Graphene-based bank of supercapacitor cells (BOSC) from electrode to system level

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ABSTRACT — Pleione Energy has been actively involved in a number of activities over the past few years exploring the use of graphene in energy storage devices. Starting the developments from material level and proceeding all the way up to evaluating the effects of graphene at a system level. The activities have been conducted under the supervision of European Space Agency, spanning from the development and optimization of the material and electrode level to the design, manufacturing, and optimization of supercapacitor cell, and lastly the development of supercapacitor power module. More specifically, in ESA-GRACE II activity (4000137745/22/NL/FE/mkn), the main objective was to achieve the production of electrodes, and as a result the development of high-performance supercapacitor cells, with increased specific energy and power density (compared to the currently commercially available products) using proven and simple manufacturing procedures that can be easily scaled-up and offer competitive products.

KEYWORDS — graphene, energy storage, supercapacitors, power module

INTRODUCTION

Technology advances in space power and energy storage offer significant benefits to spacecraft, launch vehicles, landers, rovers, spacesuits, tools, habitats, communication networks, and anything that requires power and energy. Such advances may even enable missions that were previously considered technically unattainable. As far as the energy storage is concerned, primary goal for any space energy storage technology is to provide power at the highest possible specific energy with sufficient durability in the mission environment and, in the case of rechargeable storage, sufficient cycle life.

The investigation of novel, low-cost, environmentally friendly, and high-performance energy storage systems has been under an ever-increasing demand [1]. The three main devices are primary batteries, rechargeable batteries, and capacitors. Supercapacitors (SC) have lately captured the attention for power applications in space environment. They differ from conventional capacitors due to their fast charge–discharge rates, longer life cycle, high power, and high energy density. They bridge the gap between conventional electrolytic capacitors and batteries[2], [3]. They can support pulses of elevated power while the cell temperature rises tolerably, they have an ample operating temperature range (typically -40 °C to 65 °C) and long cycle life (>1×10^6) [4].

The last decade graphene has shown immense potential and has been extensively studied for its ability to enhance the performance of batteries and supercapacitors. Graphene's unique properties, such as its high electrical and thermal conductivity, large surface area, mechanical strength, and chemical stability, make it a promising material for energy storage applications such as lithium-ion batteries and supercapacitors. Ongoing research and development efforts are focused on optimizing graphene's properties, improving its production scalability, and reducing costs to facilitate its widespread adoption in the energy storage sector. In the field of supercapacitors, graphene's high surface area and excellent electrical conductivity enable the development of supercapacitors with increased energy storage capacity and improved cycling stability [5].

Since supercapacitors have found applications in several different industries, where there is the need to store and release huge amount of power in a very short time, their combination with graphene might provide an enhanced performance that will fit the needed requirements. Supercapacitors are used primarily used in hybrid electric vehicles (HEV), electric vehicles (EV) and fuel cells vehicles like passenger cars, trains, trolleybuses. Another area of application for supercapacitors is the industry of electronic devices such as uninterruptible power supplies and volatile memory backups in PCs. Third and very promising area of application is in the field of energy harvesting systems like solar arrays or wind turbines, where supercapacitors play a supplementary role next to conventional batteries. In addition, in space sector, it has been demonstrated that a characteristic cell type is tolerant in proton and gamma radiation and thermal-vacuum tests screenings have evaluated some existing supercapacitor designs, and they are sufficient for space applications. From ESA Study Contract No. 21814/08/NL/LvH entitled “High Power Battery Supercapacitor study” completed in 2010 by Airbus D&S, supercapacitors for launchers and satellites, were demonstrated as possible applications for space. The study showed that most promising ones, could be optimization of pyrotechnical activation system, high power mechanisms, electrical thrust vector control, high power radar supply or even hybridization of Supercapacitor banks with Lithium-Ion batteries [6].

Though out this activity, a thorough trade off analysis both on material and processes level has been performed, providing the best combination of materials and the most efficient processes in order to develop up-scaled graphene-based electrode and high-performance supercapacitor cells, reaching values of capacitance higher that 100F. Following the identification of the materials to be used and having established a small-scale in-house line, the design, manufacturing and assembly of a graphene-based bank of supercapacitors (BOSC) for space application, was performed.

