EVS26
Los Angeles, California, May 6-9, 2012

RECENT ADVANCES ON PHOSPHATE, TITANATE AND BIPOLAR LI-ION CELLS FOR µHYBRID, HEV or EV

Florence Fusalba[1], Sébastien Martinet[1],
Sébastien Patoux[1], Séverine Jouanneau[1], Marianne Chami[1], Yvan Reynier[1]

[1] Department of Electricity and Hydrogen for Transportation, CEA (French Alternative and Atomic Energies Commission), 17 rue des Martyrs, 38054 Grenoble Cedex 9 – France
E-mail: florence.fusalba@cea.fr

Abstract

To face increasing needs in battery demand for electric and hybrid electric vehicles, both high energy and high power Li-ion cells together with new architectures designs are under development. Several routes are possible, and in this paper the focus will be put on the so-called “safe” chemistries including phosphate materials coupled either with graphite or lithium titanates. Over the last ten years significant efforts have been invested by CEA in developing high energy LFBP (Boron "doped" $LiFePO_4$) based Li-ion cells. This technology is shown to demonstrate either relatively high energy or high power rate capability together with high stability and safety behaviour, depending on its cell conception. Aside, as high rate charge - high peak power candidates, batteries based-Lithium Titanate negative electrodes will be discussed as a promising technology to sustain frequent use of quick charge without detrimental effect on the lifespan. New cell architecture will also be addressed with giving the recent advances obtained on bipolar Li-ion technology. The bipolar design consists in identical cells which are stacked together. This technology offers several advantages because it simplifies cell-to-cell connections and so a lowering internal resistance for the whole battery. The bipolar battery can be designed to present a large capacity, a high voltage and an appreciable flexible form factor. The patented bipolar battery developed at CEA for the µHybrid Electric Vehicle (µHEV) is based upon the use of $Li_4Ti_5O_{12}$ as negative active material (fast charging with high capacity retention, life time, safety/reduced reactivity compared to Lithiated Graphite.) allowing the use of a common bipolar aluminium current collector and $LiFePO_4$ (cycle life, safety, low cost) as positive material. Such bipolar technology can also address other energy storage devices as super capacitors & hybrid systems potentially finding applications in other mobile & stationary fields as power tools or storage enhanced grid charging systems.

Keywords: “Li-ion Batteries”, “Energy Storage”, “Power”, “Fast charge”, “Micro-Hybrid & Electric Vehicles”

---

1. Introduction

Introducing new technologies requires respecting safety behavior, affordable cost and environmental aware. Respecting these criteria, to increase the battery autonomy, several active materials are currently on improvement. On the other side, quick charge power is deployed to reduce range anxiety and turbo-charge the mass acceptance of electric vehicles. Thus, battery and capacitor designs are being developed to expand range and shorten charging times. However, “5 minutes” fast charge is not even feasible reducing the battery life quickly with high heat evolution because of extreme charge/discharge conditions resulting in batteries heating up thus increasing the rate of degradation. Beside the battery limitation, 5 minute charging for a large capacity size battery requires significant electrical facilities. Indeed, to enable fast charging and sustain high currents for power systems, high capacity retention with high stability materials in innovative designs becomes necessary. Several solutions are in competition to face these specific needs.

Thus, lithium iron phosphate ($LiFePO_4$ or LFP) is a technology of choice for electric vehicles (EVs) because of its low cost since it doesn't include precious metals (also non toxic material) and also for its high stability in temperature compared to conventional lithium metal oxides based on Nickel and/or Cobalt. For power chemistries, most promising approaches are the use of high-ionic conductivity materials, zero strain materials like Lithium Titanate (but with lower conductivity) or other Titane-based oxides negative electrode materials. When coupled with LFP positive electrode, this electrochemistry exhibits extended life cyclability as confirmed in a recent paper from A. Gerfi et al.[1] showing above 15,000 deep cycles. While the major drawback remains the voltage reduction of the cell by 1.4V compared to graphite ($Li_4Ti_5O_{12}$ or LTO redox potential of 1.5V vs. Li^+/Li) leading to a reduction of the corresponding cell energy, this makes this technology of interest for very high specific power applications combined with high safety and high cycle life.

On the other side, to enable fast charging and sustain high currents for power systems, in addition to high capacity retention with high stability materials, innovative designs have to be developed. Especially integrating LTO, the major drawback being the cell voltage reduction, can easily be counter balanced using several accumulators put in series. This is what suggests the bipolar battery design, an innovative battery concept to compensate low cell voltage building identical cells stacked together with simplified cell to cell connections thanks to specific core cells architectures as the one patented by Yardney Technical Products in 1994 [2] using a bi metallic (Copper/Aluminum) current collector or the one patented by CEA in 2001 introducing a singular aluminum current collector [3] with LTO.

In this study, we will present last results obtained at CEA on technologies integrating Boron doped LiFePO4 (LFBP) positive electrode material for energy applications & LTO negative electrode for power rate capability, giving data on materials and performances of "standard" stacked or wound Li-ion cells and of bipolar LFBP/LTO cells, using studies of cases to light targeted markets applications.

