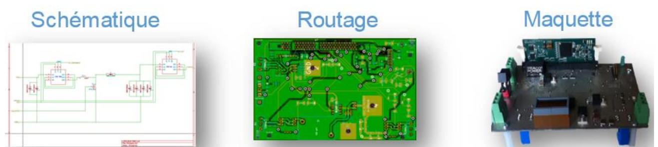
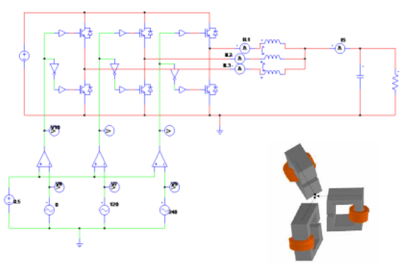
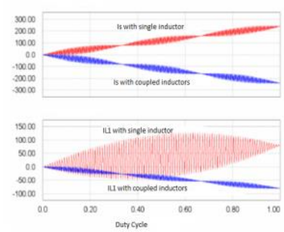
Electrochemical batteries management and applications

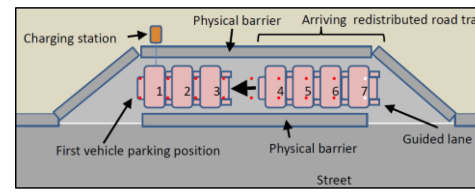
Daniel Chatroux



Test d'un convertisseur BOOST 175W régulé par DSP – synthèse du correcteur numérique réalisé avec la bibliothèque SFRA de Texas







ELECTROCHEMICAL BATTERIES MANAGEMENT AND APPLICATIONS

2/11/2016 - 4/11/2016 | ESARS ITEC 2016 | Daniel Chatroux

AGENDA

- Criteria of choice for energy storages and some orders of magnitude
- Overview of the different technologies of electrochemical accumulators
- Aqueous batteries (Lead acid, NiCd, NimH)

  => Results on electric vehicles in the 1990’s
- Lithium ion technologies

  => Security of Lithium-ion battery packs
- Markets for the different technologies

  => Overview of electric and plug-in vehicles
- Future trends and conclusion

CRITERIA FOR ENERGY STORAGES

Main parameters :

- Gravimetric energy (Wh/kg)
- Volumetric energy (Wh/l)
- Efficiency
- Safety

Unities :

Energy unit is the Joule (1 Watt for a duration of 1 second)
In electrochemistry domain, higher units are preferred:

- Wh (3600 J)
- kWh (3.6 MJ)

CRITERIA AND ORDERS OF MAGNITUDE FOR DIFFERENT ENERGY STORAGES

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

ELECTROCHEMICAL ACCUMULATORS TECHNOLOGIES

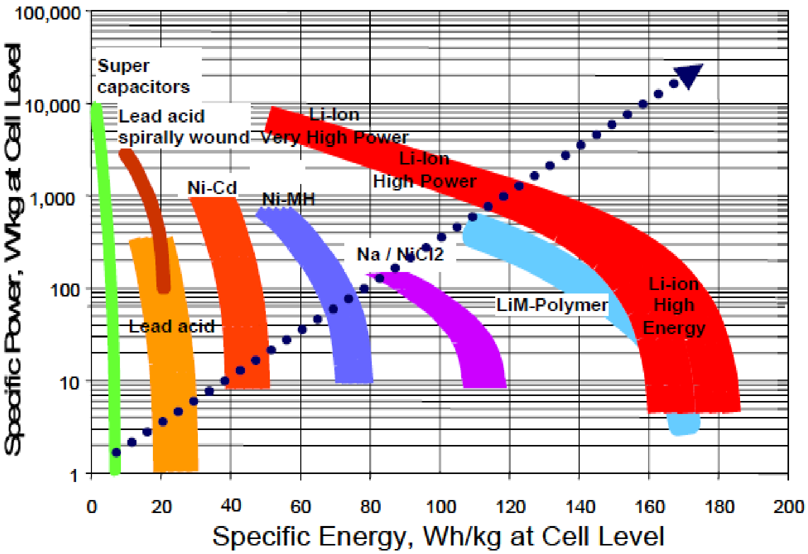
	Lead acid	NiCd	NimH	ZEBRA	LiFePO4 Iron phosphate Li-ion	Li ion (1)	Li Polymer
Gravimetric energy (Wh/kg)	30-50	45-80	60-110	120	120-140	150-190	150-190
Energy density (Wh/l)	75-120	80-150	220-330	180	190-220	220-330	220-330
Power density (2) (W/kg)	up to 70 0		up to 900	200	up to 800 (3)	up to 1500	up to 250
Number of cycles	400-600 (1) 1200(2)	2000	1500	800	>2000	500-1000	200-300
Self discharge pe r 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

