Lithium-sulphur batteries for space applications

Géraldine Palissat and Valéry Gineste***

* *Airbus Defense and Space, Space Systems,*
51-61 Route de Verneuil, 78130 Les Mureaux, France
** Airbus Defense and Space, Space Systems,
31 rue des Cosmonautes, Z.I. du Palays, 31402 Toulouse Cedex 4, France

Abstract

The current lithium-ion cells are limited to about 175 Wh kg^{-1}. In contrast, the first lithium-sulphur cells tested exhibited promising performances around 200 Wh kg^{-1}, and the technology evolves very quickly enabling to achieve more than 400 Wh kg^{-1} on cell level in the next years. The characterisation of Li-S cells is performed using standard capacity measurement, electrochemical impedance measurement, cycling at various C-rates and temperatures and lifetime assessment. Thermal stability of Li-S technology is reported. By the same way, improvement of the Li-S technology cycle stability is reported with 1600 cycles reached by the tested cell.

1. Introduction

Energy storage devices, which are used in many space applications, are facing unique challenges. Most of such applications (typically geostationary and low-earth orbit satellites, next-generation launchers, reusable launch vehicles and human exploration missions) depend on high performance, delivered by highly specialised batteries. Indeed, the electrical power subsystems designed today for space applications, are required to cope with new trends driven by the fast-growing business: more powerful payloads meaning more power stored on-board, global increase of mission duration, ever more constraining safety requirements, lower satellite masses and smaller volumes made available for the battery subsystem. The particular characteristic that all battery engineers and researchers strive to optimise is the specific energy. Indeed, this energy per weight ratio is a major criterion in the battery choice as every gram sent in orbit has to be paid for dearly in launch costs.

Rechargeable batteries in combination with solar arrays are popular for powering earth orbiting satellites where batteries can constitute a significant proportion of the total mass of the spacecraft. Launch vehicles use high capacity batteries requiring high energy density to power avionics systems. Weight reductions resulting from the use of Lithium Sulphur batteries offer significant cost advantage and increased load carrying capacity for space applications.

In this context, lithium-sulphur batteries are an interesting candidate due to their high energy density compared to current batteries used in launchers and current spacecrafts. Indeed, Sulphur cathode offers a theoretical capacity of 1675 mAh / g and a theoretical energy density of 2600 Wh / kg with the fully utilization of sulphur in the following process:

$$16\ Li^+ + S_8 + 16\ e^- \leftrightarrow 8\ Li_2S \qquad \textbf{(1)}$$

A rechargeable Lithium-Sulphur Battery (LSB) is composed of a lithium metal anode and sulphur-based cathode, as shown in the figure below.

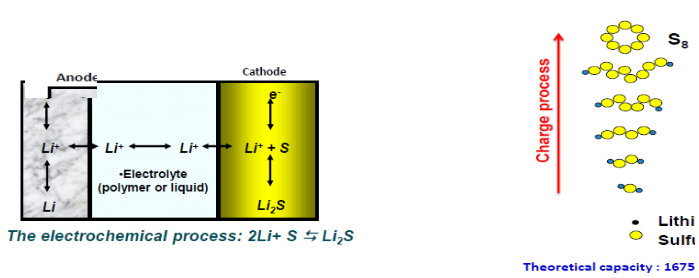

Figure 1: Lithium-sulphur battery cell overall reaction [1]

Lithium-Sulphur battery (Li-S battery) works on the basis of redox reactions between lithium metal anode and sulphur cathode. The extreme reactivity of lithium has hindered many an attempt to safely harness its power as a pure metal anode. In spite of this, lithium has always been a desirable choice as an electrode material due to its low equivalent weight, highly negative reduces ion potential and high specific energy [2; 3]. For these reasons, considerable research and development has been dedicated to making this a safe and viable commercial option. Those reversible reactions enable the cycling of the lithium-sulphur cell. Cycle life of rechargeable batteries is critically important in satellites applications, and is one of the challenges of the Lithium-sulphur technology.

2. Experimental methods

It is common practice to perform screening assessments on each cell prior to any characterisation tests. This ensures that the manufacturer's specifications are met, that any defective cells are found and that the variation in cell characteristics across the batch is determined. This is especially necessary for the Li-S cells used in this work, as the cells are produced in low batch numbers and so batch uniformity may be variable. Indeed, the screening tests provided as much information about the cell as possible with minimal impact on its future performance**.** The electrochemical behaviour of the cell was also investigated using discharge at various C-rates, charge / discharge at various temperatures, satellites cycling at various Depth of Discharge (DOD) and Electrochemical Impedance Spectroscopy (EIS) at different depths of discharge and charge. A screening test algorithm was completed for each Li-S cell tested, as follows:

- Charge cell at the manufacturer's recommended current rate of 0.35 A to 2.45 V,
- Rest for 30 seconds,
- Impedance measurement in the range of frequency 100 Hz; 100 kHz,
- Rest for 15 minutes,
- Discharge cell at the manufacturer's recommended current rate of 0.68 A to 1.50 V,
- Charge cell at the manufacturer's recommended current rate of 0.35 A to 2.45 V,

2.1 Standard capacity measurement (SCM)

The capacity found in a screening cycle can also be used to define a "Standard Capacity Measurement" (SCM), which tells the user how much of the full capacity is available using a predefined current rate. A standard capacity measurement (SCM) is used to determine a cell's nominal capacity at a predetermined current rate and is referenced as a percentage of the cell's total capacity. This is useful information because determining an accurate measurement of the total capacity of a cell requires a very slow discharge (~2 days) in order to minimise resistive losses. If it were necessary to perform a full capacity measurement each time a cell was used in a test, that test would be very time consuming. Therefore, knowing what percentage of capacity an SCM cycle yields means the total capacity can be accurately determined from a much shorter test (~10 hours in the case of the C/10 rate).