1.1 Today positive electrodes

So far, three main positive electrodes technologies are competing for electric or hybrid vehicle batteries: i) one of the most advanced is the $LiNiCoAlO_2$ (NCA) oxide developed first by SAFT and further commercialized by JCS for hybrid vehicles with very high stability in performances but which requires specific safety care, ii) for electric vehicles applications, many companies are now proposing Mn-based chemistries for their interest in cost reduction and safety improvement by coupling compounds or mix of compounds such as $LiMn_2O_4$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) for instance with first commercialization in 2011, and last iii) the most recent technology concerns the $LiFePO_4$ compound, also developed by most of the industrial battery manufacturers in the world with already commercialization by Asian companies or US companies such as A123 and more recently SAFT for high power needs.

As above mentioned the stability advantage of lithium iron phosphate technology makes its lithium ion cells not combustible and not reacting violently with electrolyte when exposed to high temperature or if the cell is damaged [4]. It was then shown during abusive tests that cells do not exhibit any reaction when nail test is performed and only a thick white smoke is observed, without explosion nor flames after being overcharged or overheated.

1.2 Today negative electrodes

Replacing graphite by $Li_4Ti_5O_{12}$ material as negative electrode in addition to enable fast charging [5] with high capacity retention thus increased life time, also improves safety due to the reduced reactivity of LTO compared to Lithiated Graphite. These two last points are totally in accordance with micro and mild hybrid applications. However, the major drawback of LTO is the voltage reduction of the cell leading to a reduction of the corresponding cell energy, as for Enerdel technology ($LiMn_2O_4/Li_4Ti_5O_{12}$) which exhibits life time of interest for vehicles application however with a low cell voltage of 2.3V or for SciB Toshiba Lithium Cobalt Oxide/LTO cells with a mean voltage of 2.4V. This drawback can be compensated either with an innovative cell design (See bipolar design) or by coupling LTO with high voltage/capacity materials.

1.3 Both $LiFePO_4$ and $Li_4Ti_5O_{12}$ materials can be processed at nano scale level for power applications

Nano-particle materials have attracted much interest for lithium battery electrodes. Nano-sized particles show faster lithium ion diffusion and larger solid solution region than micron-sized particles. The Li-ion diffusion coefficient, D_{solid}, determines the minimum particle size of the electrode materials required for their full utilization at the highest rates of charge and discharge ($D_{solid} = l^2/t$ where l is the radius of an electrode particle and t is the time required for the Li ion to fully diffuse into it). When $D_{solid} = 10^{-9} - 10^{-10}$ cm^2/sec (as in layered electrode materials such as $LiCoO_2$, $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ and graphite), the average particles have to be in the 1-5 micron range or less in order to achieve full utilization in 60 sec. On the other hand if $D_{solid} = 10^{-13}$ to 10^{-14} cm^2/sec as in $Li_4Ti_5O_{12}$ and $LiFePO_4$, the particles have to be on the order of ~ 15-120 nm to realize full capacity in 60 sec [6]. The interest of LTO compared to graphite also coming from its lower reactivity in order to avoid any lithium plating event.

1.4 Current Status on Safe $LiFePO_4$/Graphite cells for electric vehicles (EV) application

$LiFePO_4$ technology as a possible candidate for Li-ion positive electrode was first discovered by Dr. John Goodenough at the University of Texas. So far, the biggest player in the $LiFePO_4$ marketplace for electric vehicles is A123 Systems that has teamed up with GM to develop these batteries for the Chevy Volt plug-in hybrid. Today, A123 cells energy density is increased by 30%, from 110Wh/kg to 140Wh/kg.

CEA has been working on Li-ion technology for around 15 years. In particular, over the last ten years significant efforts have been invested in developing high energy boron doped lithium iron phosphate material, LFBP based Li-ion accumulators [7], now in partnership with Prayon material manufacturer. Safe CEA LFBP based accumulators were shown to exhibit intrinsic safety, high cycle ability & expected reduced cost. CEA succeeded in transitioning the $LiFeBPO_4$ synthesis to the kilogram scale for technology transfer and is now supporting Prayon [8] under CEA License for industrial development at the ton level.

2. Materials & Methods

CEA growing lithium battery research group is a ca. 180 people team devoted to the preparation and development of electrode materials and electrolyte membranes, the setup of small to large lithium-ion cells and the complete battery assembly and testing. We are working on the development of future battery generations demanding higher power, higher capacity, lower cost and safer performances than the currently commercialized cells. Our researches are dedicated to the electric and hybrid vehicles, and also to other applications like professional, military, space, defense, aeronautic, medical, security, textile, stationary or electronics… Research on advanced Li-ion batteries at CEA is under development through three complementary platforms:

- A platform dedicated to (nano)materials developments and pilot scale production up to several kg per batch. As examples, our group has a great expertise in the well-known LFP material with 4 patents, an upscale demonstration at the kg level. CEA also develops LTO technology through 4 patents. More over, high energy Lithium rich layered oxides, new high energy density 5V spinels with $LiMn_{2-x}M_xO_4$ compositions, and higher energy density phosphate materials are under investigation giving rise to a dozen of innovations carried on materials development which have been patented.