ELECTROCHEMICAL ACCUMULATORS TECHNOLOGIES

	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 temp erature	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
Disadvantages	Poor energy instantaneous death	Low energy, toxicity	Raw material cost (8), temperature behavior	Power limitation, energy losses	Low temp erature charge (7)	Security for big accumulators cost (7)	Low temperature performance cost (7)
Cost estimation (€/kWh)	200 to 250 (a) 200 (b)	600	1500 to 2000	800 to 900	1000 to 1800	2000	1500 to 2000

TEMPORAL CRITERIA FOR STORAGE CHOICE

Ragone diagram:
Storage in the axes:
gravimetric energy,
gravimetric power.



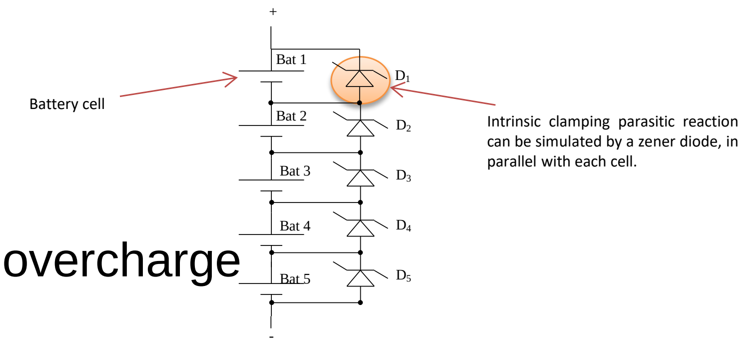
Another presentation is time parameter.
Storage selection can be done with time criteria.

- < 100 ms => electrochemical capacitor
- Some seconds to some minutes => ultracapacitors
- Some minutes to one or two hours => batteries of electrochemical accumulators
- More than two hours => genset, fuel cells

To compare different technologies or size of batteries a good parameter is **RC/V**

AQUEOUS ELECTROCHEMICAL ACCUMULATORS

Aqueous technologies : Lead acid, NiCd, NimH,
Electrolyte made of water and sulfurous acid or KOH
A lot of parasitic reactions: water electrolyze,…



Disadvantages :

- Self discharge
- Water loses
- Waste of energy, lower efficiency, especially if overcharge
- End of charge cooling for large batteries
- Difficulty of the end of charge detection
  For NimH, negative dV/dt and temperature rise is adapted for fast charge at ambient temperature
- Difficulty to have a precise gauge

Advantages :

- Intrinsic clamping
- End of charge balancing only done by overcharge
- No electronic for each stage of accumulators in series

RESULTS ON ELECTRIC VEHICLES IN THE 1990'S

For aqueous technologies, the energy performances are limited. The energy of the pack allows only less than one hour drive in normal use.
But the batteries technologies are adapted only for slow discharge, for example, a three hours discharge specification.
On vehicle, energy delivery is lower than specified, for example half of the specification.
Aqueous technologies are not adapted for electric vehicles.
For lithium batteries, there's only the additional weight of the mechanic of the pack.

	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 ?	?

LITHIUM ION REACTION

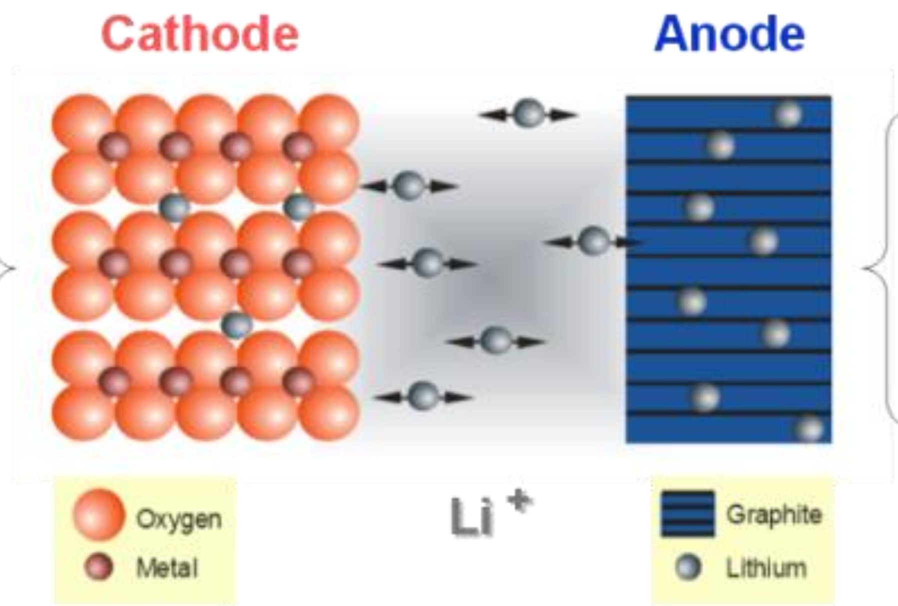
Cobalt ($LiCoO_2$)