2.2 Electrochemical Impedance Spectroscopy (EIS)

EIS studies the system response to the application of a periodic small amplitude alternative current (ac) signal. Direct Current (dc) transient response of electrochemical systems is usually measured using potentiostat. In the case of EIS an additional perturbation is added to the dc signal in order to obtain the frequency response of the system.

These measurements are carried out at different ac frequencies and, thus, the name impedance spectroscopy was later adopted. Analysis of the system response contains information about the interface, its structure and reactions taking place there. Cell's impedance is measured from 100 Hz to 100 kHz with differential current probes. The system impedance may be measured using frequency response analysis. The initial cells internal resistance at 1 kHz shall be measured.

2.3 Lifetime

The lifetime of the Li-S cells studied in this paper, corresponds to most common scheme of satellites applications. The cycling tests will be performed at 20°C.
A first one is given for a Li-S cell discharged by approximately 20 % at – 680 mA (C/5) of its full charge before being recharged again at 340 mA (C/10) to 2.35 V. A reference measurement has been done each 200 cycles.
A second cycle life mode is given for a Li-S cell discharged by 100 % at – 680 mA (C/5) of its full charge before being recharged again at 340 mA (C/10) to 2.35 V. A capacity measurement is automatically done at each cycle.

2.4 General characterisation

Cell Potential

The cell voltage for the Lithium-Sulphur couple is determined by comparing the standard reduction potentials for each electrode. Equation 2 gives the reaction at the Sulphur cathode.

$$S_{(S)} + 2e^- \leftrightarrow S^{2-} \qquad \textbf{(2)}$$

The standard reduction potential of this reaction relative to the Standard Hydrogen Electrode (SHE) is -0.48 V.

Equation 3 gives the reaction at the lithium anode.

$$Li_{(S)} + 2e^- \leftrightarrow Li^{2+} + 2e^- \qquad \textbf{(3)}$$

The standard reduction potential of this reaction when compared to the SHE is -3.05 V.

It is convention to determine the total cell potential by calculating the difference between the potentials of the cathode and the anode. This potential difference ΔV determines the maximum open circuit voltage of the cell so:

$$\Delta V = E_{cathode} - E_{anode} \qquad \textbf{(4)}$$

The lithium-sulphur cell voltage, given by Equation (4), is 2.57 V. In fact, as will be shown, the potential is dependent on the concentration of different species within the cell and varies as these species undergo redox reactions during cycling.

Capacity and C-rate

The total capacity of a cell is defined as the amount of charge, given in Amp hours (Ah), that a cell can deliver when discharged from 100% State-of-Charge (SoC) to 0% SoC. To get the maximum amount of charge from a battery requires an extremely slow discharge so that there are minimal losses from resistance and heat dissipation in the cell. At high current the rate-dependent difference in potential between the EMF and the terminal voltage, caused by internal resistance, means that the cell reaches its safety voltage limits before the cell's full capacity is realized.

It is standard practice to use the capacity of a battery to define the current levels used on it. The lithium-Sulphur cell used in this work has a nominal capacity of 3.40 Ah and so it would take 1 hour to discharge the cell at 3.40 A. This is known as the C-rate and charge or discharge currents are often given as fraction or multiple of this rate. For example, C/2 would be 1.70 A and would discharge the cell, theoretically, in two hours.

3. Experimental results

3.1 Standard capacity measurement (SCM)

As indicated in the paragraph above concerning Standard Capacity measurement, the test is performed for each Li-S cell, following the completion of the algorithm mentioned. Furthermore, an Electrochemical Impedance Spectroscopy measurement is performed from 100 Hz to 100 kHz with differential current probes. The real part of the impedance at 1 kHz is equivalent to the internal resistance of the Li-S cell.

The table 1 hereafter presents the obtained results. This screening has been performed at T = 30 °C for each Li-S cell.

Table 1: initial characteristics of the Li-S cells

	Cell 1	**Cell 2**	**Cell 3**	**Cell 4**	**Cell 5**
Batch	Handmade pouch cell	Handmade pouch cell	Automated line pouch cell	Automated line pouch cell	Automated line pouch cell
Charge capacity (Ah)	2.638	3.210	3.736	3.750	3.613
Discharge capacity (Ah)	2.185	2.786	3.294	3.223	3.304
Internal resistance @ 1 kHz (mΩ)	59.99	61.28	60.72	54.27	57.92

As indicated in the table above, the charge capacity of the handmade pouch cells is slightly lower than the values of the supplier's datasheet. Also, the automated line pouch cells, produced under manufacturing control processes, exhibit electrochemical characteristics perfectly compliant with the datasheet provided by the manufacturer. That shall be explained easily by the fact that automated line pouch cells enable to obtain good and reproducible performances.

The charge capacity is not completely recovered during the discharge, due the parasitic reactions well-known under the name of polysulphides shuttle mechanism. Indeed, during the discharge of a new Li-S cell at the positive sulphur electrode, lithium ions in the electrolyte are combined with sulphur and electrons to form a polysulphide, Li_2S_8. The electrons come via the external circuit (load) from the negative electrode where lithium molecules give up electrons to form positively charged lithium ions. The Li_2S_8 that is produced immediately reacts with more lithium ions from the electrolyte and more electrons to form Li_2S_6. The process continues, and the reactions presented in figure 1 shall occur, and at each step more energy is given up and passed to the load. The discharge profile Cell potential = f (discharge capacity) at 30 ° C, using the charge / discharge profile described in paragraph 2, enable to illustrate this purpose.

The discharge profile of the 5 cells was studied and compared to theoretical discharge profile of Li-S cell found in the literature [4].

3.2 Discharge profile: cell potential

For cells 1 and 2, the charging profile was performed between 1.5 V and 2.35 V at 0.35 A and 30 °C. For the cells 3 to 5, the charging profile was performed between 1.5 V and 2.45 V at 0.35 A and 30 °C.

