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Lithium-sulphur batteries: opportunities and challenges for space applications

*Géraldine Palissat**

**ArianeGroup*
51-61 Route de Verneuil, 78130 Les Mureaux, France

geraldine.palissat@ariane.group

Abstract

Energy storage devices in many space applications are facing unique challenges. Most of such applications (Next Generation Launchers, reusable launch vehicles, satellites, human exploration missions…) depend on high performance, highly specialised batteries. Currently, there is strong interest by all stakeholders related or influenced by the battery markets on two systems: advanced lithium-ion and lithium-sulphur (Li-S) batteries. Li-S cells are one of the most promising systems for next generation batteries due to their high theoretical energy density, the abundant and low cost sulphur resources and lithium-ion comparable cathode production. Early results, comparison with the current lithium-ion batteries, opportunities and challenges will be presented.

1. Introduction

The electrification of space systems as well as the increase of the missions' duration, involves new requirements in terms of on-board electrical power and energy. Today, improved electrical power subsystems shall be developed to cope with these general trends. 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 lithium-ion batteries used in space applications. 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.

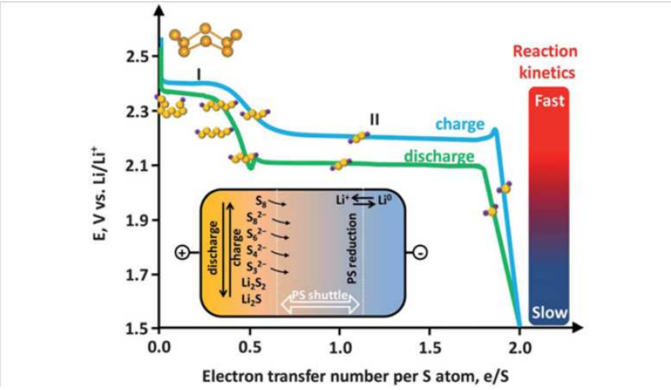

Figure 1: Electrochemistry of sulfur showing an ideal charge-discharge profile. [1]

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The various stakeholders have one critical factor that engineers strive to optimise: specific energy. Prototype cells were prototyped by OXIS Energy UK, and characterized. The results are presented here, mainly in order to enhance basic understanding, show relevant trends and present the opportunities and challenges of the technology for space applications. A comparison with the existing lithium-ion technology is also addressed in this paper.

1.1 Technical requirements specifications

The technical requirements at cell level are presented in the table hereafter.

Parameter	**Stakeholder requirement**
Open-circuit voltage (V)	2.45
Nominal voltage (V)	2.10
Cell capacity when discharged @ C/5 and 20°C to 1.9V (Ah)	> 10
Continuous discharge current (A)	8
Equivalent Series Resistance (ESR) @ End-of-Discharge (mΩ)	< 40
Self-discharge per month during storage (%)	< 5
Specific energy @ C/5 and 20°C (Wh / kg)	300
Number of cycles	10
Mass (g)	< 110 g

Table 1: technical requirements for li-S cell development

1.2 Lithium-sulphur cells specifications

20 prototype cells were provided by OXIS Energy and tested. An important remark at this stage is that due to the lack of maturity of the prototypes, the Li-S cells are handmade. The table hereafter presents the average values obtained for each parameter described above durig the initial measurements, with regard to the requirements.

Parameter	**Li-S cell Specification**
Open-circuit voltage (V)	2.45
Nominal voltage (V)	2.10
Cell capacity when discharged @ C/5 and 20°C to 1.9V (Ah)	14.00
Continuous discharge current (A)	7
Equivalent Series Resistance (ESR) @ End-of-Discharge (mΩ)	30
Self-discharge per month during storage (%)	< 5
Specific energy @ C/5 and 20°C (Wh / kg)	300
Number of cycles	>10
Mass (g)	108

Table 2: Oxis li-S cell specifications

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 1.40 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 2.80 A to 1.90 V,

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- Charge cell at the manufacturer's recommended current rate of 1.40 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 (~11 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 10 000Hz due to limitations of the impedance meter used by the Electrical Laboratory of Airbus Group. The system impedance may be measured using frequency response analysis. The initial cells internal resistance at 1 kHz shall be measured.

The internal resistance is the key parameter for determining power, energy efficiency and lost heat of a lithium sulphur pouch cell. Precise knowledge of this value is vital for designing battery systems for launcher applications.