The development of the first graphene-based BOSC prototype leads the way towards commercialization for Pleione Energy, that has already been working towards this direction and has successfully developed its first graphene-based supercapacitor power bank. More specifically, a Bank of Supercapacitors was successfully designed, assembled, and assessed. The design has been based on requirements that have been provided by ESA and LSIs (Large System Integrators) and are strongly connected to specific applications. Further improvement can be achieved in all levels of the development from material to cell and system level to deliver a more efficient Graphene -Based BOSC.

EXPERIMENTAL

For the final development of the BOSC, the processes were separated in three levels. The first level was on the investigation and manufacturing of the upscaled graphene-based electrode, that would lead to the second level of the assembly and characterization of the supercapacitor cells. Lastly, the third and final level was of the design and assembly of the BOSC.

Graphene Based Electrode

Upscaled-Graphene based electrode has been prepared with a roll-to-roll (R2R) method. Initially, in lad scale, various slurry configurations have been investigated, including active material, binder, addition of conductive additive and transition metal oxides contents, before proceeding to the upscaled electrode manufacturing. For the preparation of the graphene-based electrode, the slurry was mixed using a dissolver with a water-cooled vessel. For a good dissolving quality, a high viscous mass is needed, therefore only a part of the solvent (water) is propounded in the vessel and the solids are added. Water was added until reaching the appropriate rheological properties for coating. The selected slurry configuration for the upscaling electrode, apart from graphene as an active material, contained also conductive additive and water-soluble polymers as binder.

The slurry was transferred to the R2R machine and coated by continuous doctor blade process using aluminium foil as a substrate. Initially various metallic substrates were also investigated as possible current collectors.
The graphene used for the electrode development was characterized through Raman and BET (Brunauer-Emmett-Teller), before being used, so that the characteristics provided from the supplier, matched the measured ones. In addition, rheological characterization was also performed, prior to the coating. For the characterization of the graphene-based electrode, scanning electron microscopy (SEM) was used for the morphological characterization and Cyclic Voltammetry (CV) and Charge-Discharge (C/D) for the electrochemical characterization. Having developed the upscaled electrode and after characterizing it, pouch supercapacitor cells were assembled.

Graphene based supercapacitor cells

Following the electrode preparation, the supercapacitor cells were assembled and characterized. A trade off analysis on the materials and components to be used for the supercapacitor cells was performed and different electrolytes, separators and designs were investigated until reaching capacitance values higher than 100F. For the SC cell assembly, the electrodes were initially conditioned under vacuum and for several hours in order to reduce humidity and then assembled into a cell. The SC were prepared in a pouch form and the electrolyte filling and sealing was performed under inert atmosphere. Following their assembly, the cells were submitted to electrochemical characterization and mechanical testing. A degassing step was added after the cell had run a few cycles to release occurring gasses.
For the characterization of the SC cells, Charge Discharge characterization, Leakage Current and Self Discharge were performed. Additionally, Vibration and Shock were used for the mechanical testing of the pouch cell.

Fig. 1. Assembled Supercapacitor cells

Graphene based Bank of Supercapacitor cells (BOSC)

The cells were assembled into a BOSC after being characterized and degassed according to requirements set together with the LSIs. A total of 6 cells were connected in series, together with aluminium busses and carbon fibre reinforced polymer (CFRP) plates, that were used for the casing. The BOSC was submitted to Charge-Discharge characterization, Seld Discharge and Leakage Current characterization. The design of the BOSC was referring to a space application of a motorization of robotic arm, with specifications required being of a useful energy of 500 J, number of supercapacitors in series: 4 to 7 and $V_{min} = V_{max}/2$. The device would be operated a few times, over a mission duration of a few years.

DISCUSSION AND RESULTS

Graphene-based electrode

Samples from the upscaled electrode were submitted to SEM morphological characterization and following small testing pouch cells were assembled and submitted to Cyclic Voltammetry and Charge Discharge characterization.

a. b.

