Supercapacitor for Launcher Applications

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1. INTRODUCTION

Although supercapacitors are widely used on ground for multiple applications such as cars, buses, trains, planes, cranes, elevators, etc. there are today no supercapacitors with space heritage in Europe. The main potential applications of supercapacitors in space are within launchers -as described in this section- and also within satellites e.g. to power antenna or solar panels movements, high pulse payload such radar or LIDAR, etc.

Historically in launchers, and specially for ARIANE, electrical power generation has not been a big issue as missions were very short (less than one hour), consisting essentially of Geostationary Transfer Orbits (GTO). As a result, power source technologies remained unchanged for a long time: AgZn batteries for avionics and NiCd batteries for pyros.

Nowadays the scope of missions as well as their duration is becoming larger and larger, varying from 1 hr (GTO) to 10 hours (GTO+, Medium Earth Orbit) thus changing dramatically the energy and power requirements.

Li-ion batteries have become the most popular power systems for space applications but are slow to charge and discharge, lose 30% of their energy through heat alone and have limited power available.

Even if supercapacitors are not currently used in launchers, they hold a tremendous potential that has been investigated for about 10 years, mostly because of their ability to charge and discharge instantly, their very high power density and their resilience to millions of life cycles.

One key difference between supercapacitors and batteries is the ratios of energy density to power density: supercapacitors have a higher power density and lower energy density than batteries. Therefore, high power Li-ion batteries are more competitive than supercapacitors in applications where discharge times longer than about 10s are needed.

For applications with charge / discharge times less than about 10s and very high number of cycles, supercapacitors will be more appropriate thanks to a higher power density and a cycle life that does not depend on the Depth of Discharge (DOD) as Li-ion batteries.

PROJECT OVERVIEW

From the first space missions to the present day's technological wonder, the energy and power needs continue to increase. Space missions come in all shapes and sizes and allow us to do things that most of us take for granted. Today, improved electrical power subsystems shall be developed to cope with the general trends observed in space applications

with powerful payloads and increase of mission duration. All space applications batteries have two critical factors that engineers strive to optimize: specific energy and specific power.

Currently the batteries used to power supply some applications, like pyrotechnics or EMTVC, are oversized. Indeed, their power need profile are mostly composed of power pulses and their energy need is thus fairly low. The batteries used are oversized to cope with the power pulses. Their replacement by high power sources like supercapacitors will enable interesting mass savings.

Aiming at disrupting the established market of high power energy storage, the Vertically Aligned Carbon Nanotubes (VACNT) developed by NawaTechnologies opens the realms of high energy capability to supercapacitors. This new strength, added to their high power capability, high cyclability and thermal efficiency has the potential to create the ultimate energy storage product.

A promising market is outlined by the possibility to use this technology in launcher applications. Three applications were reviewed: The Electro-Mechanical Thrust Vector Control (EMTVC), the Pyrotechnics and Safeguard. EMTVC was selected as long-term objective of the TRP program, while the Pyrotechnical application was selected for the short-term goal of this project, allowing to go into detailed design and put the technology to the test. Currently out of reach however, the Safeguard application has been temporarily discarded.

The potential of the technology has been compared to a thorough review of the COTS products in light of the different applications. It has been observed that the required vibration environment was unusual and inapplicable to most of the observed products.

The need for testing the technology in the high vibration environment was defined and a representative Bank of Supercapacitors (BOSC) composed of 11 cells provided by NawaTechnologies was built (See Figure 1 and 2). The packaging has been tailored to the pouch cell. It allowed to offer a good interface to the cell and prevented it from unnecessary damages.

After integration of the supercapacitor cells, tests were carried out on the BOSC assembly and on a single spare cell.



Fig. 1. Supercapacitor pouch cell by NawaTechnologies

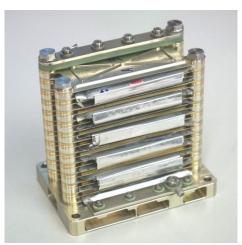


Fig. 2. ALMATECH Bank Of SuperCapacitors made out of 11 pouch cells in series

2. SUPERCAPACITOR CELL AND BOSC DESIGN

2.1 Design of cells

During the project multiple technologies of cells and electrolytes were studied to fulfil requirements given by Ariane Group. As final R&D trade-off, two technologies of electrodes were deeply investigated VACNT and P3MT with combination of multiple electrolyte composition.