2.3 Lifetime

The lifetime of the Li-S cells studied in this paper, corresponds to most common scheme of space applications. The cycling tests will be performed at 20°C. A first one is given for a Li-S cell discharged by approximately 100 % of its full charge at 1.5C before being recharged again C/5 to 2.45 V. A capacity measurement is automatically done at each cycle.
A second cycle life mode is given for a Li-S cell discharged by 20 % of its full charge at 1.5C before being recharged again at C/5 to 2.45 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.

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

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.

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

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

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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 14 Ah and so it would take 1 hour to discharge the cell at 14 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 7 A and would discharge the cell, theoretically, in two hours.

3. Experimental results

3.1 Charge profile: cycling results

The charging profile was performed between 1.9 V and 2.45 V at C/10 (1.5 A) at room temperature (around 20°C), for the cell n° 1 to cell n° 10. The figure hereafter shows a charge voltage profile for the first cycle of the 10 Li-S cells.

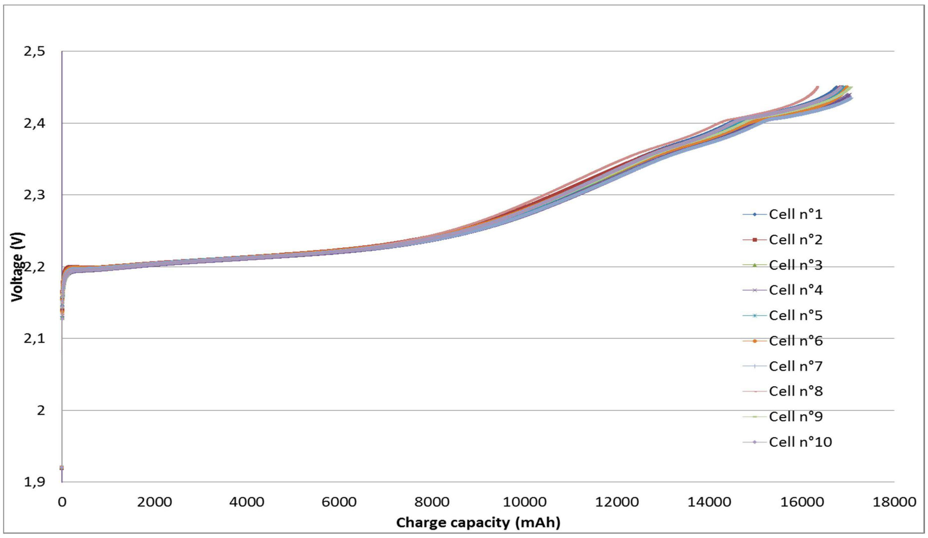

Figure 5: curves of charge of the cells n°1 to n°10 (second cycle).

As shown in the figure, the charge curves are similar for each Li-S cells. The detailed results for the first cycle are presented in the table hereafter and analysed to determine the energy density of the Li-S pouch cells at C/10 and at room temperature.

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The table hereafter presents a compilation of the obtained results for the first cycle. This screening has been performed at T = 20 °C for each Li-S cell.

	Charge capacity Acceptance (Ah)	**Charge capacity (Ah) 2nd cycle**	**Energy density (Wh / kg) Acceptance @ C/10**	**ESR @ 1 kHz (mΩ)**
Cell n°1	17.038	16.750	392	9.85
Cell n°2	17.043	16.842	385	12.44
Cell n°3	17.044	16.946	387	9.71
Cell n°4	17.036	16.817	384	8.65
Cell n°5	17.032	16.905	388	9.16
Cell n°6	17.039	16.979	385	11.68
Cell n°7	17.056	17.069	374	6.12
Cell n°8	17.064	16.330	388	11.49
Cell n°9	17.046	17.053	392	10.35
Cell n°10	17.067	16.839	388	9.08

Table 3: initial characteristics of the Li-S prototypes.

The capacity measurement is slightly lower than observed during acceptance test, except for the cells n°7 and n°9. The energy density @ C/10 and at room temperature is of the order of magnitude of 390 Wh/kg, as shown in the table above, except for the cell n°7.

The impedance measurement at a frequency of1 kHz enables to determine the internal resistance of the Li-S pouch cells. The results shown a variation of the obtained values for the internal resistance, potentially explained by the handmade production of the Li-S cells prototypes. The evolution of the charge profile in function of the number of cycles is presented for each cell in the figures hereafter.