For this study, both homemade and commercial Phosphate and Titanate materials were used. In parallel, electrode ink formulation developments have two main goals, to achieve the best performances in terms of electrochemical behavior and process ability at the lowest cost and environmental impact. Work on water-based LFP & LTO inks was therefore performed to be switched to “standard” organic (NMP-based) solvent.

- A pilot assembly line comprising 2 dry-rooms (ca. 500m²) including all the steps of cell manufacturing: mixing equipments for positive and negative inks preparation, reverse-roll/slot die coating machines, calendaring, winding, electrolyte filling, electric and laser welding in inert atmosphere, under vacuum heat-sealing machine… This line allows specific and “on demand” designs through one area devoted to new chemistries introduction and the other one to process upscale, for various applications from smart-cards, medical implants and power tools to EVs or hybrid electric vehicles (HEVs). The cell capacity may therefore vary from few mAh to several tens Ah (depending on energy or power application) with either soft-packaging or hard-casing. The line is then completed by battery pack assembly with capability to realize 20 to 40 battery packs (EVs sizes)/month. All materials & components are electronically tracked during the process thanks to bar codes.

In this study, composite electrodes were coated on lab-coater for material and electrode formulation development and on a pilot coater for full Li-ion wound/stacked cells or bipolar design. Full Li-ion cell development uses an intermediate pouch cell design referred as “CEA standard” 5x34x37mm format (see photo Figure 1) in order to adjust process parameters before large capacity manufacturing on pilot line.

CEA designed preliminary mechanical assembling tool and tightening plates to perform bipolar architecture assembly and connection steps respecting design rules. Automated assembly line for industrialization assessment is under progress.

- A testing platform with more than 1000 ISO-9001 certified channels. In addition to its Grenoble facilities (Electrical test benches: High power ~300 channels/Low power -Includes formation- 480 channels), CEA is already internationally recognized for its expertise in photovoltaic applications, especially through its National Solar Energy Institute (INES) in Chambery (France). These testing facilities which enable medium to high power electrical tests associated to climatic chambers are coupled with electrochemical modeling and expertise in both lead-acid and Li-ion technologies. CEA has also developed specific know-how in the optimization of battery management which is one of the key points in the increase of the battery cycle life.

- Major Partnerships allow CEA battery activity to ramp up steadily like Renault-CEA signed cooperative research and development agreement in June 2010, which encompasses work on electric vehicles, new energies, and cleaner combustion engines.

3. Phosphate/Graphite Li-ion cells for EV & Plug-In HEV applications

The main characteristics of the CEA LFBP cells are shown here. Intermediate capacity Li-ion pouch cells (5x34x37mm-CEA standard format) are used to adjust materials, formulations & process before larger capacity manufacturing (Figure 1). Large capacity prototype cells manufactured on our pilot line and their electrical characteristics are summarized below:

- High cycle ability
- Improved Safety behavior
- 15 to 33Ah Cell up to 150Wh/kg @ C/3 rate
- Expected Low cost
- Hard casing or Soft Package

Intermediate capacity Li-ion pouch cells (5x34x37mm referred as 53437) used by CEA as standard format for new chemistries investigation

Soft-Package
Stacked Cell
Dimensions: 195x165x10 mm
Practical Capacity: 32,7Ah [3,6V-2,5V]
150Wh/Kg -700g
Mean Discharge Voltage: 3.2V
Rinternal (1kHz): 1.7 mOhm

Cylindrical Hard Casing
Dimensions: 125 mm Height – 50mm Diameter (referred as 50125)
Practical Capacity: 16Ah [3,6V-2,5V]
120Wh/Kg – 3C Rate

Figure 1: CEA LFBP/G prototype cells designs & corresponding electrical characteristics

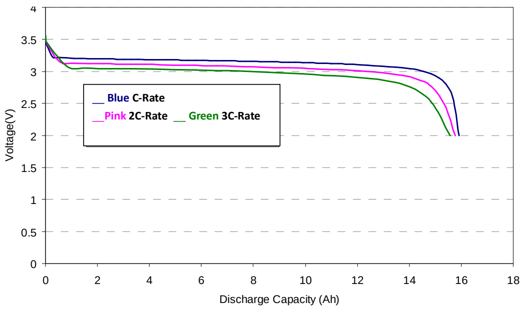


Figure 2: LFBP/G Li ion 50125 cells discharges at C, 2C and 3C Rates after charge@C/5 followed by CV @3.6V

Power capability was also checked with 230mAh@C/3 (5x34x37mm) soft-packaged LFBP / Graphite (G) Li-ion cycling at charge CC-CV@5C, discharge 5C (Figure 3). It was reported only 12.5% capacity loss after 7500 cycles at 5C rate therefore 0.0017% capacity loss per cycle. These prototypes are manufactured with low electrode loading for active materials high power rate assessment therefore they exhibit low specific energy for such small capacity level.