Cell voltage increase was also investigated. Indeed, the cyclability, capacitance and the Voltammogram form were measured by increasing the voltage from standard 2.7 Volts by steps of 0.1 Volt. A voltage of 3.3V was achieved for Et4NBF4 1M PC: A good cyclability is reported at room temperature for EDLC (benchmark) and VACNT. But an improvement is still needed due to poor self-discharge and leakage current results.

Other secondary axes of improvement were also investigated such as:

- Decrease encapsulation mass
 - Pouch mass is currently 3.47g.
 - New configuration with more layer inside is on-going
 - Decrease the mass of the electrodes stack
 - Separator, no significant gain (only a few mg)
 - o Reduce tabs thickness from 40µm to 20µm and verify VACNT synthesis and tabs weldability

A VACNT representative cell in mass and dimensions of the future cell was provided in order to perform a vibration test and vacuum tests. The mass of the cell was somewhat higher than the specification: 27g.

The vibration test objective was to test the packaging interfacing and the VACNT supercapacitor pouch cell at launch loads.

The final consolidated design of the pouch cell was defined as reported in Table 1 below and performances were below those expected with a large range of variation.

				Resume Energy cell						
W3			1	At RT	Spec (PDR)	Measured (Average)	Measured (Deviation / %)			
L3		11	12	Capacitance / F 200		84.1	+/- 20			
				mass cell / g	16.5	9.7	+/- 5			
-	W1			ESR (EIS) at 1Hz / m Ω	35-45	74.9	+/- 18			
H2 I	W2			ESR (EIS) at 1kHz / m Ω	-	49.2	+/- 16			
			H1	Maximum voltage* / V	2.7	i.	-			

L 1/ cm	L 2/ cm	L3 / cm	W1/cm	W2 / cm	W3 / cm	H1 / cm	H2 / cm	NAWA Treconcisional
8	7	5.5	4.6	3.6	≥ 1.5	0.2	0.02	

*To avoid a plausible degradation, during the preliminary characterisations, the cell voltage is limited to 2.5V at room temperature

Table 1. Design of the pouch cell

2.2 Design of the BOSC and preliminary test

In order to encapsulate the pouch cell, stacks were designed that had to be light but strong enough to sustain launch environmental loads. Total mass of one single stack including cell: 72g.

Preliminary vibration and vacuum test on one single encapsulated cell were performed. The verification of the good sake of the cell was assessed by the electrical test (see §3.2).

The complete BOSC was then designed and manufactured based on this cell encapsulation. Concept designed is modular and allow to increase or decrease number of cells. Random and Sinus simulations were performed to validate

the mechanical design of the Bosc. These simulations demonstrate that the frequency of the first Eigen Mode is higher than 840Hz and that the designed structure is stiff enough to support environmental launch conditions.

Output Set: Mode 1, 841.034 Hz, Deformed(2.264): Total Translation, Nodal Contour: Total Translation

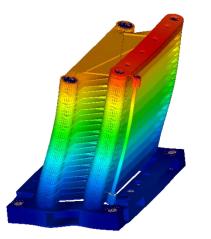


Fig. 3. First Eigen Mode shape

During assembly, a major leak tightness issue occurred during the glue curing at high temperature that destroyed all the cells that were manufactured. This major NCR had an important impact on project planning and cost. A new BOSC was finally re-manufactured that contained only 2 VACNT supercapacitor functional cells in series and 9 dummy cells (containing no active material) in series. Total mass of the assembled BOSC was 552g.



Fig. 4. Picture of the BOSC

3. SUPERCAPACITOR CELL AND BOSC TESTING

3.1 Objectives

General objectives of the tests were to demonstrate that the cells and the BOSC can survive and work properly as required in the specific pyro application under stringent environmental conditions of launch and space.

Specific objectives of electrical tests are to measure and qualify the electrochemical performances of the cell during different conditions. Such tests lets to follow the ageing of cells during their use and their storage. The functional tests are performed to ensure the supercapacitor cells are compliant with the technical requirements specification.

Electrical and environmental tests have been conducted at Cell and BOSC levels in order to detect issues at different levels.

3.2 Preliminary tests on representative cell

Preliminary electrical and environmental tests have been conducted in preliminary prototype VACNT cell and associated single stack structure. The outcomes of the tests were that structure held well the pouch cell during the environmental loads, and moreover that no electrical performance degradation was observed even after stack reached vacuum level.