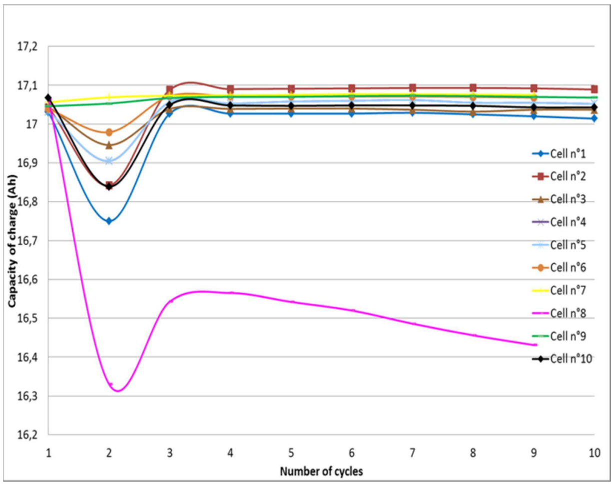

Figure 6: evolution of the charge capacity of the Li cells n°1 to n°10.

The charge capacity for the first cycle corresponds to the acceptance capacity of the Li-S pouch cells.
As shown in the figure above, the charge capacity of the cells n°7 and n°9 is very stable following the increase of the number of cycles.
A slight loss of the charge capacity during the second cycle is observed for the 8 other Li-S cells. This is maybe due to the precipitation of lithium sulphide on the anode side, enabling a loss of active material from the cathode to the anode and the associated capacity fading. The cell n°8 seems to have a particular behaviour, probably linked to the manufacturing handmade process.

3.2 Discharge profile: cycling results

During operation (discharge), solid sulfur from the cathode dissolves into the electrolyte, forming S_8. Liquid S_8 is then electrochemically reduced at the cathode to form intermediate products, so called lithium polysulfide species (Li_2S_x) with an accompanying oxidation of Li metal to Li^+ ions at the anode. The polysulfides species (Li_2S_x $2 < x < 8$) are soluble in the liquid electrolyte and diffuse out from the cathode to the electrolyte/separator side. When the discharge proceeds, the length of the polysulfide chain is getting reduced, which in turns affects the viscosity, mobility and solubility of Li_2S_x compounds. At the end of discharge, S_8 is fully reduced to S^{2-} (Li_2S) and the anode is fully stripped of Li metal. The final discharge product, Li_2S_2/Li_2S, is a solid and insulating material which passivates the electronically conductive surface of the cathode, causing premature end of discharge, the increase of the internal resistance, which eventually can lead to increased heat generation in large format cells. The discharge profile of the 5 cells was studied and compared to theoretical discharge profile of Li-S cell found in the literature [4]. The discharging profile was performed at C/5 (3A) between 2.45 V and 1.90 V at room temperature (around 20°C), for the cell n° 1 to cell n° 10. The figure hereafter shows a discharge curves during the first cycle for the 10 Li-S cells tested.

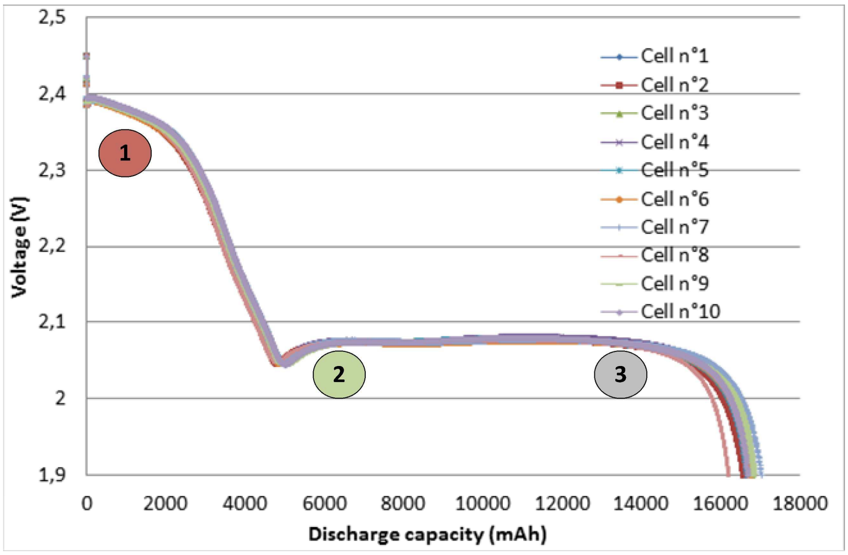

Figure 7: first cycle discharge curves of the cells n°1 to n°10.

As observed, the capacity is not completely recovered during the discharge, due the parasitic reactions well-known under the name of polysulphides shuttle mechanism and described in the beginning of this paragraph.