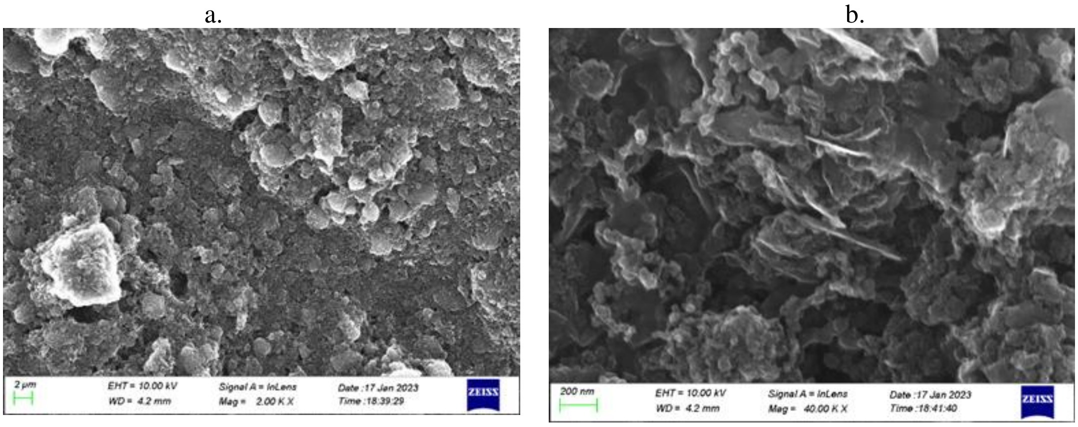
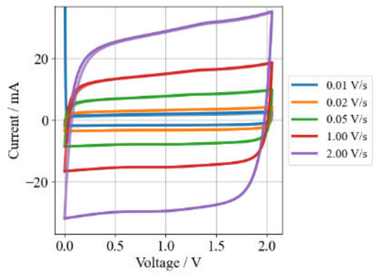


Fig. 2. SEM images of the electrode at a. 2K X and b. 40K X

For the SEM images, samples from different parts of the electrode, throughout the length of the upscaled electrode, were selected and images were received. In all images, the graphene flakes were visible at 40K X magnitude. Similarly, samples thought the length of the electrode were prepared into small testing cells and submitted to Cyclic Voltammetry and Charge Discharge, both with a 2V upper potential window.

a.



b.

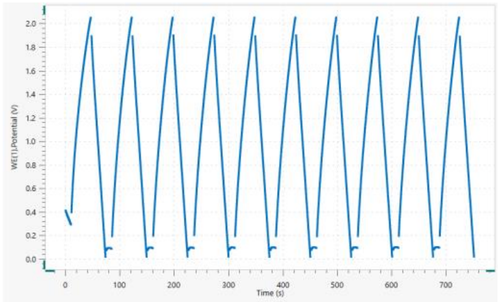


Fig. 3. a. CV curves at different scan rates. b. Galvanostatic Charge discharge curves of the small testing pouch cell

The specific capacitance of the graphene electrode can be calculated according to the following equation:

$$C_{cell} = \frac{1}{2} \frac{\int IdV}{m_t \, v \, \Delta V} \qquad (1)$$

where I is the current (A), V is the potential (V), v is the potential scan rate (mVs^{-1}) and m is the mass of the graphene in the electrodes (g) [7]. In a symmetric SC though each electrode, the negative and the positive can be expressed as two capacitors connected in series, where the capacitances can be expressed as C_p and C_n and are equal [8], [9]. So, from the equation of calculating capacitance when connected in series and equation (1) above, the capacitance of the electrode is calculated to be

