Rechargeable Lithium-ion Batteries For Wireless Smart Designs

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ABSTRACT

Wireless communication is today considered as a disruptive technology. Indeed, even if wired systems can easily achieve 100% of reliability, it induces high amount of wiring, which has non negligible impact on the mass and so on the lifetime. In order to save time and planning, wireless communicating sensors appear as a wiring optimization, allowing rapid installation without modification of the general electrical network. But such systems need embedded energy. In order to demonstrate the validity of wireless technology concept adapted to various environments including the space, the aeronautic or the building ones, the developments of miniature & autonomous Li-ion batteries are described in this paper. Their prototypes performances in space, aircraft flights, cold environments or harvesting conditions are discussed. New chemistries for higher energy density, above 250Wh/kg, or low temperature operating electrolytes, below -20°C, are also introduced.

Keywords: Secondary Lithium-ion Batteries, extreme environments, high energy, aerospace, harvesting

1 INTRODUCTION

To face the increasing demand for high energy, lightweight rechargeable batteries in aerospace, Li-ion technologies have to be designed taking into account environment constraints such as temperature, gravity, vacuum or vibrations. These considerations have led to engage the development of miniature and autonomous Li-ion batteries in order to demonstrate the validity of wireless technology concept adapted to those various environments including the space, the aeronautic, the military or the public one, with range from missions that require very few cycles, such as launch applications, to missions that require tens of thousands of cycles. Chemistries operating in high temperature (above 100°C) or low temperature (down to -40°C, -60°C), with high energy or power capability in conception withstanding vacuum or very low pressure with extra thin configuration and/or flexible, very small 3D dimensions (less than a few mm3) become here a necessity. Concerning satellites, tests on ground and storage between -40°C and +60°C, and tests simulating launch phases with temperature decreasing to -40°C in 30mn have to be done for instance. Low pressure proof packaging and also hermetic packaging towards vacuum are needed. The stability of the battery core, the strong cohesion between the battery and the electronic part and the integrity of the connections are crucial for sustaining vibrations.

2 PROTOTYPES DATA

2.1 Li-ion Battery for autonomous µ-system in wireless transmission for space environment

The interest of wireless sensor network for space is shown through the field of multiple applications, for example during the assembly, during integration, during thermal and vibrations test phases in order to monitor the satellite. In order to save time and planning of the phase of integration (AIT phase), wireless communicating sensors appear as a wiring optimization, allowing rapid installation without modification of the general electrical network. Indeed, a high number of sensors is needed in space applications, so wireless sensors allow to save time of integration due to the simplification of links and connections. But such systems need embedded energy, since each node has to monitor data and transmit them to the master one. In 2008, CEA with the companies Astrium (Toulouse) and 3DPlus (Buc in France) engaged, in the framework of the ASTRAL project (EADS Fundation funding) the development of miniature and autonomous communicating sensor network, in order to demonstrate the validity of wireless technology concept adapted to the space environment. The selected application consists in a wireless sensor network allowing the monitoring of satellite through the measurements of vibrations during (i) the Assembly, Integration and Test (AIT) phase on ground: satellite monitoring during the thermal and vibration system tests and during (ii) the satellite/launcher/shuttle monitoring during launch: shocks, sine 1 random vibration data. The satellite/launcher/shuttle monitoring in flight: temperature, pressure, radiation data would be another application field. The network for the demonstration is composed of a master node and 5 slave nodes (or sensor module). The master ensures the communication between the satellite and the RF network. It sends orders to the sensor modules and receives their data. The modules acquire data and send them to the master. The slave nodes have to exhibit a compact format and be autonomous: each module has its own power source in order to supply the sensor (a tri-axes accelerometer), the electronic components and the RF emitter. Its weight is limited to 150g and its overall size is below 3 x 3 x 2 cm.