NCA ($LiNiCoAlO_2$)

NMC ($LiNiMnCoO_2$)

Manganèse ($LiMn_2O_4$)

Phosphate ($LiFePO_4$)



Graphite

Hard Carbone

Titanate

Li-ion picture: courtesy of Prof. M. Winter

$$e^- \longleftrightarrow Li^+ \longleftrightarrow e^-$$

- Only one electrochemical reaction
- Process with deposition of layers on metallic sheets
- Low or very low internal resistance => adapted for fast charge and discharge

LITHIUM-ION ELECTROCHEMICAL ACCUMULATORS

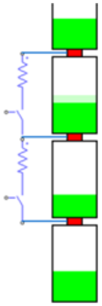
No parasitic electrochemical reaction

Advantages :

- Energy storage for months or years
- End of charge detection is very easy
- Faradic efficiency near 100% (discharge capacitance / charge)
- Gauge with voltage measurement or coulombmetry (charge counting)

Disadvantages:

- Overvoltage and undervoltage detection is necessary for each stages of accumulators in series
- Electronic for balancing for each stages



Other specificities:

- Process is done in dry room (expensive)
- Electrolyte filling is done under inert gas
- Balancing is necessary but not at each cycle
- The choice of Lithium ion chemistry is a compromise between energy, life time, number of cycle, power, security, cost
- Low internal resistance
- Charge in some minutes are possible
- High level of short circuit current
- Efficiency as high as 95% are possible

LITHIUM-ION ELECTROCHEMICAL ACCUMULATORS

Other specificities :

- Graphite electrode is limiting because of instability in the electrolyte, but protected by the SEI (like aluminum)
- Lithium metal deposition potential is near graphite one.
  => risk at low temperature below 0°C
  => no fast charge
  => life time impact
- Titanate hasn't these limits
  => adapted for fast charge
  => adapted for low temperature
  => high number of cycles
  But lower energy (one volt less)
- Discharge at low temperature => loss of energy. Heating or keep in temperature.
- Only two standard formats:
  18650 (Laptop and electric tools)
  26650 (power tools)

Bluecar of Bolloré is a Lithium metal electrochemistry and not a Lithium-ion one.
To avoid dendrite problem a full solid polymer electrolyte is used.
For polymer electrolyte conduction, battery is keep hot (60°C).

COMPARISON OF AQUEOUS AND LITHIUM ION BATTERIES TECHNOLOGIES

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

THE DIFFERENT LITHIUM-ION CHEMISTRIES

Cobalt oxide

- The oldest
- Very reactive – Oxide decomposition with oxygen release
- Was used on laptop by Japanese
- Used on Boeing
- Cobalt cost

Nickel Cobalt Aluminum (NCA)

- SAFT
- Panasonic accumulators of TESLA (18650 format)
- Very reactive
- Good life time and high number of cycles
- Cobalt cost

Nickel Manganese Cobalt (NMC)

- Reactivity, cost, life time and number of cycle depending of the percentages of Nickel and Cobalt (from 1/3, 1/3, 1/3 up to 5% 90% 5%)

Manganese oxide

- Lowest cost material
- Low reactivity
- Low life time at high temperature
- Low number of cycles

THE DIFFERENT LITHIUM-ION CHEMISTRIES

Iron phosphate

- Safest chemistry
- Good life time
- High number of cycle
- Low cost raw material
- Nano-structuration and doping of phosphate is necessary
- 3,3V plateau from 10% to 90% of state of charge
- Lower energy
- Can be used to 3,3V +/- 10% (3V – 3,3V – 3,6V)
- Overvoltage tolerance => 4,5V
- Matrix of accumulators with fuses or electronics for defect tolerance developed in CEA for five years

The safety of the chemistry allows:

- High capacity accumulators mainly in China (hundreds of Ah) with moderate energy density (safety)
- Used by Valence for ten years to provide modules to replace lead acid batteries by matrix of 18650 with BMS in an adapted package.
  Replacement or used is made by the customer/integrator.