The figure hereafter shows a discharge voltage profile for the first cycle of the 5 Li-S cells tested in this paper.

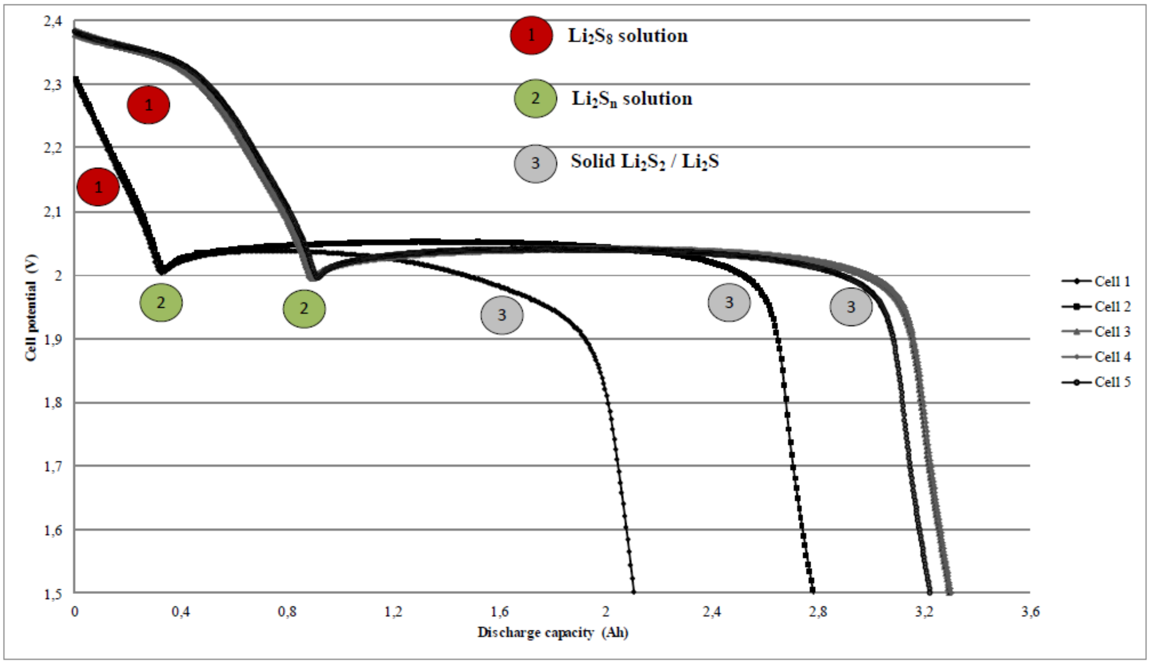

Figure 2: Discharge profile of the lithium-sulphur cells tested at 30°C.

As shown in the figure 2, during the discharge the following sequence of reactions takes place:

- Formation of polysulphides Li_2S_8, by combination of electrolyte with sulphur and electrons (Region 1),
- Reaction of Li_2S_8 with lithium ions from the electrolyte to form low-order polysulphides Li_2S_n (Region 2),
- the reactional mechanism described above continue and involves the formation of Li_2S_2 and finally Li_2S in the Region 3, which corresponds to the voltage plateau 2V – 1.9V.

The difference of end-voltage applied during the charging profile of the cells 1 and 2, explains a part of the variations observed on the presented curves.

3.3 Charge / discharge profiles: capacity measurement

Repeating the measurement of capacity using the algorithm described in the paragraph 2, enabled to observe the stability of the electrochemical performances of the Li-S cells tested. Furthermore, that enables to show the reproducibility pf the performances during the first cycles and to calculate the capacity fade due to parasitic reactions observed between the first and the second charge cycle. The obtained results are presented in the figures hereafter for charge and discharge.

The figure 3 presents the charge capacity curves of each tested Li-S cell for the three first cycles.

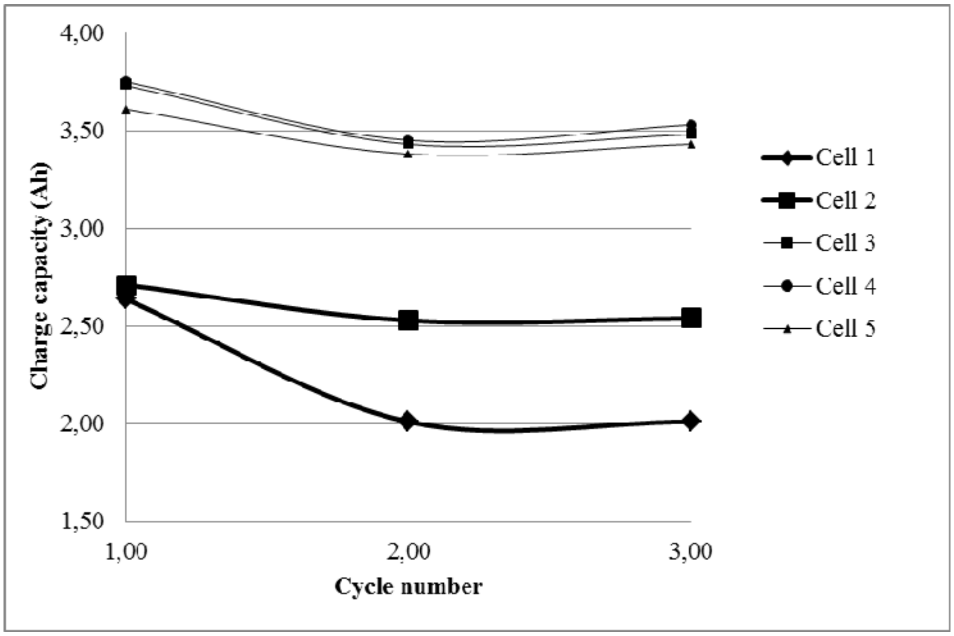

Figure 3 : Charge curves at T = 30°C for each Li-S cell

The five curves have the same shape and present a decrease of the charge capacity at the second cycle, typical of the Li-S cells. Indeed, this irreversible capacity loss is widely described in the literature. As it was shown in [5], some of the Li_2S that forms during discharge remains on the cathode even after full charge. This Li_2S does not contribute to any future electrochemical reactions causing irreversible capacity loss.
This decreases the active area of the cathode and removes the Li_2S, to which it is attached, from future electrochemical reaction.