$$C_{electrode} = 2C_{cell} \qquad (2)$$

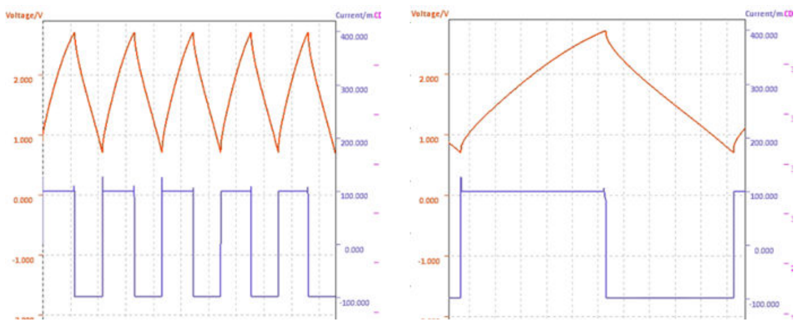
Cyclic voltammetry (CV) measurements were carried out within the potential range of 0-2V, to analyse the electrochemical behaviour of the graphene electrode. Figure 3a. shows CV curves of graphene electrode at scan rates varying from 10 to 200 mVs^{-1}. The typical rectangular curve without obvious oxygen and hydrogen evolution peaks can be observed at all scan rates, indicating good charge propagation within the electrode. In addition, the obvious increase of current with scan rates means a good rate capability for graphene electrode [10]. For the graphene-based electrode, the capacitance calculated was about 140F/g with an Ionic liquid electrolyte, a promising result regarding the performance of the material. Having characterized the electrode and proving its performance, Supercapacitor pouch cells were assembled.

Graphene-based Supercapacitor cells

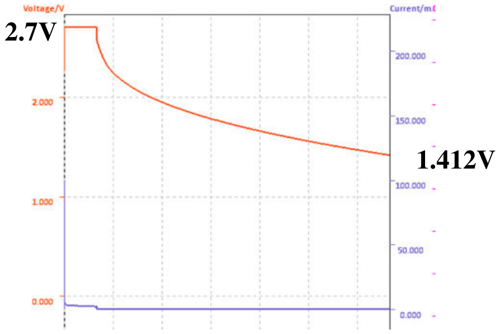
Following the established assembly process the first upscaled cells were developed and tested. The requirement for the upscaled cells was to reach capacitance values higher than 100F. The cells were submitted to galvanostatic charge discharge characterization and mechanical testing. Additionally, Leakage Current and Self Discharge characterizations were carried out.

Electrochemical characterization

a.



b.



c.

Hours (h)	Leakage Current (μA)
0	2500
24	103
48	55
72	51

Fig. 4. a. GCD (galvanostatic charge discharge) curves of the upscaled SC cells., b. Self-Discharge of the SC cell, c. Leakage current after 24, 48 and 72h

In the galvanostatic charge/discharge studies, graphene supercapacitors were charged up to 2.7V at a constant current and were discharged under the same current rate. From the slope of the discharge curves, capacitance was calculated. The charge - discharge curve of a graphene supercapacitor used in this study is given in Figure 4 (a). It is very clear that the charge - discharge curves are almost linear. The cells were also submitted to life cycle analysis. From the capacitance calculation of the cells, an average of 160F was measured for the upscaled cells.

The study of self-discharge of supercapacitors has great significance in the practical scenario as it determines the available energy for stand-alone applications. However, the self-discharge characteristics of supercapacitors mostly remain unexplored. Self-discharge phenomenon keeps supercapacitors away from energy intense applications. The involvement of ions and various electrode structures makes the self-discharge mechanism more complex in supercapacitors.

The mechanism of supercapacitors cannot be attributed only to the leakage resistance model, but to material properties such as ionic size of the electrolyte, porosity of the electrode, accessible surface area, structure of the electrode, presence of impurities, also play major role in controlling the self-discharge mechanism [11], [12]. For the self-discharge characterization, of the upscaled supercapacitors, the cells were Constant Current (CC) charged with 100mA up to 2.7V and then Constant Voltage (CV) charged at 2.7V for 8h. After 8 h, the self-discharge was studies for 72h. The leakage current is usually modelled with a resistor which is connected in parallel with a capacitor. The leakage current of the cells was calculated from the self-discharge profiles above. The leakage current was calculated at 0h, 24h, 48h and 72h, as provided in Figure 4 (c).

Mechanical testing

The pouch cells were also submitted to mechanical testing of Vibration and Shock. The capacitance of the cells was measured prior to the mechanical testing, after the vibration and after shock. Lastly the performance of the cells was also investigated after all tests had been performed. It has been concluded that the values of capacitance remained very similar in all phases of the characterization plan applied to the cells, showing no damage to the cells or degradation.