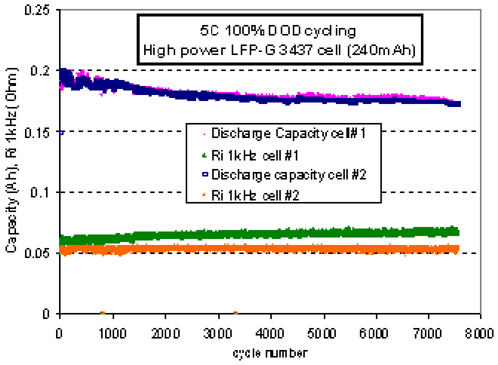
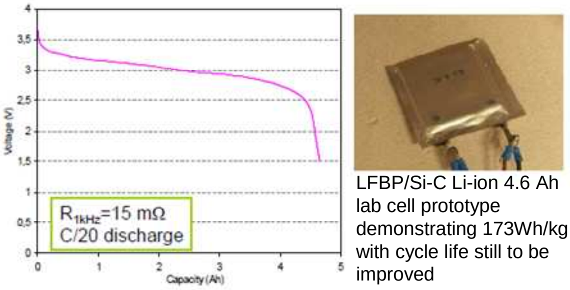


Figure 3: 230mAh (5x34x37mm CEA standard format) LFBP / G Li-ion cell– Cycle Life in a power mode (5C charge-discharge rates)

In parallel, CEA still targets an increasing energy density of the “phosphate cells” either by working on other phosphates derivatives ($LiMPO_4$, M = Co, Mn… with higher redox potential) or by replacing graphite negative electrode by carbon-silicon composite material. Indeed, Silicon-Carbon composites are today an attractive alternative to graphite due to the high theoretical capacity of 3579mAh/g of Si (Li-Si alloy forming), compared to 372mAh/g with graphite. However, a large capacity fade is observed upon cycling as a result of a large volume change in the material during alloying and de-alloying with Lithium. Nano sized particles and design of new binders are some of the investigated ways to limit this issue. In a complementary manner, several silicon/silicon carbon composites synthesis routes are investigated at CEA. The material approach is combined with electrode formulation development due to the huge impact of the constitution of the porous volumetric composite electrode for capacity retention in cycle life. Improvements are so far reached in aqueous media.

Finally, the most pragmatic strategy according to us consists in starting from conventional graphite, improving its capacity by adding Silicon (C-Si). Therefore, the corresponding negative electrode capacity depends on added silicon content. For instance, 5% silicon in active material results in a capacity experimentally measured at ca. 440mAh/g, and in cell capacity increased by ca. 25% (small scale demonstration, <1Ah -not shown). Today more than 170Wh/kg were obtained for LFBP/Si-C electrochemistry and our target is to reach 190Wh/kg (Figure 4).



LFBP/Si-C Li-ion 4.6 Ah lab cell prototype demonstrating 173Wh/kg with cycle life still to be improved

Figure 4: A path to increase LFBP Cells energy density up to 190Wh/kg, introducing silicon-carbon composite negative electrodes

3.1 High power Phosphate Li-ion cells including LTO negative electrode & Bipolar Technology for µHybrid and HEV Li-ion applications

3.1.1 Safe & High power LFBP/LTO Li-ion cells

CEA is now involved in the development of large LFBP/LTO cylindrical and prismatic cells. Today, promising results are shown on intermediate format (5x34x37mm or 53437) pouch cells (Figure 5).

- 80 % of capacity charged at 7C – less than 7 minutes, no impact on cycle life
- Target = Full Charge in less than 5 minutes or less than half an hour for PHEV without reducing cycle life

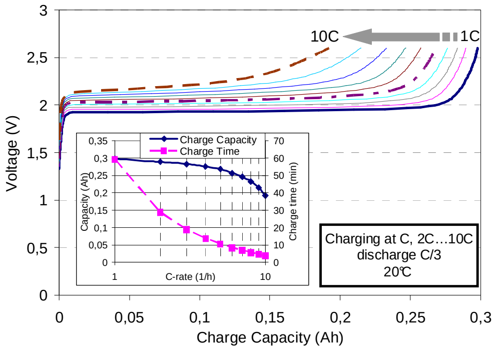


Figure 5: LFBP / LTO Fast Charging Ability. 0.3Ah Li-ion pouch cell (5x34x37mm): Charging from C to 10C, discharge at C/3 @20°C

Stability upon cycling was also controlled using 53437 CEA Standard Li-ion cells at C-rate 100%DOD/100%SOC (Figure 6). Almost no capacity loss is reported after 1500 cycles.

