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Safe Li-Ion Technology for Micro and Mild Hybrid application based on CEA Bipolar $LiFePO_4/Li_4Ti_5O_{12}$ technology

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Abstract

The bipolar design consists on identical cells which are stacked together. This technology offers several advantages because it simplifies cell-to-cell connections and so offers 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 in CEA for the Hybrid Electric Vehicle (HEV) is based upon the use of $Li_4Ti_5O_{12}$ as anode material (allowing the use of a common bipolar aluminium current collector, and high power application) and $LiFePO_4$ (cycle life, safety, low cost). The main target has been first to achieve a sealed system with no electrolyte leakage, and then to demonstrate the advantage of the $Li_4Ti_5O_{12}$ / $LiFePO_4$ couple (1.9V) for high power Li-ion bipolar battery. To increase the battery cycle life, a new design has been elaborated and has allowed to develop standard energy battery of 15Wh (24V, 0.65 Ah).

In this paper, first results on 15Wh cells, using the $Li_4Ti_5O_{12}$ / $LiFePO_4$ couple and a new bipolar battery design, will be presented according HEV profiles.

Keywords: "Battery" Lithium-ion" "bipolar" "Power" "Safety" "High cycle life" "Low cost"

1 Introduction

To face increasing needs in batteries demand for electric and hybrid electric vehicle applications, both high energy density and high power Li-ion cells are under development. To increase the battery energy density, the voltage and/or the capacity have to be increased. Thus, to improve the lithium-ion battery capacity, several active materials are on development, but specific electrolytes have to be employed to sustain high voltage and cycle life still has to be improved. In another manner, the lithium-ion battery voltage can easily be enhanced, using several accumulators put in series, and this is what suggests the bipolar battery design, an innovative battery concept based on patented singular aluminium current collector [1] with $Li_4Ti_5O_{12}$ (LTO) to compensate low cell voltage and built with identical cells stacked together.

Such bipolar battery offers a high voltage with simple cell-to-cell connections, and a small electric resistance between adjacent cells. The cell-stack provides uniform current and potential distributions over the active surface area of each cell component. Conventional electrolytes can be used (no needs to have a large electrochemical stability window). Moreover, due to series architecture which allows higher cell voltage, active materials such as $LiFePO_4$ and $Li_4Ti_5O_{12}$ can be selected as technology to be integrated in bipolar Li ion cells aiming to reach safe and high power batteries.

Indeed, the two main advantages of lithium iron phosphate (LFP) technology consist in its low cost since it doesn't include precious metals (also

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non toxic material) and high stability compared to conventional lithium metal oxides based on Nickel and/or Cobalt. Thus, LFP as integrated in lithium ion cells is not combustible and does not react violently with electrolyte when exposed to high temperature or if the cell is damaged [2]. 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.

Replacing graphite by LTO material as negative electrode enables fast charging [3] with high capacity retention, increases the life time and the 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 of 1.5V leading to a reduction of the corresponding cell energy.

Consequently, concerning LFP/LTO couple, the most important point for hybrid electric vehicle application is that this chemistry is totally safe and exhibits very high cycle life (targets at 15 years and 500 000 charge-discharge cycles at 20C & death of discharge of 3%) due to very stables materials with biphasic structures and low volumetric expansion. Moreover, both materials are low cost when compared to cobalt based compounds, and assembled in bipolar cells. Thus, LFP/LTO electrochemical couple assembled in a bipolar cell is expected to demonstrate very high reliability and safety behaviour when abusively tested. Such system displaying high rate capability is therefore well suited for micro and mild hybrid applications requiring both power and mild energy densities.

2 Experimental

Lithium iron phosphate material synthesis is performed by CEA using a 3 steps mechanical chemical method. Lithium titanate spinel oxide ($Li_4Ti_5O_{12}$) is also in house manufactured. The bipolar electrode is an aluminium current collector foil which is coated on each side with $LiFePO_4$ and $Li_4Ti_5O_{12}$ electrode inks based materials. Electrolyte leakages are prevented by using specific resins on the outline of each electrode. $LiFePO_4$ and $Li_4Ti_5O_{12}$ couple exhibits a low cell voltage of 1.9V compensated by the bipolar "series" architecture.