Indeed, the electrical measures showed that the properties were kept within variation of test benches measurement errors, with a slight increase in capacitance to be noted, supposedly due to the effect of forming the cycling had on the cell.

Visual and Low Sine vibrational inspections showed no evidence of structural degradation, while providing characteristics of the packaging, as its first natural frequency at 600 Hz, its damping factor of 3.8% and its Quality factor Q of 13.3. These last two numbers show that the glue interface of the SPYRO plays a non-negligible role in its structural integrity, as the usual damping factor for metals lies within 2%.

The high natural frequency of 600 Hz shows that the design is rigid enough to avoid a too large response during the sinusoidal tests that go up to 375 Hz. However, the damping caused by the glue and cell interfaces allow the initiation of the response at 100 Hz already.

This will need to be monitored to limit the stress and the eventual fatigue in larger BOSC integrations. The stack reached the level of vacuum of 10-5 Torr without issue. Despite some grid noise at 50Hz, electrical tests showed that performance of the cell stay stable after the two tests.

The Figure 5 indicates that the structure was not spared by the different tests. It has however stayed stable and showed no sign of unusual wear.

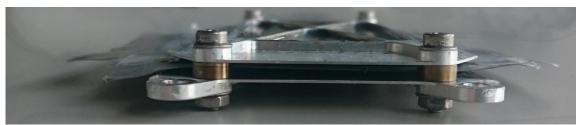


Fig. 5. SPYRO at the end of the test campaign

3.3 Test on final Cell and BOSC

The following tests have been performed on a final cell reference cell alone and in a BOSC composed by 2 functional cells and 9 dummy cells in series. Approximatively the same sequence of test have been followed by the reference cell alone and the BOSC. In the BOSC three additional tests have been added. The first is an electrical test at low temperature the second is a mission profile after the thermal cycling and the third is a thermal vacuum test with an additional functional test to check eventual degradations.

3.4 Functional Test conditions

The cell under test and the BOSC were submitted to electrical functional test at various temperatures, thermal cycling, vacuum and mission profile according to test plan and test scheme sequence presented in Figure 6.

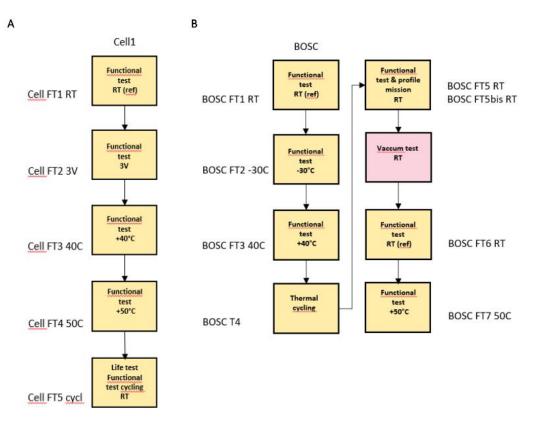


Fig. 6. Test sequence for cell 1 and BOSC

Three Main electrochemical tests are performed on the cell and on the BOSC assembly to test electrical performance and health of the cells. These tests are Cyclic Voltammetry (CV) used to determine the capacitance of the cell /BOSC, Galvanoamperometry (Galvano) which determine the discharge capacitance and ESR and finally Electrochemical Impedance Spectroscopy (EIS) at different frequencies to measure ESR at different frequencies. These three kind of tests are different, their results cannot be compared between them as they uses different boundaries.

3.5 Electrical tests results 3.5.1 Cell1 test results

Lifetime on cell1 was demonstrated for more than 100 cycles. The Cell1 successful passed the different functional tests high voltage 3V and high temperature 40° and 50°C. Cell1 presents a capacitance around 50F with a resistance ESR at 1Hz around $20m\Omega$ and $15m\Omega$ at 1 kHz.