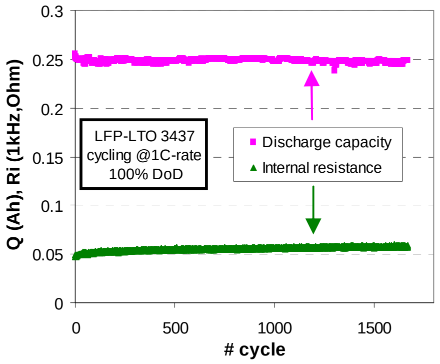


Figure 6: 53437 CEA Standard Li-ion cells cycled at C rate 100%DOD/100%SOC

Abusive testing on 10Ah CEA wound cells in soft-packaging (Figure 7) externally performed by a French battery manufacturer clearly concluded to $LiFePO_4$ technology intrinsic safety.

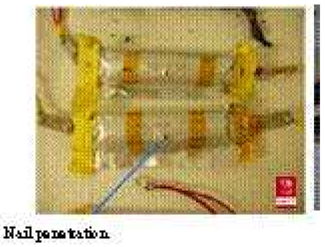


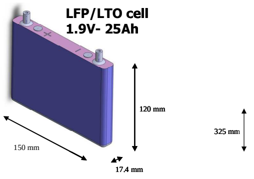
Figure 7: $LiFePO_4$ technology abusive testing: Nail penetration performed on 10Ah LFBP/G wound cells prototypes (soft-packaging) exhibits no fumes, nor fire, nor explosion without any added safety device (i.e. w/o PCB)

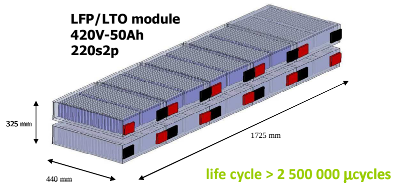
Perspectives for LFBP/LTO technology in conventional cell architecture (wound or stacked core) deal with high power markets where technology has to sustain high power peaks with long life cycle and where specific energy is not the prior parameter because of its low operating voltage. Such applications include stationary storage/charge stations & heavy duty vehicles like subway, tramway or buses… autonomous between stations. One example of battery cell & pack sizing exercise for public transport electric vehicle is given below with LFP/LTO– Prismatic cells conception & 5-10% DOD assumption:

LFP-LTO Li ion cell capacity : 25Ah
Cell volume : 312cm³
Cell energy : 46Wh
Gravimetric energy : 52Wh/kg
Volumetric energy density : 139Wh/L
Total cell mass : 822g
Internal resistance : 0.24mΩ

Pack Solution #1: 73kWh
380V-192Ah DOD 6.8%
Storage System total weight: 1500kg
Storage System total volume: 1150L

Pack Solution #2:
49kWh
410V-120Ah DOD 10%
<1500kg; <2 m³





3.1.2 Innovative cell design using bipolar technology

The major drawback of LTO, the cell voltage reduction, can easily be counter balanced using several accumulators put in series. This is what suggests the bipolar battery design, an innovative battery concept based on individual identical compartments assembled in series in one cell to compensate low chemistry voltage thanks to single common current collector either made of bi metallic (i.e. copper/aluminum) [2] or singular aluminum [3] in a stacked or wound [9-11] core assembly.

For CEA bipolar cells [3], the bipolar electrode is an aluminum current collector foil which is coated on each side with LFBP and LTO based composite active layers (Figure 8) and stacked in a prismatic cell format.

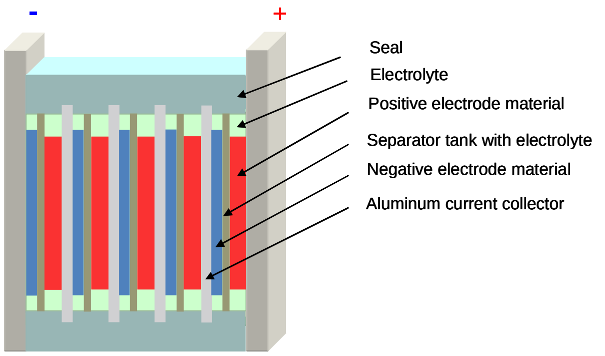


Figure 8: Bipolar Li ion cell architecture built from several cells in series thanks to a common aluminum bipolar electrode on which, as example, both lithium iron phosphate and lithium titanate oxide can be coated without any risk of alloy formation during the full cell charge step

Electrolyte leakages were prevented by using specific resins on the outline of each electrode. The whole bipolar battery has been designed with a capacity of 0.7Ah and a voltage of 24V, including 12 bipolar electrodes (13 cells of 1.88V OCV) and 2 terminal mono-polar electrodes stacked together in a flat design (see figure 9).

Patterns definition for sealing pastes/adhesives remains to be optimized. For concept assessment, a large pastes/adhesives framework was selected in order to avoid any electrolyte leakage issue while ageing. Reducing both non-coated area (increasing active electrode materials area) and current collectors (Aluminum) weight contributions (thinner foils), would give rise to energy storage improvement (ca. 50Wh/kg). Indeed, the selected fit and form design will have to exhibit ease of process respecting charge extractions and collecting tabs.