For the mechanical vibration of the cells, testing was carried out along all three main axes (X / Y / Z) with sinusoidal and random vibration. Similarly, for the shock characterization, testing was carried out along all three main axes (X / Y / Z) as well.

a. b.

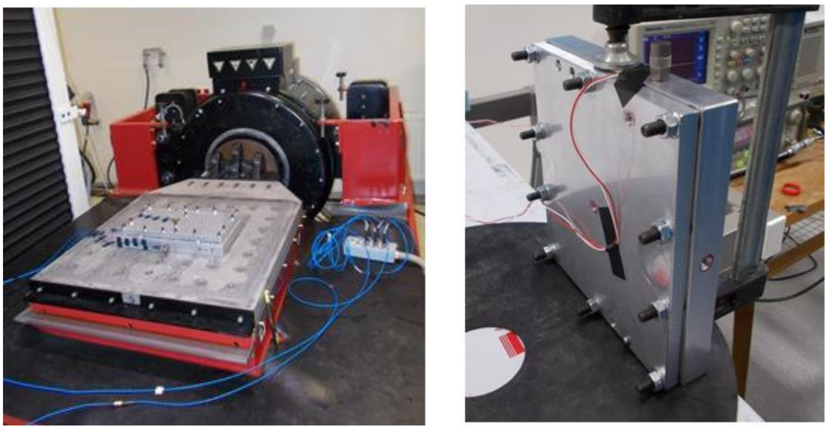


Fig. 5. a. Apparatus for vibration tests, b. Apparatus for shock tests

Before the sinusoidal and the random vibration in all axes, resonance research was performed priorly. For axes X and Y, no resonance peak was observed, as presented in Figure 7, 8 and 9 below. For Z axes, the sinusoidal resonance search peak evaluation, provided the values described on the table 1 below.

Table 1. Sinusoidal resonance search peak evaluation, Z-axes

	Before Sinusoidal		After Sinusoidal						
Peak	Frequency (Hz)	Level (g)	Frequency (Hz)	Level (g)	Delta Freq. Measured (%)	Delta level measured (%)	Delta Freq specified (%)	Delta level Specified (%)	Ok/NOK
1	**2062**	**0.8**	2062	0.7	0.0	-5.2	+/-10%	+/-50%	OK
	Before Random		After Random						
Peak	Frequency (Hz)	Level (g)	Frequency (Hz)	Level (g)	Delta Freq. Measured (%)	Delta level measured (%)	Delta Freq specified (%)	Delta level Specified (%)	Ok/NOK
1	**2062**	**0.7**	2062	0.7	0.0	1.4	+/-10%	+/-50%	OK

The peaks for Z axes are showed in the picture below.

a. b.

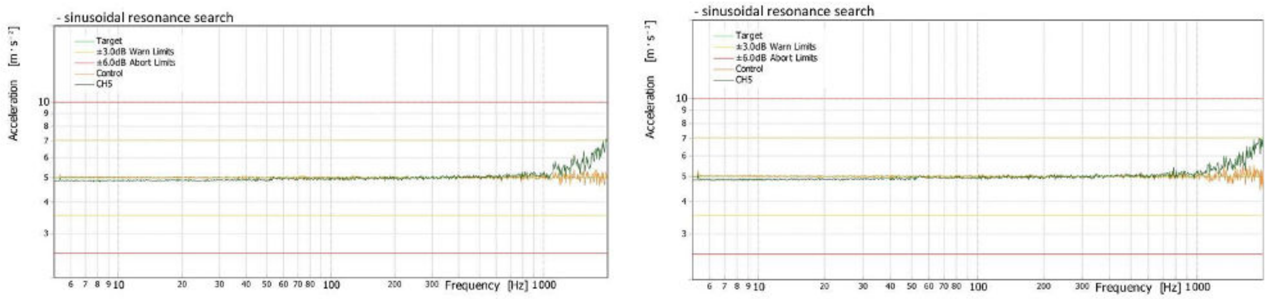


Fig. 6. a. Peak on Resonance search before sinusoidal vibration, b. Peak on Resonance search before random vibration

Below the graphs for the three axes for the Sinusoidal vibration, Random vibration and Shock testing are provided.