Based on Li-ion technology the battery was specifically developed for withstanding the environmental constraints with a nominal voltage of 3.6V and a required useful capacity of at least 285mAh. This capacity was calculated from the using conditions during the integration phase on ground and the consumption of the slave nodes, estimated during the phase of launch. Designed in a metallic rigid can (30 x 30 x 13 in mm) its pins are directly integrated into the cage jacks of the electronic part. Finally, two versions of battery were realized: one in stainless steel and the second one lighter in titanium with a nominal capacity of 450mAh (Figure 1).

Hermeticity of the casing : < 10^{-8} mbar.L.s^{-1}

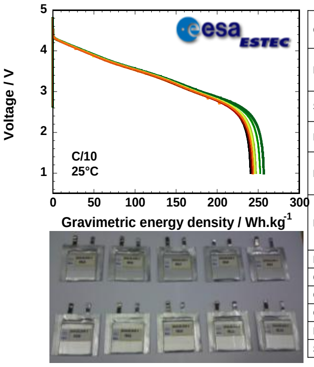
Technology	**NCA / Graphite** (CEA electrodes)
Nominal Capacity (mAh)	450
Nominal voltage (V)	3.6
Nominal Energy (Wh)	1.62
Cut-off Voltages (V)	3.0 - 4.0
Internal Resistance (mΩ)	175
Overall dimensions without pins (mm)	30 x 30 x 8.4
Volume (cm^3)	7.6
Mass (g)	15.5
Volumetric Energy Density (Wh/L)	213
Gravimetric Energy Density (Wh/kg)	105

Figure 1**:** Wireless Sensor Titanium battery for space application specifications data sheet.

Several networks with autonomous modules were thus realized. Tests have shown their good working after process and very low consumption (typically 15mA in active mode at 1kS/s). Some experiments of validation have been then organized by ASTRIUM, in order to test the transmission of data in simulated conditions in a satellite mock up. From this demonstrator, CEA battery is shown to operate with the required performances in space conditions and to allow WSN transmission [1]. New versions of wireless system based on this concept will be able to be designed for other space applications.

2.2 High Energy Li-ion Battery for space application

Among various parameters, high specific energy is the most important criteria for GEO and LEO satellites. ESA (+ EADS-Astrium) granted project allowed CEA starting developments in 2006 for high energy density (>250 Wh/kg) Li-ion cells for space application [2]. High energy Li-ion technology for space so far used is below 200Wh/kg (e.g. SAFT VES 180 SA Li ion modules for communications satellites -E3000 batteries = 2 modules of 40 cells: High specific energy of 170Wh/kg at pack level). A breakthrough is expected in this domain to be able to prepare prototype cells with at least 250Wh/kg. Cycle life and self-discharge are also crucial parameters. Low self-discharge and capacity above 80% of the nominal capacity after 500 cycles are expected (@C/2 at 100% State of Charge (SoC)), operating with high reliability & efficiency, under specific environment including large temperature range (-10°C to +50°C). In this framework, high energy density (~250Wh/kg) Li-ion cells delivered by CEA (Figure 2) were evaluated by EADS-ASTRIUM. Results stressed satisfaction of the main requirements for space application i.e. a low self-discharge (<5%/day), a large temperature range (-10°C to +50°C) but with a low life cycle.



Cell design	**Stacked** (4x4 cm²)
Packaging	Soft Density = 1.74 g/cm^3 Thickness = 110 µm
Separator	M824-type Celgard® **12µm trilayer membrane**
Electrolyte	$LiPF_6$ in three carbonates 30% < excess < 40%
Negative electrode	**Silicon/Carbon composite** Porosity = 42% 10µm copper collector
Positive electrode	**Layered-layered oxide** $yLi_2MnO_3 \cdot (1-y)LiMO_2$ Porosity = 37% 20µm aluminium collector
Electrodes loading	**~5.5 mAh/cm²**
Cell weight / thickness	~19.3g / ~5mm
Cell capacity (C/10; 25°C)	~1.5 Ah
Cut-off limits	1.0 – **4.8 V**
Mean operating voltage	~3.21 V
Specific energy (C/10; 25°C)	**242 – 257 Wh/kg**

Figure 2: 10 prototype Li-ion cells delivered to ESA after 2 formation cycles at 25°C@C/10 between 1.0 and 4.8V.