BIPOLAR CELL DATA SHEET

Technology : $LiFePO_4/Li_4Ti_5O_{12}$
Design : Bipolar 13 unit cells

Nominal electrical data :
Capacity @ C/10 20°C: 0.7 Ah
Nominal voltage : 24 V
Max. voltage (continue charge) : 33 V
Min. voltage (continue discharge): 6.5 V

Mechanical data (hard casing excluded)
Length: 615 mm
Width: 205 mm
Thickness: 2.5 mm
Weight: 0.7 kg

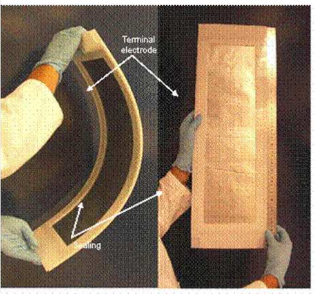


Figure 9: High power, safe and low cost $LiFeBPO_4/Li_4Ti_5O_{12}$ 15Wh bipolar cell for µHEV

The most important point for hybrid electric vehicle application is that the LFBP/LTO chemistry is totally safe and exhibits very high cycle life (target at 15 years and 500 000 charge-discharge cycles at 20C & depth of discharge of 3%) due to very stables materials with biphasic structures and low volumetric expansion. Thus, LFBP/LTO electrochemical couple assembled in a bipolar cell exhibits relevant stability (Figure 10) and is expected to demonstrate very high reliability and safety behavior when abusively tested. Such system displaying high rate capability but with lower energy density is therefore well suited for micro hybrid applications where both power and sufficient energy recovery are required.

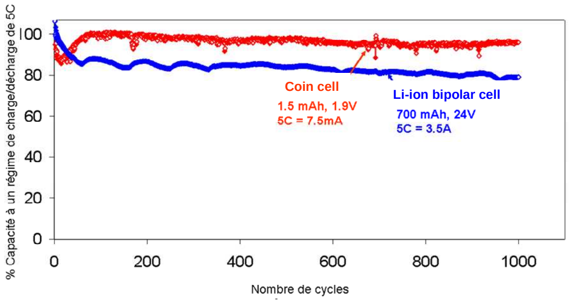


Figure 10: High stability over cycling, low polarization for LFBP/LTO chemistry (Coin cell) and in a bipolar design assembly

High power, safe and low cost $LiFePO_4/Li_4Ti_5O_{12}$ bipolar system for µHEV displays:

- High rate-power (charge/discharge)
- Low internal resistance for the whole battery adapted to high rates
- Simplified cell-to-cell connections
- Sustains NEDC urban cycle with 80C (RT) restarts (~2kW/kg for a 150Wh pack)
- 1s pulse possible at 170C (~4kW/kg)
- Long cycle life (7.5 years life time in µHEV profile

with at least 35-40% of usable capacity)
- An appreciable flexible form factor in a 2D volume (Stacked electrodes & flat geometry) (few mm thick)
- Lower heat generation (RI^2) and better heat dissipation (in flat cell design)
- No safety issue. No visible cell degradation during nail penetration abusive test except the nail hole and no thermal run away nor fumes, nor flames, nor sparks during overcharge –not shown)
- Well adapted for regenerative breaking (KERS)
- Rough and very preliminary cost analysis leads to expected battery element cost of ca. 1.6€/Wh, less than 15€/kW

Safety data and especially overcharge, overheating (see Figure 11), deep discharge and nail penetration result in no fumes, no fire, no explosion without any added safety device, confirming that this technology is maybe the safest Li-ion technology.

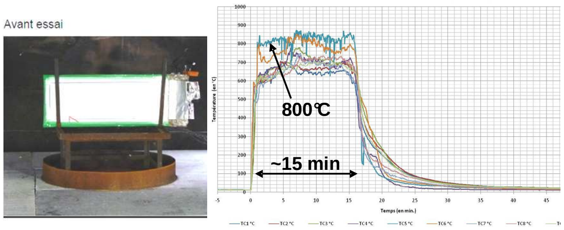


Figure 11: Overheating abusive testing. No event reported

Further, coupling LTO with high voltage $LiNi_xMn_{2-x}O_4$ opens up the opportunity to both improve the operational cell voltage to reach a "3V" system (figure 12) and to decrease the self discharge, improving power capability and cycle life if compared with "5V" system ($LiNi_{0.4}Mn_{1.6}O_4$/Graphite). A loss of capacity of 0.06% per cycle is reported. It corresponds to a cycle life of about 300 cycles. 80% (End Of Life) of the nominal capacity is recovered at 10C (figure 12-Insert).