The whole bipolar battery has been designed with a large capacity (0.7 Ah), a high voltage (24 V), with 13 cells stacked together (Figure 1), and offers an appreciable flexible form factor.

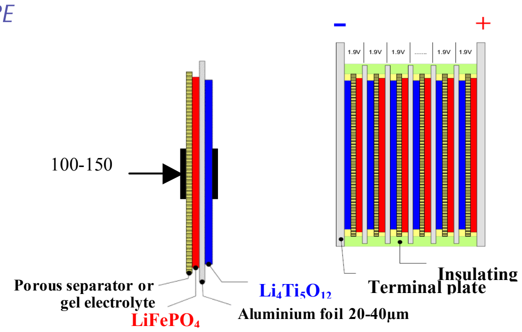

Figure 1: Bipolar Li ion cell architecture built from several cells in series (right) thanks to a common aluminium bipolar electrode (left) on which both lithium iron phosphate and lithium titanate oxide can be coated without any risk of alloy formation.

Typical electrode loading corresponds to high power electrodes with an electrode area of about 750 cm^2. Electrode coating requires on line process in regular –interruptive- patterns on both substrate sides and a sensitive alignment to avoid over heating. Prototypes are assembled and activated in inert atmosphere. The battery is soft packaged in order to enable a significant increase in energy and power density thanks to its light weight (Figure 2).

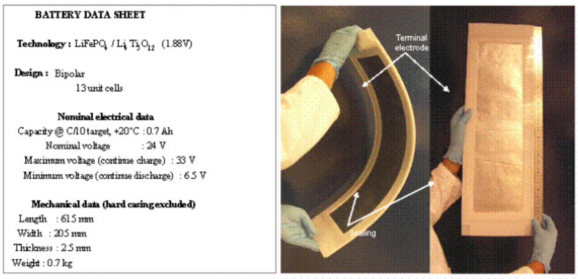

Figure 2: CEA 15Wh Li ion bipolar cell data sheet and photography.

Such bipolar design allows simplifying cell to cell connections and reduces internal resistance for the whole battery. Increasing electrodes areas enables to integrate large capacities and the wide developed active surface area improves thermal dissipation. CEA designed preliminary mechanical assembling tool and tightening plates to perform bipolar architecture assembling and connection steps (Figure 3). Automated assembling for production is expectable if requested.

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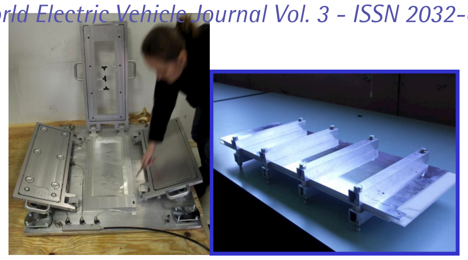

Figure 3: Mechanical assembling tool (left) and tightening plates (right) for bipolar cells prototyping.

Electrochemical tests performed allow following the battery performances in a hybrid electric vehicle (micro hybrid) application. This hybrid profile simulates battery life under hybrid electric vehicle strains. Micro-cycles include discharge and charge phases for instance, respectively, to start the engine and during breaking step. It consists in repeating twenty times micro cycles alternating with low rate charges (1C) in between the 20 micro cycles so far that the operating single cell voltage falls down to 1V.