As shown in the figure, 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 involves the formation of Li_2S_2 and finally Li_2S in the Region 3, which corresponds to the voltage plateau 2,05V – 1.9V.

3.3 Coulombic efficiency

Coulombic efficiency (CE), also called faradaic efficiency or current efficiency, describes the charge efficiency by which electrons are transferred in batteries. CE is the ratio of the total charge extracted from the battery to the total charge put into the battery over a full cycle.

The coulombic efficiency corresponds to the following formula:

$$\eta_C = \frac{\int_0^{t_d} I_d dt}{\int_0^{t_c} I_c dt}$$

Where: I_d is the discharge current, t_d is the discharge time, I_c is the charge current and t_c is the charge time.

The table hereafter presents the coulombic efficiency for the 10 Li-S prototypes at acceptance.

	Coulombic efficiency (%)
Cell n°1	89
Cell n°2	81
Cell n°3	91
Cell n°4	84
Cell n°5	91
Cell n°6	92
Cell n°7	87
Cell n°8	81
Cell n°9	94
Cell n°10	90

Table 4: coulombic efficiency after acceptance test of the Li-S cells n°1 to n°10

As shown in the table, the coulombic efficiency of the Li-S prototypes is in the range 81% to 94%, with an average value of 88%. For the first cycle, this value seems to be lower than for the value of this parameter for lithium-ion batteries. Knowing that for Li-S prototypes, the coulombic efficiency seems to increase after the first cycle, its evolution is presented hereafter and an average of the coulombic efficiency after 10 cycles is calculated.

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The figure hereafter presents the evolution of the coulombic efficiency following the cycling tests, for the 10 Li-S cells charged at C/10 and discharged at C/5 10 times.

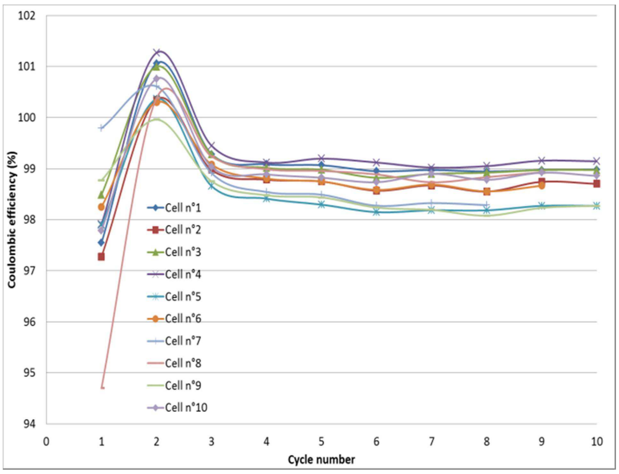

Figure 8: evolution of the coulombic efficiency @ C/5 and room temperature.

As shown in the figure, after 3 cycles, the coulombic efficiency is steadier and becomes constant. Finally, at C/5, the average value of the coulombic efficiency is of the order of magnitude of 99% and it's similar to those of lithium-ion batteries. Furthermore, the stability of the coulombic efficiency at C/5 after 10 cycles means probably that the presence of soluble active material species in the electrolyte is negligible after 10 cycles.

3.4 Energy efficiency

Energy efficiency is defined as the ratio of the discharged energy to the energy needed to be charged to the initial state before discharge. The energy efficiency corresponds to the following formula

$$\eta_W = \frac{\int_0^{t_d} U_d I_d dt}{\int_0^{t_c} U_c I_c dt}$$

Where: I_d is the discharge current, t_d is the discharge time, U_d is the discharge voltage, I_c is the charge current and t_c is the charge time and U_c is the charge voltage. U_d and U_c are functions of time.

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The table hereafter presents the energy efficiency for the 10 Li-S prototypes at acceptance.

	Energy efficiency (%)
Cell n°1	76
Cell n°2	75
Cell n°3	76
Cell n°4	76
Cell n°5	76
Cell n°6	76
Cell n°7	77
Cell n°8	73
Cell n°9	77
Cell n°10	76

Table 5: energy efficiency of the Li-S prototypes.

As shown in the table, the energy efficiency of the Li-S prototypes is of 76%. For the first cycle, this value seems to be lower than for the value of this parameter for lithium-ion batteries.

The figure hereafter presents the evolution of the energy efficiency following the cycling tests, for the 10 Li-S cells charged at C/10 and discharged at C/5 10 times.