Sinusoidal vibration

Axes X | Axes Y | Axes Z

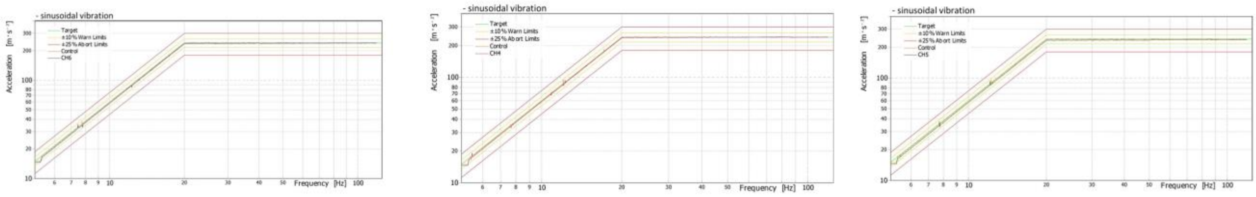


Fig. 7. Sinusoidal vibration on axes X, Y and Z respectively

Random vibration

Axes X | Axes Y | Axes Z

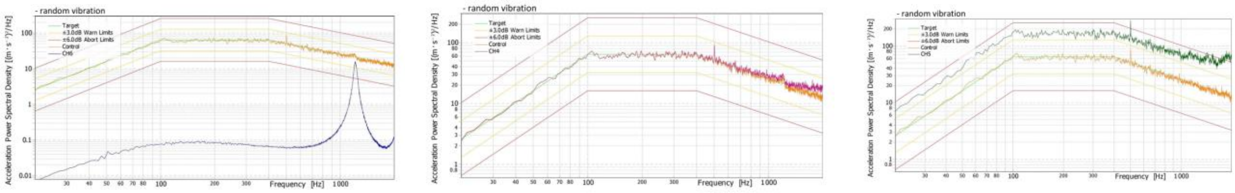


Fig. 8. Random vibration on axes X, Y and Z respectively

Shock testing

Axes X | Axes Y | Axes Z

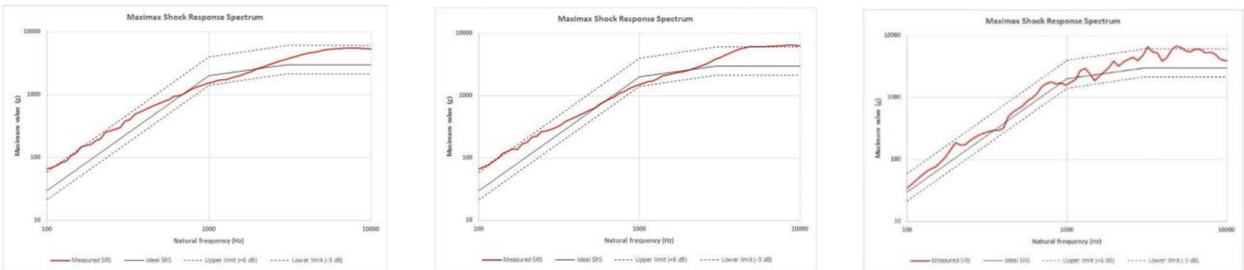


Fig. 9. Shock tests on axes X, Y and Z respectively

The cells were undamaged and the performance regarding the capacitance, Equivalent Series Resistance (ESR) before and after the mechanical testing was very similar.

Bank of Supercapacitor cells (BOSC)

Testing and characterization

Since the cells reached the required capacitance and were fully characterized, a total of 6 additional cells were prepared for the BOSC assembly, according to the manufacturing plan. The prepared cells were connected in series and assembled with CFRP plates for the BOSC to be developed. Following the assembly, the BOSC was submitted to charge discharge characterization.

a. b.

Fig. 10. a. Assembled BOSC connected with a LED tape, b. Testing of the BOSC

The capacitance of the BOSC was measured on the fourth cycle of the charge discharge characterization. Apart from the capacitance measurement, a floating test was performed, where the BOSC ran a total of 400 cycles. Additionally, the BOSC was also submitted to Self-Discharge and Leakage current characterization.