The figure 4 presents the discharge capacity curves of each tested Li-S cell for the three first cycles.

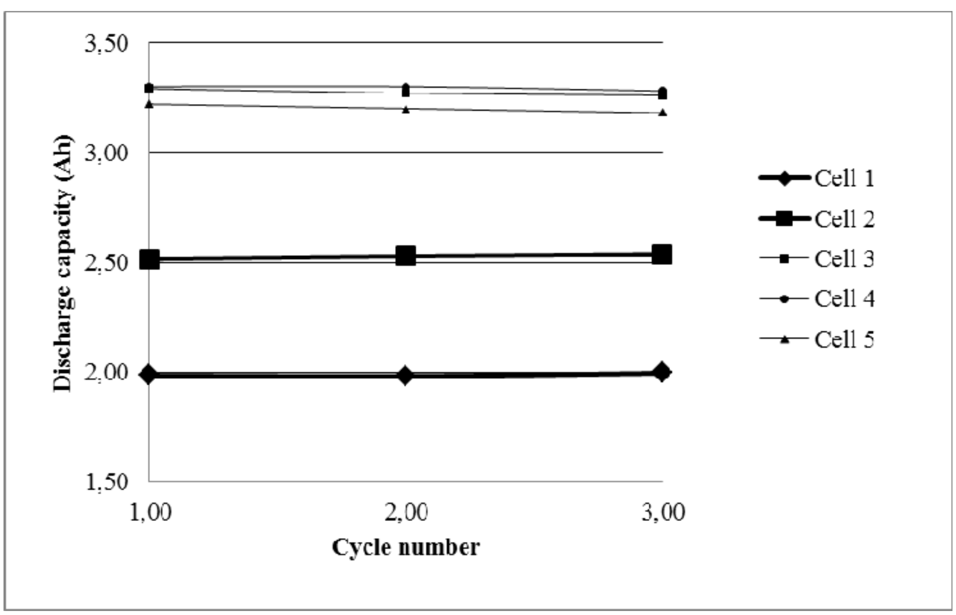

Figure 4 : Discharge curves at T = 30°C for each Li-S cell

As shown in the figure just above, the discharge capacity is stable for each Li-S cell tested, independantly of the manufacturing process, handmade or automated line pouch cells. The figure indicates that for each automated line Li-S pouch cells (cells 3, 4 and 5), the experiments conducted shown that the discharge capacity couldn't reach the maximum value (i.e. the charge capacity). Indeed, the reduction of high order polysulphides on the anode would have a measurable effect on the discharge capacity. For the handmade Li-S pouch cells, the behaviour is slightly different. Indeed, for the cycles 2 and 3, the discharge capacity of these cells reached the maximum value which shall correspond to an inhibition of the polysulphides shuttle, as described in the literature [6].

3.4 Preliminary gravimetric energy assessment

A preliminary gravimetric energy assessment has been performed on the automated line Li-S pouch cells to give an idea of the achieved energy for these first tested cells, which are the first developed by the manufacturer. The table 2 hereafter presents the results.

Table 2: preliminary gravimetric assessment of the Li-S cells

	Cell 3	**Cell 4**	**Cell 5**
Charge capacity range (Ah)	3.736	3.750	3.613
Charge energy (Wh)	9.153	9.187	8.851
Gravimetric energy (Wh / kg)	187	195	185

3.5 Discharge at various C-rates

It is a standard practice to use the capacity of a battery to define the current levels used on it. The lithium-sulphur cells used in this work have a nominal capacity of 3.4 Ah and so it would take 1 hour to discharge the cell at 3.4 A. This is known as the C-rate and charge or discharge currents are often given as fraction or multiple of this rate. For example, C/2 would be 1.7 A and would discharge the cell, theoretically, in two hours. The figures hereafter present the discharge of three Li-S cells performed at T = 30 °C for the following C-rates: -680 mA (C/5), -1 700 mA (C/2), and - 3 400 mA (C)