Trends were then reported for performances improvements (mainly life cycle improvement) and work started in 2011 [3] with the key driver for GEO satellite application of ca. 180Wh/kg End of Life (EoL) at battery level or ca. 220-250Wh/kg EoL at battery level.. Optimizing high energy Layered-Layered oxides ($Li_2MnO_3 \bullet LiMO_2$) synthesis process, use of nano-metric silicon rather than sub-micro size one, adding metal in the matrix with sub-micro size Si, optimizing electrode preparation, limiting the Depth of Discharge (DoD) upon cycling and working with C/Si (increase of carbon content) allowed increasing significantly life cycle by a factor of 5. However, today life cycle is still not sufficient to sustain satellite requirements where very low capacity loss per cycle is needed (<-0.01%/cycle) to reach 2000 cycles 80%DoD-typically.

2.3 High Energy Li-ion Battery for military/soldier

As for the previous application, among various parameters, high specific energy density (Wh/kg) is the most important criteria for Energy Efficient Soldier program. A high energy Li-ion battery pack was then developed for a military radio application with ROCKWELL COLLINS FRANCE (RCF). High energy Li-ion cells prototypes manufactured by CEA, assembled with cell protective control unit (PCB) were packaged by AGLO-DEV including cell to cell connections in a 4S5P mode and Battery Management System (BMS also developed by AGLO-DEV), the pack being presented in figure 3. Very high energy, intrinsic safety and high life cycle of the active materials are the most important parameters for this application. While the time allocated to this project was not sufficient to fully demonstrate the whole specifications, we proposed to investigate as prior solution a Li-ion technology demonstrating more than 50% autonomy increase compared to the commercial competitor integrating $LiCoO_2$/Graphite chemistry in 3S2P configuration, at equivalent weight. A Silicon-based active material was selected as negative electrode in a first version with $LiNi_{0.8}Co_{(0.2-x)}Al_xO_2$ (noted NCA) [4] and in a second version with $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC not shown) [5] at the positive side. Li-Si has been chosen for Soldier applications because it shows very high energy density together with addressing as well "energy" domain as "power" domain. The theoretical capacity obtained with Li-Si is 10 times higher than with conventional negative compounds (graphite). The drawback for such a technology is the large capacity fading upon cycling due to material expansion. The cycling limitation is not a show stopper because solutions are already under investigation and have been experienced at electrode level by other research centers worldwide. Limitations come from "popcorn" effect (destructive absorption of Lithium by Silicon) and surface fixing of Lithium on Silicon (stopping the Lithium transfer). Solutions based on additives or new electrolytes or nano-silicon are in progress. This kind of problems (swelling) is very identical to the one that was faced 10 years ago during the development of first graphite-based anode for Lithium batteries. So far it is controlled by using less Silicon capacity to capture Lithium. This does not alter the energy density of the Silicon and allows significant decrease of the swelling. The competition is rough and similar technology is used by competitors with various strategies.

Battery	HE (4S)	Competitor (3S)	Δ
Capacity @C/5 20°C (Ah)	5	*4.2*	+20%
Weight (g)	371	370	+0.3%
Nominal voltage @C/5 20°C (V)	13.6	10.8	+25%
Energy @C/5 20°C (Wh)	68	45	+50%
Gravimetric energy @C/5 20°C (Wh/kg)	183	120	+50%
Volumetric energy @C/5 20°C (Wh/L)	285	225	+25%
Internal resistance (mΩ)	220	330	-33%
Specific Autonomy 20°C (h) (µcycles 4,5A (6s) – 0,1A (54s))	8h30	7h20	+15%
Specific Autonomy 20°C (h) (µcycles of 45W (6s) – 1W (54s))	**12**	8	+50%
Specific Autonomy -20°C (h) (µcycles 4,5A (6s) – 0,1A (54s))	7h15	3h50*	+85%
Specific Autonomy -20°C (h) (µcycles of 45W (6s) – 1W (54s))	**10**	3h30*	+185%
Specific Energy density 20°C (Wh/kg)	163	103	+60%
Specific Energy density -20°C (Wh/kg)	136	48*	+180%

Table legends:
Italic= Calculated value
Bold = Corrected value due to additional interface resistance at electrical test bench (Pressure connection for the commercial battery not for HE battery)
*only between 80-50% SoC

Figure 3: (Left) High Energy battery pack (71Wh) made of silicon based Li-ion technology: Weight: ca. 370g. Volume: ca. 0.22L (Right, Table) HE battery performances measurement compared to commercial competitor.