Since each cell was of 160F, as provided above, the theoretical capacitance of the BOSC was calculated to be about 26F using equation (3) below.

$$\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2} + \cdots etc \tag{3}$$

From the experimental calculations performed on the fourth cycle, the capacitance was measured to be 20.8F, with a current of 0.35A, and an upper potential applied of 18V, with the discharge potential not reaching values lower than 10V. The capacitance was also measured from charge discharge cycles performed with a current of 1A and a potential window between 18V to 3V. From the discharge curve the capacitance was calculated to be of 8.09F.
Following, the BOSC was then let for a floating test at 16.2V. For the first 100 cycles, the capacitance with 1A discharge current is provided in the picture below.

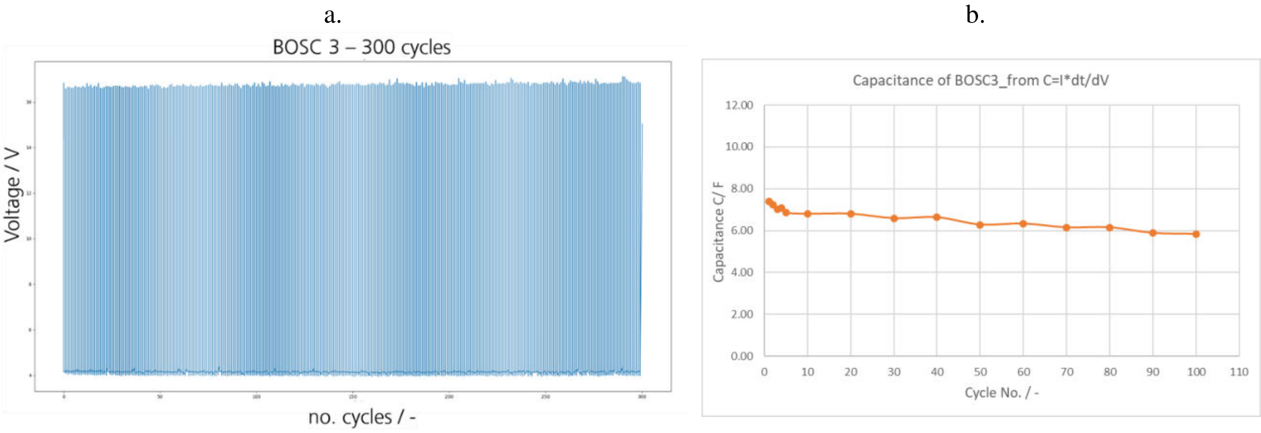


Fig. 11. a. Charge Discharge curves of the BOSC, b. Capacitance with 1A current through the first 100 cycles

There is a distinguishable difference in the capacitance measured on the fourth cycle, and the one measured at a higher current range. When the BOSC was cycled at lower currents, no issues were observed through the testing, whereas, when a higher current was applied, the cells inside the BOSC were observed to swell causing the capacitance to drop through the charge discharge cycles.

After the first 100 cycles of charge discharge characterization, the Leakage current and the self-discharge characterization were performed as provided in the figures below.