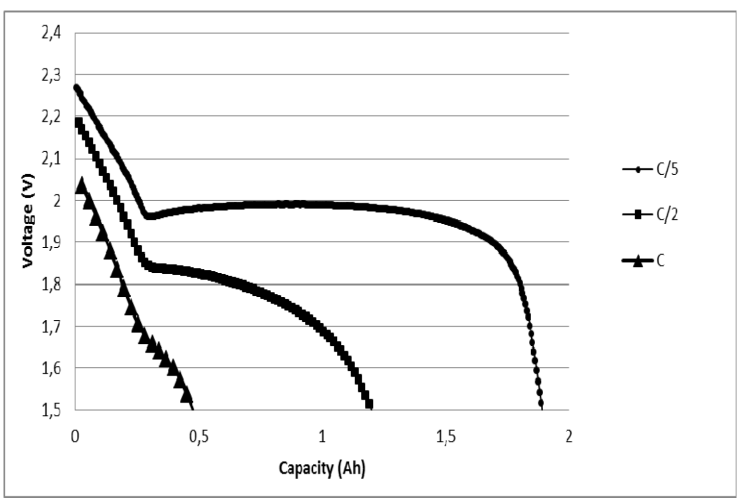

Figure 5: Discharge curves at various C-rates and T = 30 °C for the Li-S cell 1

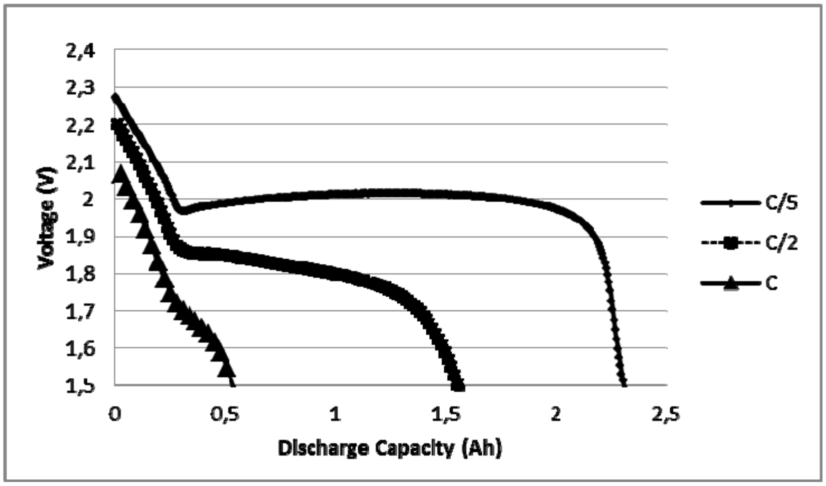

Figure 6 : Discharge curves at various C-rates and T = 30 °C for the Li-S cell 2

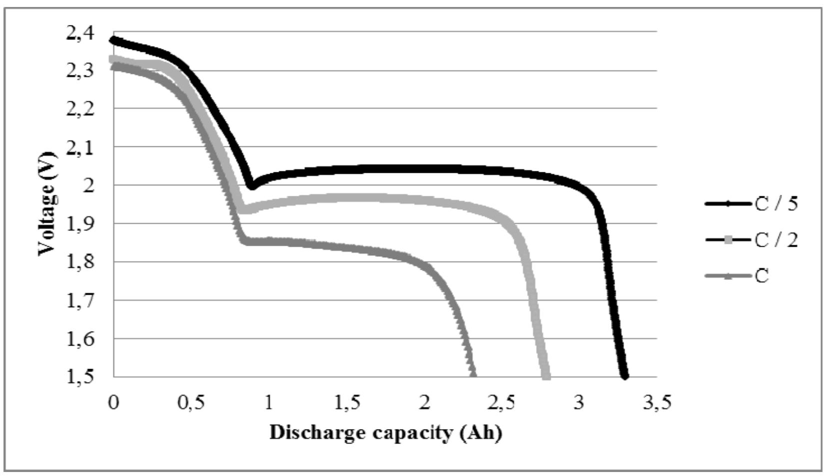

Figure 7 : Discharge curves at various C-rates and T = 30 °C for the Li-S cell 3

The figures show that at low-discharge current, the terminal voltage closely follows the open circuit voltage (or EMF) and the discharge capacity is closed of the nominal capacity of the Li-S cells. This is particularly true for the automated line pouch cells (cell 3 in our case). However, the same behavior is observed also for the handmade pouch cells (cell 1 and cell 2). Furthermore, the figures show using higher rates, when Li-S cells are discharged at high current rates, the available capacity of the cell decreases. This is certainly explainable by an increase of the Li_2S layer on the outer surface of the cathode which restricts ionic transport to the sulphur contained in the cathode, ad described in the literature [7].

3.6 Thermal behaviour at C/5

The study of the thermal behaviour of the cell is interesting due to the wide temperature range encountered in launchers and spacecrafts. The thermal behaviour of the Li-S cells is performed for a cycle of charge at C/10 and full discharge at C/5 for the three Li-S cells, at various temperatures: 5 °C, 10 °C, 20 °C, and 50 °C.

The figure hereafter presents the results obtained for Li-S cells 1, 2 and 4 cell discharged at a current rate of C/5 to 1.50 V.