Battery capacity was 21.1Ah or 71.5Wh (Nominal voltage =3.39V at C/5 & 20°C). The cells weight (excluding pack assembly components) is 180 g, therefore an energy density of 255 $Wh.kg^{-1}$. While silicon technology is swelling or "breathing" upon cycling or depending on state of charge (SoC), volumetric energy density has to be associated with its SoC. Therefore, specific energy of ca. $500Wh.L^{-1}$ at 100% SoC is reported. Voltage reaches around 10.5 volts with 4 series cells. The commercial reference is a prismatic pack size 85mm (height) by 70mm (wide) by 40mm (thick); similar weight (370g). Test protocol was provided by RCF: repeated 1 min micro-cycles, made of 4.5A - 6s pulses, corresponding to radio emission, followed by constant current at 100mA during 54s, for reception or stand-by operating modes. From these data the battery specific autonomy was assessed and compared to the competitor. Higher autonomy at 20°C (+60%) & even more at low temperature -20°C (+180%) compared to commercial battery is shown (see Table in figure 3).The specific pack design developed by AGLO-DEV for this « breathing » technology exhibits a high reproducibility in term of weight (<0.5%) and resistance (<0.5%).

2.4 Thin battery for structural health monitoring sensing devices in aeronautics

Within an European granted seventh framework Aero R&D program, named TRIADE, a battery thin (<1mm) & hermetic (for low pressure environment), hard casing is developed aiming powering autonomous sensors integrated into planes wings and helicopters rotors within a smart tag format. This battery is expected to be recharged when the aircraft is on ground, with life expectancy of about 10 years, to be resistant to very severe environmental conditions, to corrosive environment, to mechanical strain (vibrations, acceleration…), operational on a large range of pressure (50 to 1100mbars) and on a large range of temperature (-50°C to 95°C). A rigid metallic casing in stainless steel welded by laser using glass to metal seals is here suggested to withstand low pressure. A specific configuration of the cell with connections by pins going through the electronic PCB to use all the available volume and to withstand vibrations is also proposed. Moderate energy density chemistry ($LiFePO_4$/Graphite) with high cycle life (known > 800 cycles), operating between 2.6 and 3.7V (nominal voltage 3.2V) together with a specific electrolyte for working at very low temperature (down to -40°C) is integrated. The electrodes and separators of the inner cell are stacked in order to optimize embedded capacity. More than 10 cells were manufactured and delivered exhibiting a nominal capacity of about 170mAh (Figure 4).

Technology	$LiFePO_4$ / graphite
Nominal Capacity (mAh)	170
Nominal voltage (V)	3.2
Nominal Energy (Wh)	0.544
Cut-off Voltages (V)	2.6 – 3.7
Internal resistance (mΩ)	TBD
Overall dimensions without pins (mm)	57 x 55 x 1.5
Volume (cm³)	4.7
Mass (g)	17.2
Volumetric Energy density (Wh/L)	115
Gravimetric Energy Density (Wh/Kg)	31.6

Figure 4: Aero Li-ion Cell electrical and mechanical specifications.

A stable electrical behavior is reported for the first set of operational batteries. Integration tests are currently under progress. A low temperature electrolyte was especially developed to operate with $LiFePO_4$/graphite technology. Testing different solvents, salts, additives and mixtures allowed stressing two families working at -40°C for this system, made of binary or ternary mixtures with additive which allow a capacity recovered at 40-50% (Figure 5). To succeed in this development, a deep work has been carried out on both cell and components conception (casing design, electrolyte filling opening…), the glass-metal connections under small and tight dimensions constraints, the electrochemical core design (electrodes, separator, stacking assembly, connections…), the electrical insulating of internal casing to avoid short-circuits, and the low temperature operating electrolyte in order to restore capacity below -40°C.

