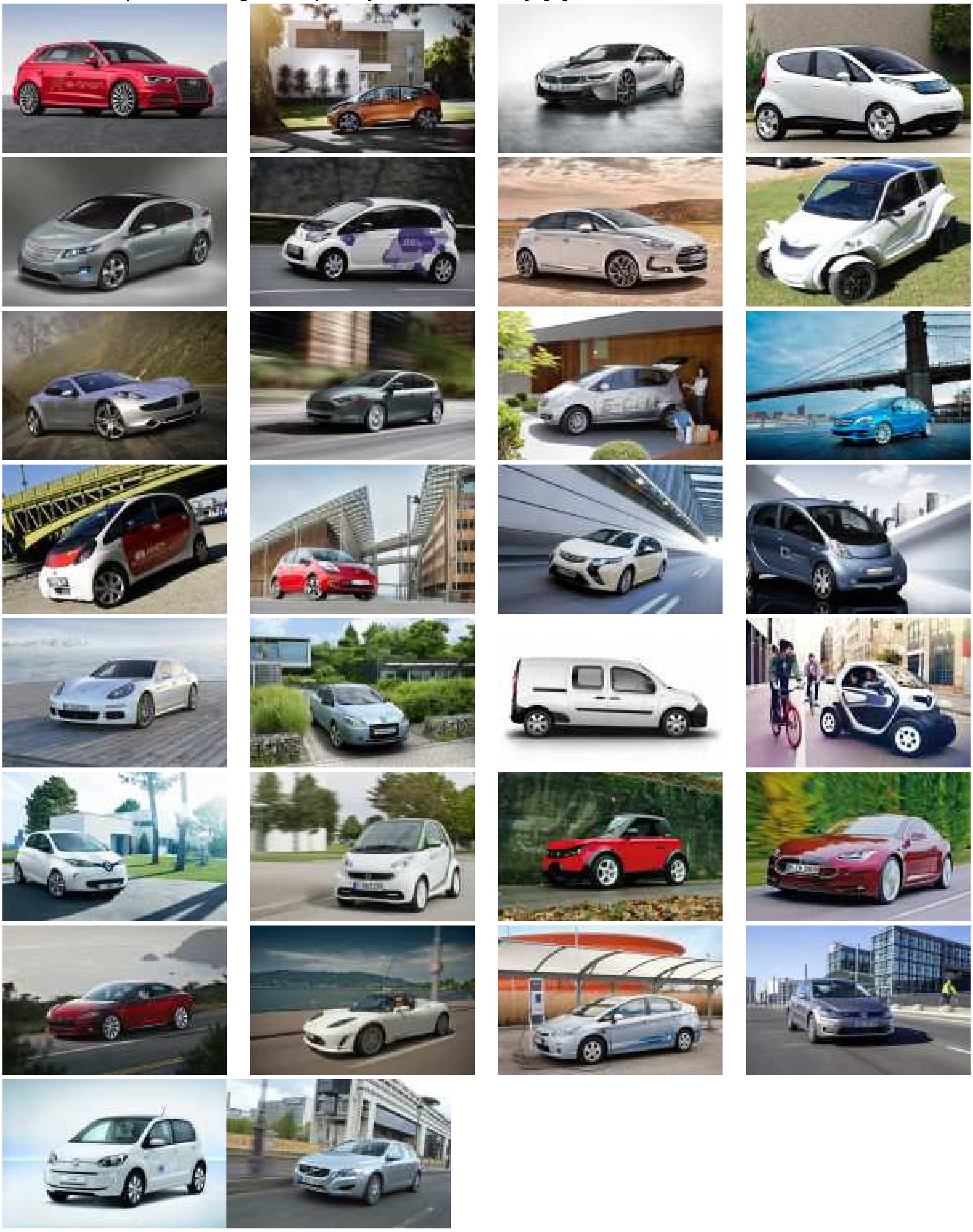

Figure 9: Electric or plug-in vehicles: Audi, BMW, Bolloré , Chevrolet, Citroën, Courb, Fisker, Ford, Mercedes, Mitsubishi ,Nissan, Opel, Peugeot, Porsche, Renault ,Smart ,Tazzari, Tesla, Toyota , Volkswagen, Volvo

4. Conclusion

Lead acid and NiCd technologies are well adapted for engine starting or energy storage for applications where uninterruptible power supply is necessary.

Laptop, cellular phones and tablet use Lithium ion battery to provide the autonomy. The mutation of electric tools has just been done from NiCd and NimH to Lithium ion. The improvement is very interesting with no self-discharge and autonomy improvement with an affordable cost.

Lead acid, NiCd, and NimH have too poor real performances on electric vehicle to be a viable solution. The mutation to Lithium allows good vehicle performances, a sufficient level of range, the possibility of promising improvement and good cost perspectives. We are in this mutation phase.

A large accumulator should be less expensive than twenty small ones, but because of the mass production of small accumulators, the level of cost is lower. The association of thousands of them is used by some manufacturers, for module production or car production. It should be only a transition phase of starting of the electric and hybrid vehicle market.

Range is presented as the main problem for electric vehicle. In 2009, we gave a presentation to indicate that the main brake to electric and plug-in hybrid vehicles was the cost of battery storage used. In fact, the battery cost was three times too expensive. Five years later, the level of cost seems to be competitive and an important progress margin is in front of us..

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