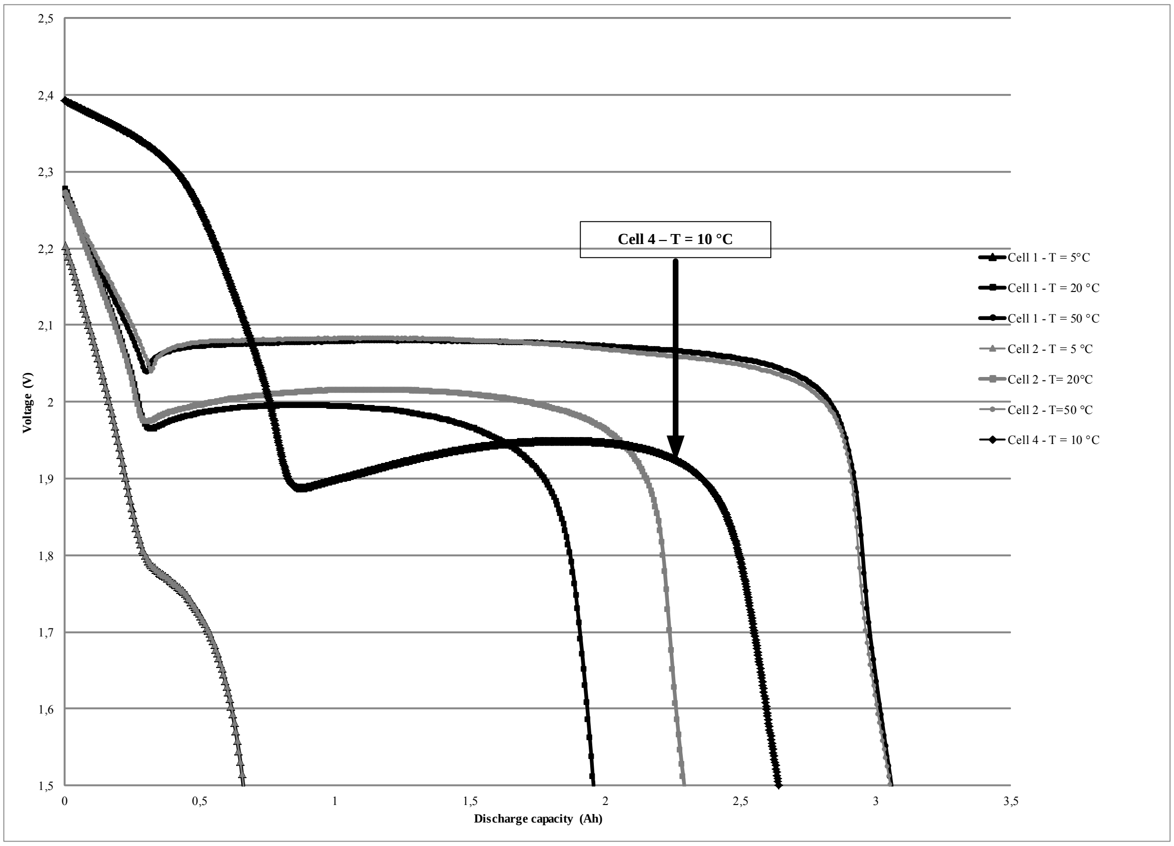

Figure 8 : Thermal behaviour of Li-S cells discharged at C/5 for various temperatures

The curves of the figure 8 indicate that in cold case (5 °C) the performances are degraded for handmade Li-S pouch cells. The automated line pouch cell 4 tested at 10 °C presents promising performances. Indeed, as shown in the figure, the performances for the cell 4 at 10 °C are better than the performances of the handmade pouch cells 1 and 2 at 20°C. This result is interesting because it shows that Li-S cells can operate at low temperature. The next step is the testing of a launcher sizing profile at 30 °C and 50 °C for the handmade pouch cells 1 and 2, and at 10 °C and 30 °C for the automated line pouch cell 4, in order to assess these first promising results.

3.7 Launcher's mission profile and thermal behaviour

The aim of this experiment is to check the capability of Li-S cells to perform a typical Ariane's launcher profile. The cells will be charged at C / 10, before performing the test. The profile is deducted of a typical launcher's mission profile scaled for testing 1 Li-S cell.

The mission profile is applied on the handmade Li-S pouch cells (cell 1 and cell 2) and automated line pouch cell 4 for various temperatures. The figure hereafter presents the obtained results.

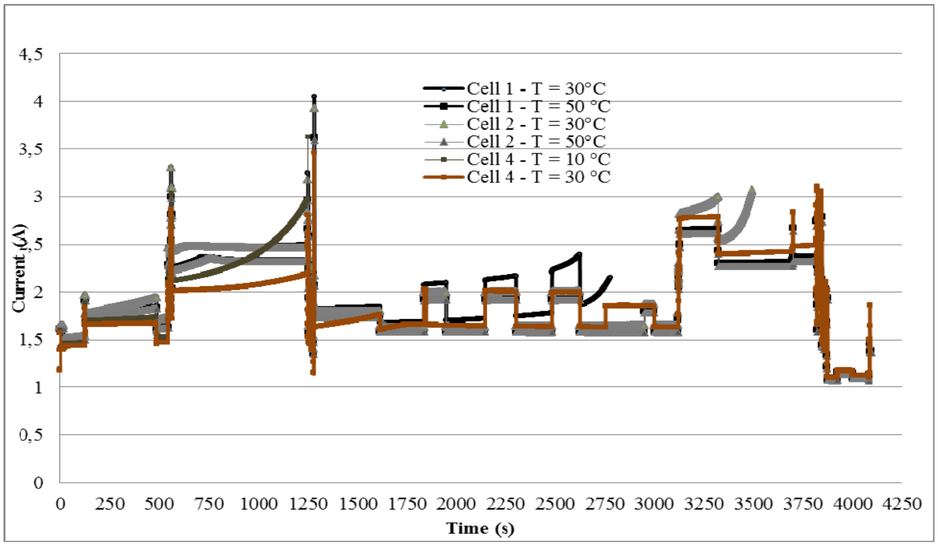

Figure 9 : Li-S cells discharged following launcher's typical profile

The typical mission profile passed successfully for the handmade Li-S pouch cells at 50 °C, and for the automated line pouch cells cell at 30 °C. At the temperature of 10 °C, the cell didn't pass the test. It's important to note that the Li-S cells used are well-sized to perform discharge tests at C/5. The launcher mission profile involves a discharge of the Li-S cells in the C-rate range C/2 up to C, all along the mission duration. Furthermore, the Li-S technology has to be improved to enable efficient operation at 10 °C.

The thermal behaviour of the Li-S cell 4 measured during mission profile testing at T = 30 °C is presented in the figure hereafter