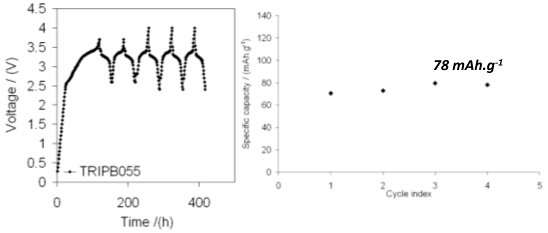
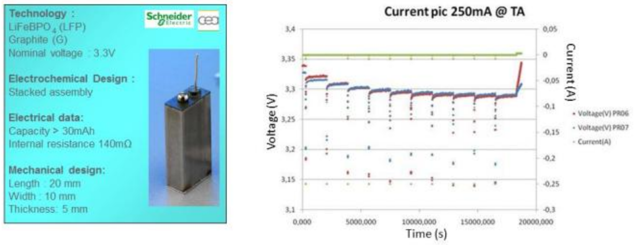


Figure 5: Aero battery cycling curve at -40°C (Left) and recovered specific capacity at - 40°C (Right) @C/20 rate.

Further work is currently under progress to improve process robustness, to qualify the cell over accelerating and vibration tests and for low temperature electrolyte improvement. Work is also under progress in order to develop high temperature operating Li-ion technology, above 100°C. This requires innovative cell conception introducing advanced components like separator, electrolyte, casing materials. Preliminary tests on CEA High Temperature cell display 90% capacity restituted at 150°C after 5 cycles @C/20 rate (not shown).

2.5 Rechargeable smart battery for energy storage from photovoltaic energy harvesting within a self-powered wireless multisensory platform

For small volume, high autonomy, long life autonomous products, Li-ion technologies become prior candidates. CEA with Schneider demonstrated a smart battery (figure 6) that sustains discharge peak currents at extended temperature range, in various humidity conditions for indoor and outdoor with low self-discharge current and long life time, in a competitive cost.


Technology :
$LiFeBPO_4$ (LFP)
Graphite (G)
Nominal voltage : 3.3V

Electrochemical Design :
Stacked assembly

Electrical data:
Capacity > 30mAh
Internal resistance 140mΩ

Mechanical design:
Length : 20 mm
Width : 10 mm
Thickness: 5 mm

Figure 6: Smart battery data sheet (Left) and voltage-current in function of time (Right) under pulses testing (250mA, 5ms, 30min relaxing) at ambient temperature.

The ca. 30mAh Li-ion cell was shown to sustain current pulses between 30 and 250mA (5-10ms), from ambient to -40°C temperatures. The lower voltage limit is >3V except for 150mA pulses at -40°C (U pulse >1.5V). An ageing test protocol was defined in order to simulate in an accelerated mode the battery cycle life. More than 2000 cycles in a pulse mode (150mA, 7.2s without relaxing time) were computed for this promising battery that will have to operate between -40 to +60°C with relative humidity from 10 to 95% rH. A similar accumulator was also demonstrated to operate if coupled with a thermoelectric generator for wireless transmission.

3 PERSPECTIVES

CEA experienced miniatures batteries for very various domains of application including niche markets (medical, aerospace, military…), but also for high volume markets (home, lighting …). Specific performances required very high energy density, high lifetime (10 years and more), operating in high temperature (above 100°C) or low temperature (down to -40°C), withstanding vacuum or very low pressure/vibration in extra thin configuration and/or flexible or very small 3D dimensions. From this background (TRL ranging from 1 to 6), work is currently under progress to develop higher capacity cells with a nominal capacity of about 30–50Ah, in order to reach >270-300Wh/kg in cylindrical or prismatic casing, using rigid casing (Stainless steel or Al or Ti) or soft pouch. Work is also still under progress in order to develop components solutions to allow operating at both low (-55°C) and high temperature (+105°C).

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