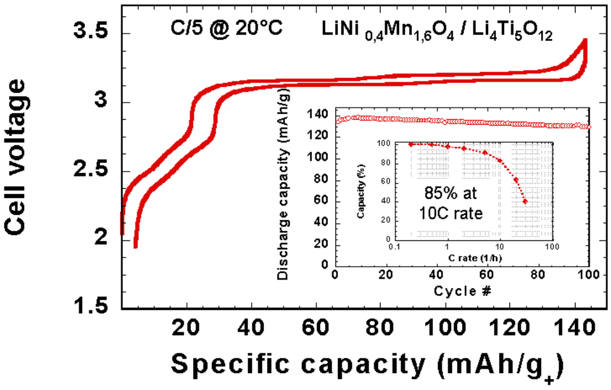


Figure 12: "3V"system coupling high voltage "5V" spinel oxide ($LiNi_{0.4}Mn_{1.6}O_4$) positive electrode with LTO ($Li_4Ti_5O_{12}$) negative electrode charge-discharge profile. Cut Off voltage: 2-3.5V. Insert: rate capability curve for high power cell

Such "3V"system is expected to deliver higher energy density ranging 120-140Wh/kg with a pulse power density of 10 to 20kW/kg, thus performances that allow expecting fast charge batteries with respectable energy for HEV-EV application.

4. Conclusion

Due to their attractive performance characteristics, lithium-ion batteries have been identified as the battery chemistry of choice for a number of applications, including Hybrid Electric Vehicles (micro, Plug-in and full electric). Electrical vehicles will be only as good as their battery: so playing with technologies, ie. coupling various active materials at both the negative & positive electrodes, gives rise to a very versatile Li ion technology thus a battery designed on demand, enabling improvements through several generations implementation.

In parallel, new cells designs are currently under development in order to better fit specific requirements. This is the case to sustain frequent use of quick charge without detrimental effect on the battery lifespan in electric vehicles. Aside from reducing the battery life quickly, quick charging would also have an adverse impact on the infrastructure costs because high voltage grid substation equipments become necessary to be constructed.

So LFP/LTO technology integrated in a bipolar design is expected to best suit Electric Energy Storage not only in low hybridization level electrical vehicles but also in charging stations, reducing the need for grid high voltages equipments, thereby reducing the cost for rapid charging.

Heavy vehicles like subway, tramway or buses therefore public transport electric vehicles that require being autonomous between stations or Storage-Enhanced Grid (Quick) Charging Systems or Grid regulation systems could also benefit from high power technology using LFP/LTO chemistry even in a fully electric mode. More other in a bipolar design because it is best suited to sustain very high power peaks with high life cycle demonstrating high output voltage capability in a 2D flat geometry with a reduced internal resistance, a lower heat generation and a better heat dissipation. Further, this bipolar design may apply to other electrochemical storage devices like supercapacitors or hybrid energy-power systems [12, 13] for applications where high voltage is a necessity.

However, LFP/LTO only allows moderate energy density that makes this technology not suitable for mild hybrid, hybrid or full electric vehicles application. To increase the battery stored energy, LTO is suggested to be coupled with high voltage and/or high capacity positive active materials ("$LiMO_2$-Li_2MnO_3") replacing LFP, the high voltage coupling being very promising.

5. Perspectives

Today, while East Penn US Company owns the UltraBattery under CSIRO Australia concept (Lead battery with supercapacitors thanks to carbon based electrodes) for hybrid vehicles (Honda) & stationary application (Edison), there is no commercial or mature Li-ion bipolar cell available. Aside, Nissan & Toyota own an important port-folio in the field. This can be explained because of technical remaining issues like full hermiticity between compartments during time. The hard point of the technology is the choice of the sealing component (glue or resin) which will be used to seal each compartment and prevent electrolyte leakage between adjacent cells. Sealing process of a bipolar compartment will have to resist electrolyte in order to prevent self discharge due to ionic short-circuit and ageing due to compartment unbalancing. Therefore, next step remains improving the CEA bipolar design improving both energy storage & ageing behavior [14], working more deeply on an industrial sealing step. More globally our bipolar design toughness still has to be strengthened and its process further developed for future industrial manufacturing with competitive costs. This work already starts on our pilot line.

Acknowledgements

The authors thank all their colleagues at CEA for their contribution to the Li-ion battery technology during the last 15 years.

6. References

[1] A. Guerfi et al. / Journal of Power Sources 195 (2010) 845–852

[2] S. Hossain: Bipolar Lithium-Ion Rechargeable Battery. Yardney Technical Products, Patent US5595839, 1997

[3] S. Martinet et al.: Lithium Electrochemical Generator Comprising at least a Bipolar Electrode with Conductive Aluminium or Aluminium Alloy Substrates. Commissariat A L'Energie Atomique, Patent US2005/0069768 (FR2832859A1 2001), 2005

[4] Development and Test of Safe, High Power Lithium Ion Main Batteries for General Aviation Aircraft"http://www.sae.org/technical/papers/2008-01-2884.