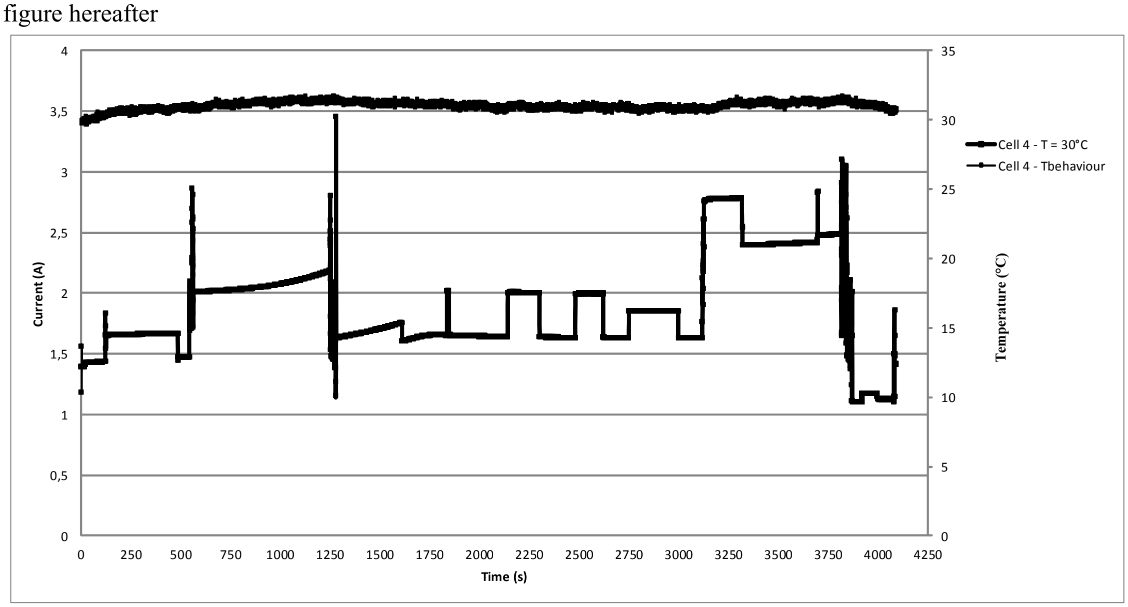

Figure 10: Thermal behavior of the Li-S cell 4 during launcher's mission profile testing

The thermal behaviour of the Li-S cell indicates a good thermal stability, which is an interesting result. Indeed, a good thermal stability indicates that Li-S technology seems to be safer than lithium-ion technologies. This preliminary result shall be confirmed by tests performed at battery level.

3.8 Satellites cycling profiles

The feasibility of the use of Li-S batteries for the GEO and LEO is studied. Here, we perform cycle stability tests on 2 Li-S cells (cells 1 and 2). The results obtained at 20°C for two different DOD are promising, and it demonstrates that the improvements make at cell raw material level enabled to exceed limited stability of a hundred cycles, which was the biggest drawback of lithium-sulphur cells.

Lifetime at 20 % of DOD

This lifetime shall show the compatibility with LEO satellites application characterised by cycling at 20% DOD. The test performed was cycling with a discharge at 20 % of its full charge at – 680 mA (C/5) follows by a charge at 340mA (C/10) to 2.35 V. A capacity measurement has been done each 200 cycles.

The figure hereafter presents the obtained results.

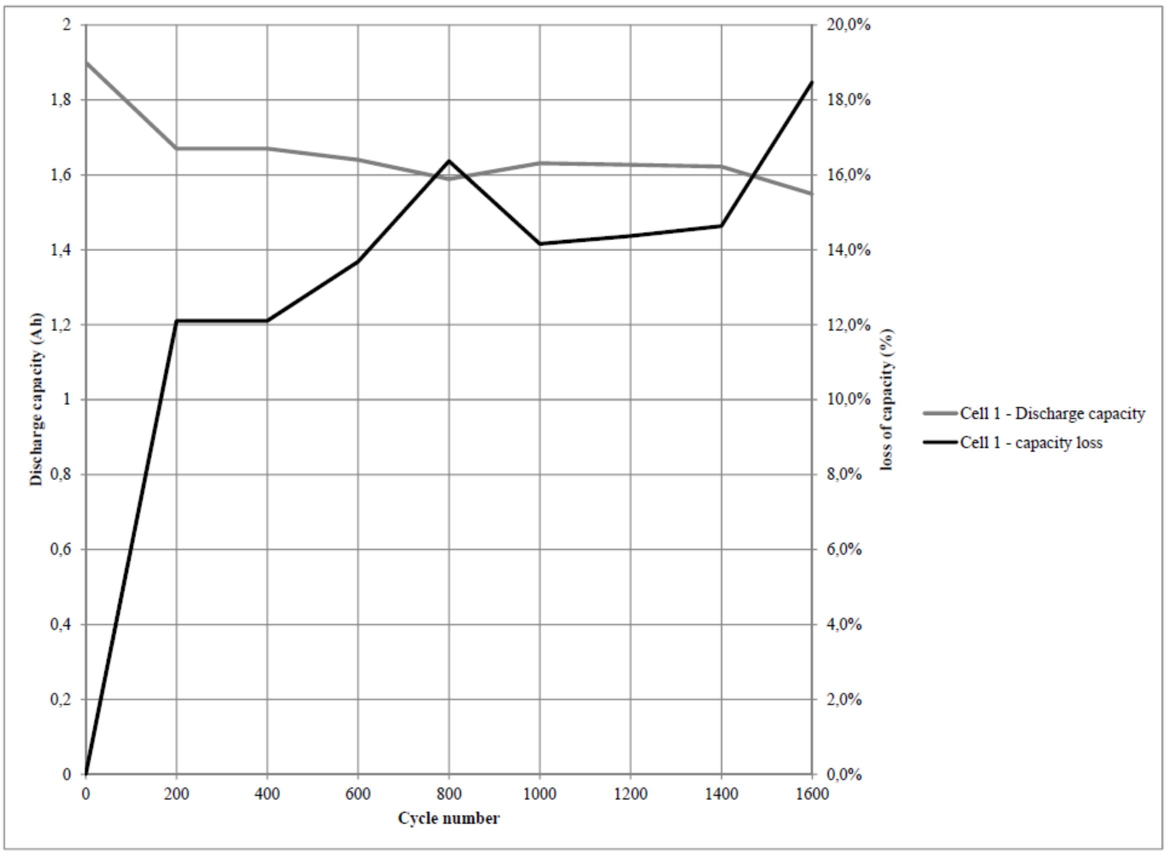

Figure 11: Cycle performance of a lithium-sulphur cell at 20 °C for 20 % of DOD

The Li-S cell exhibited 1600 cycles at 20 % of DOD at room temperature (20 °C). The figure 11 shows a high loss of capacity during the 200 first cycles. In the range 200 – 1600 cycles, the capacity of the Li-S cells is stabilised and the loss of capacity is only of 6 % for a thousand cycles. More investigations will be necessary to identify the chemical phenomenon responsible of the high fall of capacity at the beginning of the cycling test.