Except the fact that performance need to be improved, test performed on Cell 1 and presented in Table 2 show that all tests performed have no degraded the initial electrical performance of the cell.

step	т / °С	Voltag e / V	C _{cv} / F	C _{BOSC} at 1 A /F	C _{BOSC} at 3.5A / F	ESR AC / mΩ	ESR 1Hz / mΩ	ΔESR / mΩ	ESR 1kHz / mΩ
FT1 RT	23	2,7	49,5	57,0	56,9	14,1	19,9	5,7	14,0
FT2 3V	23	3	49,5	56,1	57,0	14,3	20,0	5,7	14,2
FT3 40C	40	2,7	48,8	56,7	56,0	13,5	18,6	5,1	13,4
FT4 50C	50	2,7	48,4	56,4	55,7	13,6	18,6	5,0	13,5
FT5 RT	23	2,7	46,4	54,7	54,6	15,1	20,7	5,6	14,9

Table 2. Electrical test results of the Cell1

3.5.2 BOSC assembly test results

The BOSC was functional until the vacuum test. But the electrical performance of the BOSC is not optimal. The BOSC is made of two cells in series, so we expected a BOSC capacitance around 25F and an ESR at 1Hz 50m Ω . But the BOSC presented a capacitance around 18F and ESR around 130m Ω . So we can suspected two cells too dissymmetrical. The degradation in performance was acceptable and below the required values 20%.

The Bosc was tested with a typical mission profile such as presented in Figure 7. No important degradation was observed on the BOSC electrical performances with respect to previous values. Nevertheless, due to test device limitation and the BOSC having only two cells, the test cannot be considered relevant.

Step	T/°C	C Cv / F	Csyst / F at 1 A	Csyst / F at 3.5 A/F	ESR AC / mΩ	ESR 1Hz / mΩ	ΔESR / mΩ	ESR 1kHz / mΩ
FT1 RT	23	18,1	16,9	15,3	88	130	42	91
FT2 -30C	-30	9,9	9,0	0,4	251	422	171	298
FT3 40C	40	19,2	18,3	17,3	62	90	28	63
FT5 RT	23	16,9	16,2	14,3	92	130	38	95
FT6 RT	23	5,1	N/A	N/A	1132	1411	279	1303
FT7 50C	50	7,6	5,2	N/A	623	726	104	658

Table 3. Electrical test results of the BOSC

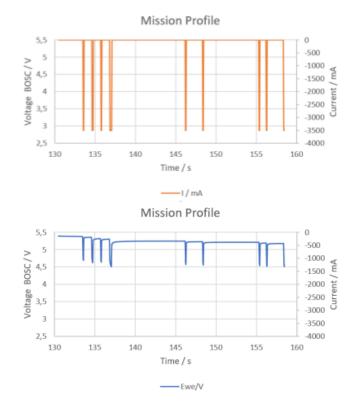


Fig. 7. Typical Mission Profile

Moreover, the electrical performance of the BOSC at low temperature (-30°C) was very low (around, capacitance half decreased and ESR increased 3 times).

During the vacuum test, the BOSC had a leak of solvent even if no visual damage was observed. The target pressure of 10-5mbar cannot be reached and Almatech decided to abort the test after 7h where pressure doesn't fall under 10-4mbar due to toxic hazard electrochemical substances inside the cell. The micro-leaks were confirmed by the loss of mass (2.27g) and the decrease in electrical performances. The electrical tests results can be observed in row starting with FT6 RT where equivalent resistivity increase significantly and capacitance drop down significantly.

4. CONCLUSION AND OUTLOOK

Currently, the VACNTs supercapacitors technology developed by NawaTechnologies present some limitations in terms of electrical performances for the aimed application which lead to a TRL limited to level 4-5 instead of 7 planned at the beginning of the project.

- Capacitance of the cells of the order of magnitude of 60F, versus the 200F expected
- Specific energy at cell level of the order of magnitude of 4.80Wh/kg, versus the 15 Wh/kg expected

Furthermore, the VACNTs supercapacitors technology developed by NawaTechnologies present some limitations in terms of cell design:

- Lack of electrical performances at negative temperature of -30°C
- Poor behaviour of the cells assembled in BOSC under vacuum conditions.

Based on the test results that were achieved, the following improvements are proposed:

- Cell material and electrolytes in order to improve the electrochemical performances.
- The goal would be to reach 15 Wh/Kg in a TRL 5-6 in 2023 / TRL 7-8 in 2025
- Leak tightness under vacuum to be improved to reach 0.0013 Pa (10-5 Torr) by increasing the sealing thickness or improving the sealing process itself.
- Improvement of the characterization of the cells: Galvano static cycling should be conducted instead of cycling Voltammetry
- BOSC must be validated including 11 functional cells in order to reach an operating voltage of 32V
- Vibration test to be conducted on the BOSC

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