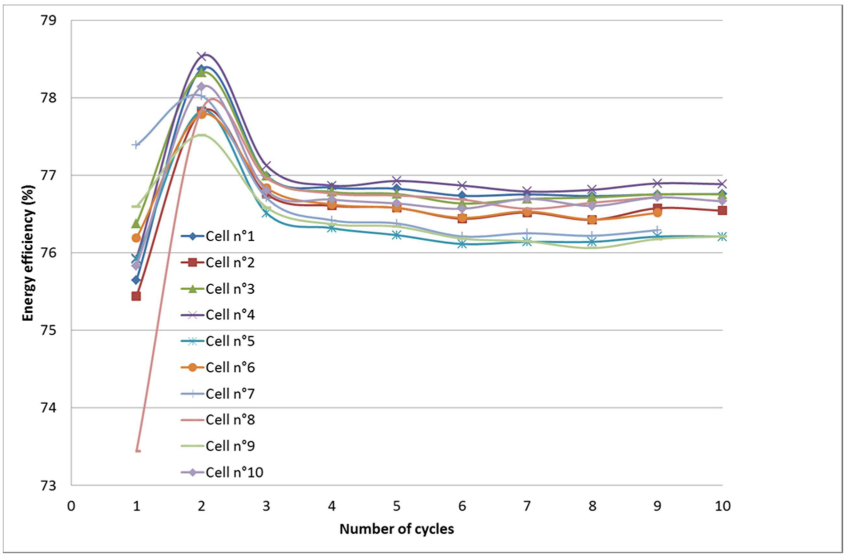

Figure 9: evolution of the energy efficiency @ C/5 and room temperature.

3.5 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 test aims at measuring evaluating the influence of discharge at different C-rate values. In order to check the reproducibility, the cells n°1 to n°10 have undergone the same test conditions and the obtained results are presented below. The figure hereafter presents the results obtained when the Li-S cells are discharged under a constant current of C/2 at 20°C.

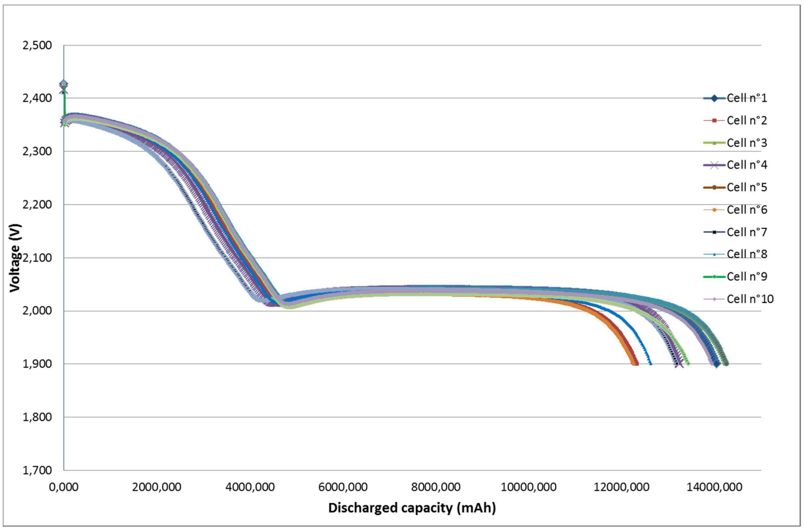

Figure 2: Discharge curves at C/2 and T= 20 °C for the 10 prototypes.

The figure below presents the results obtained when the Li-S cells are discharged under a constant current of C at 20°C.

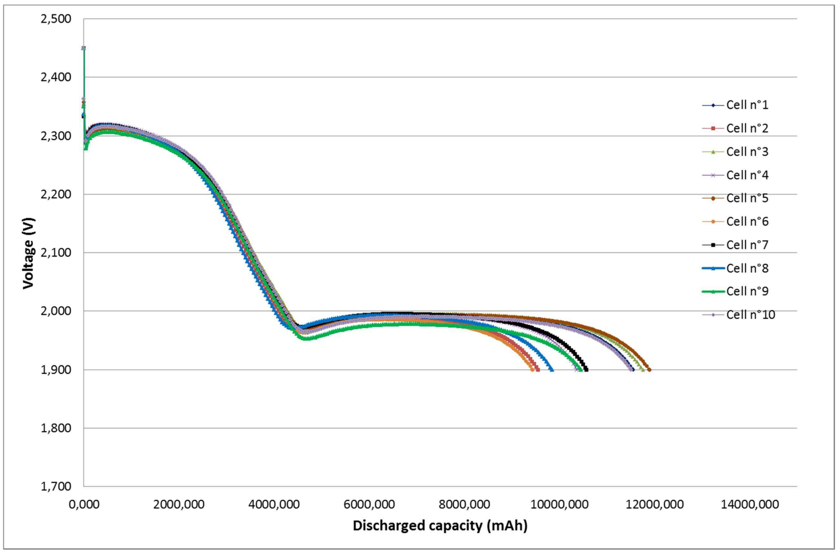

Figure 3: Discharge curves at C and T= 20 °C for the 10 prototypes.