THE DIFFERENT LITHIUM-ION CHEMISTRIES

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 te mperature
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 cycles
Hard carbon	HC	200-300	0.4	NA	High power	Low energy

SECURITY OF LITHIUM-ION BATTERY PACKS

Electrochemistry of the accumulator is only one link in the security chain
Security is a system approach with a lot of aspects:

- Lithium ion chemistry
- Electrolyte solvent (combustible now), gel electrolyte, polymer
- Separator (fusing to stop ion diffusion at high temperature, ceramic…)
- Internal fuses (CTP or pressure switches)
- Mechanical conception of the cell
- Overpressure protection
- Module conception, cells distance to avoid defect propagation, thermal barrier
- Module electric architecture
- Electric protections of the pack (vacuum or gas relays, high power fuses…)
- Mechanical protection of the packs, fire protection, auto extinguishing polymers...
- Electronic (for laptop MOSFET are used to open the circuit in case of overdischarge, overcharge or internal defect)

THE MAIN MARKETS FOR THE TECHNOLOGIES

Ultracapacitors :
Windmills safety unit
Main characteristics used reliability, temperature range, state of health only by voltage measurement

Lead acid:
Starting of vehicles (temperature range, cost)
Uninterruptible Power Suplies) : low cost/delivered energy, business model of the domain: low financial margin on equipment, high margin on maintenance contract

NiCd: starting, auxiliaries and emergency batteries for planes, auxiliaries and emergency batteries for trains

NimH: hybridation battery of Toyota PRIUS.
Epicycloidal train associated with the two
Electrical machines is a continuous variable transmission to keep the gasoline engine at higher efficiency, at lower speed and high torque. Mainly, NimH battery provide energy for some seconds for reacceleration. Microcycles allows high lifetime with low energy storage cost.

THE MAIN MARKETS FOR THE TECHNOLOGIES

Power tools:
Mutation from NiCd and NimH to Lithium-ion
The battery is now a product to improve the equipment or to use one different equipment
All a tool panel with the same pack for a supplier
Price decrease
Accumulators 18650 and 26650 formats




Laptop computers
18650 format
High performance accumulators and low cost (<300 €/kWh)
High quality mass production

Example:
60 Wh for 388 g
154 Wh/kg
310 Wh/l
30 € for replacement
500€/kWh for the final customer

THE MAIN MARKETS FOR THE TECHNOLOGIES

Smartphones, tablets, games…

Specific pouch cell accumulators for these applications.

Electric vehicle and plug-in hybrid ones

⇒ Thousand of laptop computers accumulators (TESLA), quality and low cost accumulators, know-how for design and assembling with performant cooling and secure design

⇒ Power tools LiFePO4 accumulators (Valence modules, CEA research…)

⇒ Accumulators with specific format. Lower cost for high quantity, emerging market, difficulty for starting, may switch quickly (<10 years)