Micro Cycles:

- Start engine	**(60A-1s-, 80C)**
- Help engine	(5s, 43C)
- Charge battery	(30s, 5.73C)
- Braking	(2s, 43C)
- Pause	(10s)
- Braking	**(30A-3s-, 40C)**
- Supplying consumers	(30s, 5.73C)

1 hybrid profile → Micro Cycles repeated down to 1V/cell

3 Results and Discussion

- Benchmarking $LiFePO_4$ and $Li_4Ti_5O_{12}$ materials

Several grades of $LiFePO_4$ and $Li_4Ti_5O_{12}$ have been tested as positive and negative electrodes when cell assembled, using a HEV profile. Discharge capacities (DOD 100%) during micro cycles were computed and cycling ability compared (Figure 4). It appears clearly that CEA materials used together, offer better performances than commercial grades. Indeed, while commercial sources show higher performances at the beginning of the test, their capacity loss during cycling is higher and did not allow pushing the test further than 8 000 hybrid macro cycles for some of those materials investigated. CEA materials couple remains stable over more than 15 000 hybrid cycles. Further more, It was demonstrated (not shown) that 35000 hybrid profiles (7 months ½ bench cycling computed at minimum 20 profiles per cycle) can be performed with CEA materials resulting in ~7 years operation ability (Model : 20 start functions = 20 profiles per day, 5 days/7). It is interesting to underline that the battery can be used at DOD of about 40%.

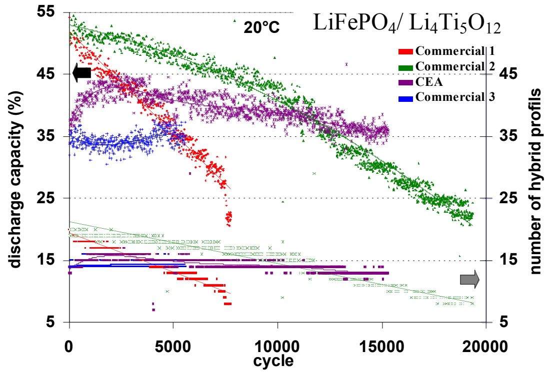

Figure 4: Discharge capacity and number of hybrid profiles (in one cycle) versus number of cycles for $LiFePO_4$/ $Li_4Ti_5O_{12}$. Tests performed in coin cells with "micro-hybrid" tests type.

- 15Wh bipolar battery

During HEV profiles (Figure 5), the 15Wh bipolar battery offers a stable energy efficiency (75 %) and a low internal resistance (~ 0.2 Ohm).

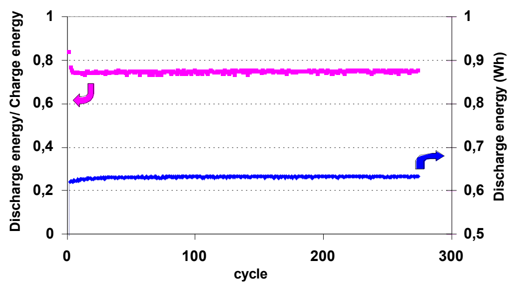

Figure 5: Energy efficiency and discharge versus number of "micro-hybrid" cycles in a 15Wh $LiFePO_4$/ $Li_4Ti_5O_{12}$ bipolar battery.

Electrochemical measurements show that the bipolar cell made of 13 stacked compartments display the expected voltage of 24V. However, restored capacity is strongly dependent on the tightening step; limited by defective cell compartments which can induce a whole capacity loss of about 25%. Homogeneity of compartments is mainly linked to stacking and electrolyte filling operations that have to be fully managed. Indeed, homogeneity plays an important role in battery efficiency and cycle life.
A tightening tool was therefore developed and improved through several steps, improving

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homogeneity in auxiliary voltages (Figure 6). The preliminary high polarization behavior reported during charge/discharge steps and attributed to surface pressure distribution issue at the electrodes was strongly reduced introducing first an aluminum tightening cell and finally a clamping system. A pressure sensor film exhibits a better pressure distribution electrochemically translated in no more voltage spread at the end of charge. Thus, bipolar cell electrochemical behavior exhibits very low polarization when charged and discharged which underlines no short circuit thus no electrolyte leakage between stacked cells (charging time is similar to discharging time).