[5] K. Nakahara, R. Nakajima, T. Matsushima and H. Majima, J. Power Sources vol. 117 (2003), p. 131-136

[6] K.M. Abraham, What does Electrode Particle Size have to do with High Power Lithium-Ion Batteries?, Paper presented at the 2009 Fall ECS meeting, Vienna, Austria, Abstract No. 692

[7] S. Franger, C. Benoit, C. Bourbon, F. Le Cras, J. Phys. Chem. Sol. Vol. 67 (2006), p. 1338-1342

[8] www.prayon.com

[9] T. Fukuzawa et al.: Bipolar Battery and Related Method. Nissan, Patent, US2004/0161667, 2004

[10] K. Hosaka et al. : Bipolar Battery. Nissan, Patent US2004/0091771, 2004

[11] G. Takayama et al.: Bipolar Battery and Method of Manufacturing the Same. Nissan, Patent US2008/0138706, 2008

[12] F. Fusalba & S. Martinet: Hybrid electric energy storage system with bipolar electrodes. Commissariat A L'Energie Atomique, Patent WO2009/101047, 2009

[13] F. Fusalba & S. Martinet: Lithium Electrochemical Generator Including Two Types Of Distinctives Electrochemical Cells, Commissariat A L'Energie Atomique, Patent WO/2011/086102, 2011

[14] M. Chami et al.: Multi Pole Battery with Improved Interplate Leakproofing, Commissariat A L'Energie Atomique, Patent US2009159582, 2009

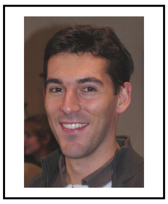
7. Authors

Florence Fusalba Ph.D
CEA-Grenoble 17 rue des Martyrs
38054 Grenoble Cedex 9
Tel: 00 33 (0)4 38 78 43 23 Fax: 00 33 (0)4 38 78 25 56
Email: florence.fusalba@cea.fr

Florence Fusalba (Ph.D) is Battery Program Manager at CEA. After seven years studying in Canada to graduate as Master M. Sc Chemistry and Ph. D Energy and Materials, on electrochemical storage devices (Lithium ion batteries and electrochemical supercapacitors), Florence Fusalba joins in 2000 STMicroelectronics as dielectric manager. In 2004, she is in charge of photovoltaic cells laboratory for CEA and since 2006, she is CEA program manager in the field of energy storage.

Dr. Sébastien Martinet
CEA-Grenoble 17 rue des Martyrs 38054 Grenoble Cedex 9
Tel: 00 33 (0)4 38 78 57 11 Fax: 00 33 (0)4 38 78 29 20
Email: sebastien.martinet@cea.fr

Dr. Sébastien Martinet is Deputy Manager of Division for transport and hydrogen at CEA. He experienced 15 years in battery field from Ni-MH batteries to Li-Ion cells, including 4 years with SAFT. From 2006 to 2010, he is in charge of the Laboratory of Components for Energy (more than 40 persons) in which all material and prototype developments for batteries are made in CEA.



Dr. Sébastien Patoux
CEA-Grenoble 17 rue des Martyrs 38054 Grenoble Cedex 9
Tel: 00 33 (0)4 38 78 57 11 Fax: 00 33 (0)4 38 78 29 20
Email: sebastien.patoux@cea.fr

Dr. Sébastien Patoux is expert in materials for Li-ion cells, as he experienced 12 years in this topic. He is in charge of the Advanced Batteries Laboratory in the Division for transport and hydrogen at CEA now.

Dr Marianne Chami
CEA-Grenoble 17 rue des Martyrs 38054 Grenoble Cedex 9
Tel: 00 33 (0)4 38 78 29 75 Fax: 00 33 (0)4 38 78 51 98
Email: Marianne.chami@cea.fr

Dr. Marianne Chami is an expert in polymer materials for Li-ion cells since she experienced in this field from 8 years, starting from gelled polymer electrolyte for lithium metal cells with Batscap (Bolloré and EDF), then project manager at CEA since 2005 working on the bipolar Li-ion technology for HEV vehicle.

Dr Séverine Jouanneau
CEA-Grenoble 17 rue des Martyrs 38054 Grenoble Cedex 9
Tel: 00 33 (0)4 38 78 30 34 Fax: 00 33 (0)4 38 78 40 34
Email: severine.jouanneau@cea.fr

Dr. Séverine Jouanneau is an expert in materials and composite electrodes for Li-ion cells since she experienced in this field from 13 years, starting from cathode material for Li-polymer cells with Bolloré and EDF, then cathode material for Li-ion with 3M. She is a project manager at CEA since 2003 working on both anode and cathode material including electrode formulation.

Dr. Yvan Reynier
CEA-Grenoble 17 rue des Martyrs 38054 Grenoble Cedex 9
Tel: 00 33 (0)4 38 78 22 88 Fax: 00 33 (0)4 38 78 29 20
Email: yvan.reynier@cea.fr

Dr. Yvan Reynier is EV-HEV battery developments project manager with 10 years experience, working for CEA since 2005.