ELECTRIC AND PLUG-IN VEHICLE PANORAMA

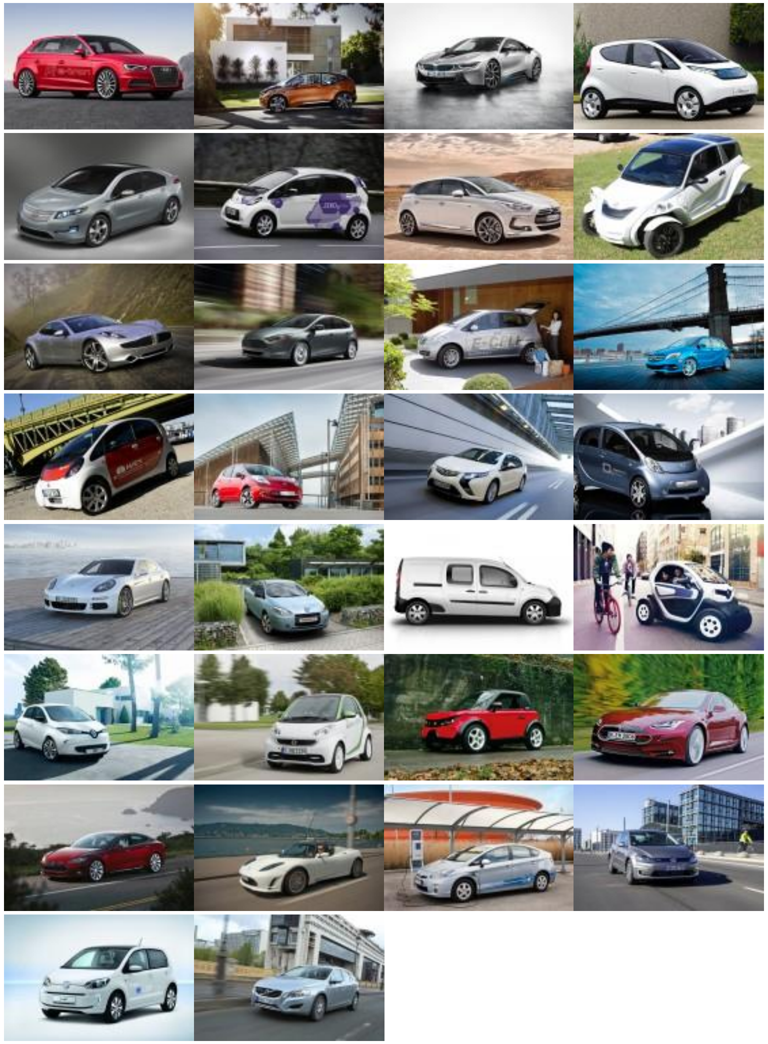


Figure 1 : Electric or plug-in vehicles : Audi, BMW , Bolloré , Chevrolet, Citroën, Courb, Fisker, Ford, Mercedes, Mitsubishi ,Nissan, Opel, Peugeot, Porsche, Renault ,Smart ,Tazzari, Tesla, Toyota , Volkswagen, Volvo

EXAMPLE OF ELECTRIC VEHICLE PROGRESS

ZOE 2013

24 kWh

210 km NEDC

150 km in summer

100 km in winter

ZOE 2017

41 kWh

400 km NEDC

300 km in summer

200 km in winter

- Packs are compatibles. Pack battery Improvements are on cells energy and less volume losses
- Electric cars are well adapted for roads (90 km/h speed limit) or low speed motorway (US), not only for towns

EXAMPLE OF ELECTRIC PLANE

- E-Fan
- Demonstration for international Paris air show Le Bourget opening
- July 10th 2015 “Travelling in the opposite direction to Louis Blériot and powered by lithium-ion batteries, the E-Fan took off from Lydd on the English south coast, completing the 74 kilometers flight east to Calais, France, in around 40 minutes. Flown by test pilot Didier Esteyne, the all-electric plane weighs around 600 kilograms and travelled at an altitude of about 1000 meters (3500 feet)”.
- Lithium-ion Battery: collaboration Airbus-CEA

FUTURE TRENDS AND CONCLUSION

Low quantity of energy in electrochemical accumulators storage

But fast delivery => risk of security, chemical reaction ignition

Aqueous technologies are not adapted for long term storage or fast charge and discharge. So, they are not adapted for electric vehicles

Lithium ion accumulator is a big progress for:

- long term storage,
- energy density,
- fast charge and discharge (some minutes, or tenth of minutes)

Lithium seems to be complicated, but end of detection and gauge are easier.

Lithium ion are adapted for electric vehicles and plug-in hybrid

Electrification of other vehicles is in rapid progress

Market laptop and power tools are very dynamic

- constant cost decrease ,
- constant performances growth

“Moore law” for battery: + 6% / year of energy in the same volume

Different technology in progress and competition (Si, Li-air, solid electrolyte…)

FUTURE TRENDS AND CONCLUSION

Revolution in the applications

Example of very fast mutation: Power tool (in 3 years)

•NiCd / NimH => Lithium

•Lithium pack is a multi tool product (work in autonomy in building site)

•Due to the huge market of laptop computer market, the constant progress of performance and decrease of cost allow commutation of all a application domain to Lithium ion.

For electric or plug-in hybrid vehicles, we are in a transition phase.

Two solution are used :

•Associate thousand of low cost high quality and performance of small standard accumulators with a lot of know-how in the association to provide thermal management, safety and security

•Associate only hundred accumulators in series. The performances, thermal exchange, security and cost are directed linked to the accumulator.
Now a specific product, in low quantity production.
Possibility of higher performances and lower cost when the electric and plug-in hybrid market will start.

FUTURE TRENDS AND CONCLUSION

In aeronautic applications, we see:

- first electric plane demonstrations with limited range
- development of batteries for starting or starting and emergency applications, security is the main challenge
- interest for fuel cells, mainly for the auxiliaries

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