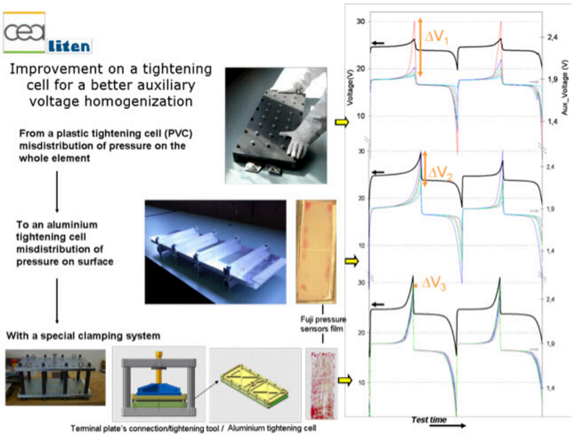


Figure 6: Bipolar cells assembling: Improvement on a tightening cell for a better auxiliary voltage homogenization

At high rate cycling (5C), capacity loss is less than 20% after more than 1000 cycles (Figure 7). Performances of 24V 13 compartments bipolar cells compare well to 1.9V button cells.

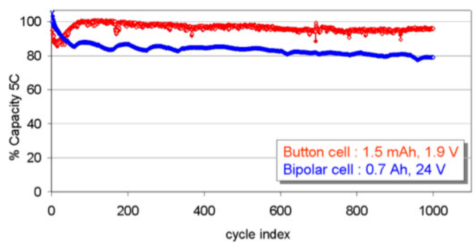


Figure 7: 24V bipolar cell, 0.7 Ah high rate cycling @5C, 20°C. Capacity loss versus cycling.

A 15Wh bipolar cell was tested during HEV profiles (Figure 8). 1 HEV profile consists mainly on a micro cycle made of discharge at max. current 60 A and 6 V cut-off voltage -60 A (1s) ⇔ 80 C rate- with a charge at max. current 30 A and 30 V cut-off voltage -30 A (3s) ⇔ 40 C rate- being repeated to simulate an accelerated duty profile -100 µcycles ~ 1 week of actual operation. It is thus reported more than 3500 HEV profiles performed by the 15Wh bipolar cell.

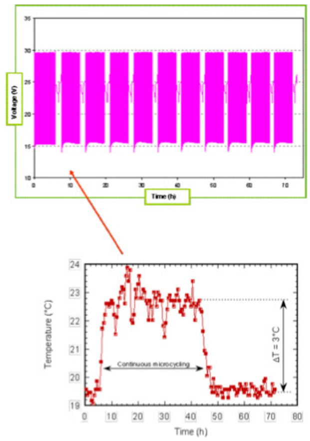
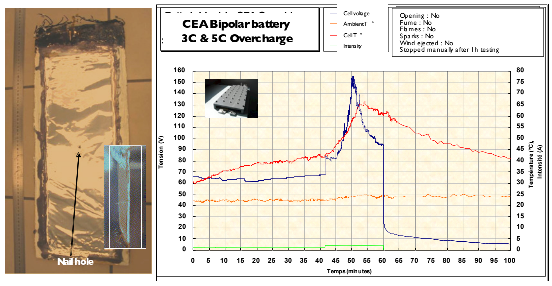


Figure 8: Ability of the 15Wh (0.7Ah, 24V) bipolar element to sustain HEV profiles

- Safety

Nail penetration did not induce any visible cell degradation except the nail hole (Figure 9, left). During overcharge (Figure 9, right), the cell temperature reached 60°C with a heat point located close to the terminal current collector but without any related safety issue. No thermal run away was observed, nor fumes, nor flames, nor sparks. As expected, a very safe system is here demonstrated.

Figure 9: Safety test. Li ion bipolar cell



photography after perpendicular nail penetration (left) and temperature monitoring during 3C & 5C overcharge (right).

Conclusion

Airtight 24V, 15Wh bipolar Li ion cells were successfully manufactured (0.7 kg, 2.5 x 615 x205 mm) exhibiting rate capability over 80C (discharge) and 40C (charge). Such storage device displays specific power up to 2-3 kW/kg with at least 35-40% of the capacity actually usable. So far energy density approaches 30Wh/kg (50Wh/L) with future perspective aiming to double or triple

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energy storage introducing higher voltage positive materials. As expected, a very safe system is here demonstrated.

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