Lifetime at 100 % of DOD

This lifetime shall show the compatibility with GEO satellites application characterised by cycling at 100% DOD. The test performed was the cycling with a discharge at 100 % of its full charge at – 680 mA (C/5) follows by a charge at 340mA (C/10) to 2.35 V. A capacity measurement is performed at each charge / discharge cycle. The figure below presents the results obtained.

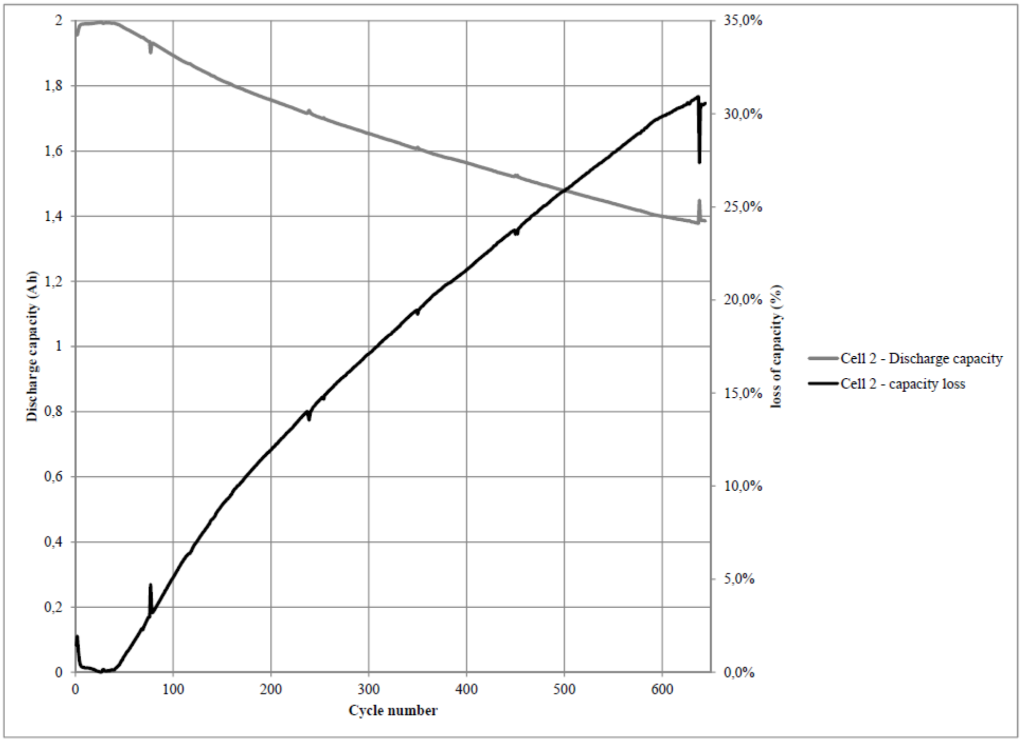

Figure 12: Cycle performance of a lithium-sulphur cell at 20 °C for 100 % of DOD

The Li-S cell cycle stability is reported at 100 % of Depth of discharge (DOD) where the tested cell has exhibited 600 cycles. The figure 12 shows a capacity loss of 12% during the 200 first cycles, which is similar to the capacity fall obtained with the Li-S cell cycling at 20 % of DOD. In the range 200 – 600 cycles, the capacity of the Li-S cells has decreased and the capacity loss has reached 30 % after 600 cycles. The obtained results at 100 % of DOD are very promising knowing that less than 1500 cycles at 80 % of DOD are necessary to perform geostationary missions dedicated to telecommunication.

4. Conclusions

Our results demonstrate the interest of Li-S cells for space applications. Indeed, the gravimetric energy of the first generation is promising and higher than for lithium-ion cells. Also, Li-S technology presents a good thermal stability under launcher's mission profile testing and interesting thermal behaviour at T = 10 °C. Moreover, we demonstrated the capability of cycling of the lithium-sulphur technology. At 20 % of DOD, the handmade Li-S pouch cell tested reached 1600 cycles. Another handmade Li-S cell has been cycled at 100 % of DOD and has reached 600 cycles, which is a promising result for telecommunication missions (GEO satellites application). The cycling stability test of this Li-S cell at 100 % of DOD is in progress. The expected performances of the next generation in terms of gravimetric energy (400 $Wh.kg^{-1}$), thermal behaviour and cycle stability (several thousand of cycles) shall enable to foreseen lithium-sulphur technology as a good candidate to breakthrough lithium-ion technology for space applications.

References

[1]: B. Scrosati, J. Hassoun, Y-K Sun, *Energy & Environmental Science*, 2011
[2]: M-Y. Chu, L. C. De Jonghe, S. J. Visco, and B. D. Katz, «Liquid electrolyte lithium-sulfur batteries," *US Patent 6030720*, February 29, 2000.
[3]: SAFT, *Lithium Batteries*, 1st ed., J-P. Gabano, Ed.: Academic Press, 1983.
[4]: S. S. Zhang, "liquid electrolyte lithium / sulfur battery: fundamental chemistry, problems, and solutions", *Journal of Power Sources 231 (2013) 153 – 162*
[5] V.S. Kolosnitsyn, E.V. Kuzmina, E.V. Karaseva, and S.E. Mochalov, A study of the electrochemical properties in lithium sulphur cells by impedance spectroscopy, *Journal of Power Sources, vol. 196, pp. 1478K1482, 2011.*
[6] : Y. V. Mikhaylik and J. R. Akridge, " polysulphide Shuttle Study in the Li/S Battery System," *Journal of the Electrochemical Society*, vol. 151, no. 11, pp. A1969-A1976, 2004.
[7] R. Spotnitz, Simulation of capacity fade in lithium-ion batteries, *Journal of Power Sources*, vol. 113, pp. 72K80, 2003.