The figure below presents the results obtained when the Li-S cells are discharged under a constant current of 2C at 20°C.

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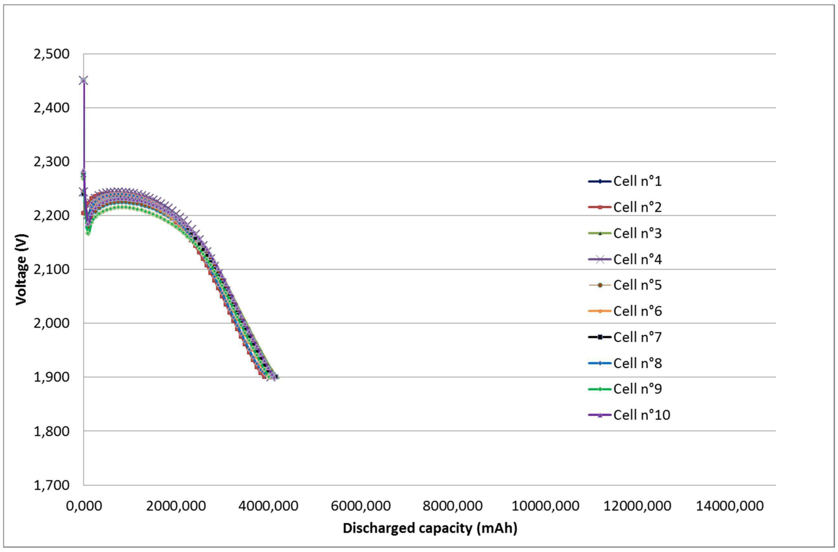

Figure 4: Discharge curves at 2C and T= 20 °C for the 10 prototypes.

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. Furthermore, the figures presenting the discharge curves at higher rates show the decrease of the available capacity for each prototype. 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, and described in the literature [4-6].

4. Opportunities and challenges

Our results demonstrate the interest of Li-S cells for space applications. Indeed, the gravimetric energy of the Li-S prototypes is promising and higher than for lithium-ion cells. It presents an interest for space applications, and particularly for launcher missions, where important mass savings are foreseen. Despite the research conducted these last years and the improvement realized on the cells, there are still some drawbacks due to the electrochemical characteristics of the system. The principal points and research challenges are summarized hereafter, as well as the consequences at the cell level.

4.1 Mass savings

Due to high energy densities (400 Wh / kg @ C/10 and 300 Wh / kg @ C/5) and interesting power density target for a secondary battery (600 W / kg continuous and 1100 W / kg peak), interesting weight savings are foreseen in comparison to the current technologies.
Taking into account all the estimated weight impacts on the electrical system of the launcher, a preliminary calculation indicates 30% of weight savings at Upper Stage level, concerning the functional power supply.

4.2 Cyclability

Due to the use of lithium metal negative electrode, which implies the formation of a solid-electrolyte interphase (SEI), the Li-S cells present a poor number of cycles. Indeed, a continuous loss of lithium, an irreversible consumption of the electrolyte, and the formation of a corrosion layer upon cycling.

Consequently, the current prototypes of Li-S cells present a number of cycles of the order of magnitude of 400 cycles, really lower than the needs of telecommunication and/or earth observation missions needs.

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4.3 State-of-charge

Nowadays, the methodology to perform a measurement of the state-of-charge of the lithium-sulphur battery technology is unknown. Indeed, the discharge curve of Li-S cell with a plateau @ 2,1V doesn't allow determining easily the capacity of the battery.

Consequently, the controllability of the Lithium-sulphur technology has to be studied, to enable the follow of the discharge capacity during the launcher system operation. It's one of the big challenges of the technology with its ability to ensure a high number of cycles (1000 to 5000 cycles).

5. 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. This technology shall enable to foreseen lithium-sulphur technology as a good candidate to breakthrough lithium-ion technology for space applications. However, this technology is facing important challenges in terms of cycling capabilities and state-of-charge measurement.

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