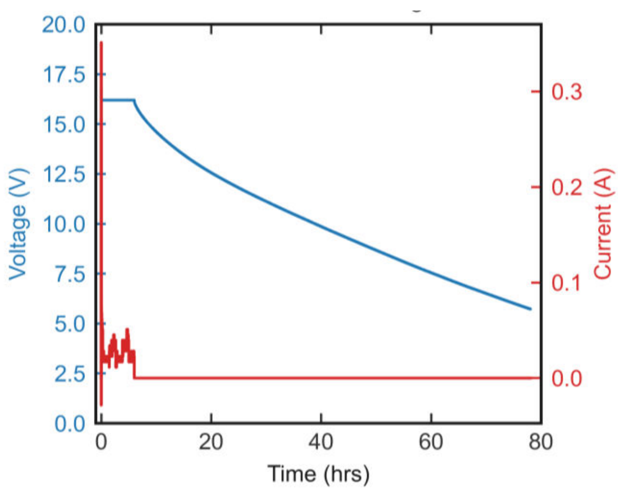


Fig. 12. Self-Discharge characterization

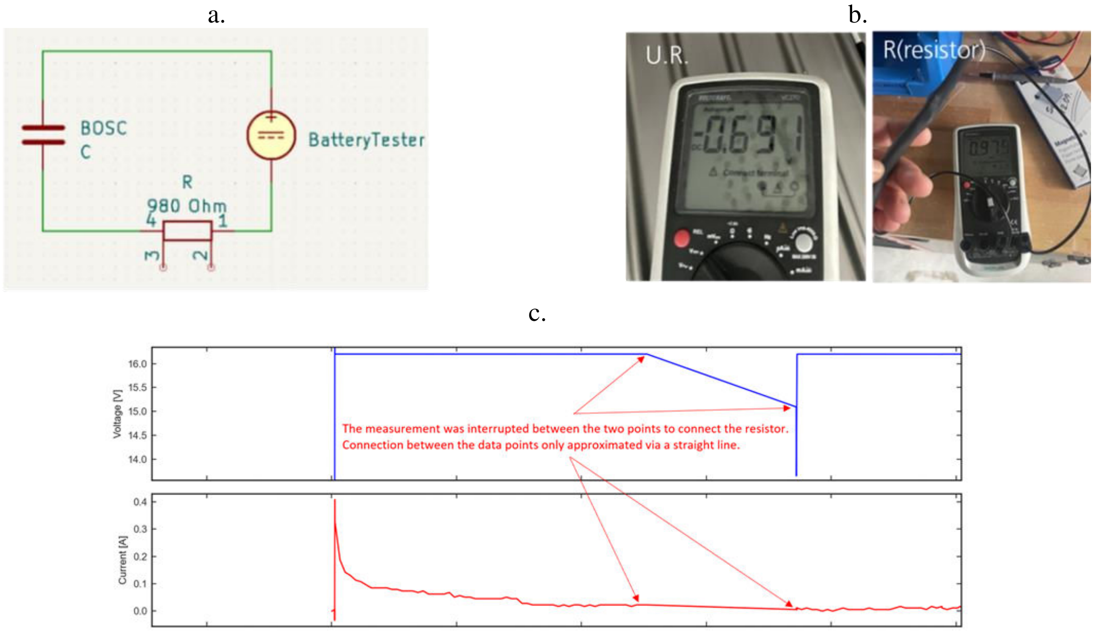


Fig. 13. a. Schematic of the test set-up to determine leakage current after 72 h., b. Resistance of the Resistor, c. Leakage Current graph of the BOSC

The voltage of BOSC during the self-discharge characterization dropped to 5.73 V from 16.2 V after 72 h. Whereas the leakage current after 72 h was 0.71 mA.

Lastly, after the testing of the BOSC was fully completed, the BOSC was disassembled, and the cells were opened for evaluation of their state. Cutting the cells open, led to the observation that the electrolyte was transformed to gases, leaving the cells almost dry, which explains also the capacitance drop through the cycles.

CONCLUSIONS

Throughout the activity, there was successfully developed an upscaled aqueous graphene-based electrode that was fully characterized and provided promising specific capacitance of 140F/g on material level. The upscaled electrode was integrated into high performance supercapacitor cells reaching values of average capacitance of 160F and submitted to life cycle characterization, leakage current and self-discharge. The Supercapacitor cells stayed also undamaged through mechanical testing, while maintaining their initial performance.

During GRACE II activity, a prototype of graphene-based bank of supercapacitors was designed, based on requirements set from LSIs for a motorization of robotic arm application. The manufacturing process of assembling a BOSC was successfully established and the first prototype device of graphene-based cells was developed. The BOSC was submitted to electrochemical characterization, proving that it can operate and provide promising results. A capacitance of 20.8 F was achieved on the fourth cycle of charge discharge characterization, with an upper potential of 18V.

Having successfully developed the first prototype provides the ground to further optimise the performance of the supercapacitor cells and improve the design and assembly of the BOSC, so that it can fit the applications needed from the LSIs. By double coating the electrodes and proceeding to the developments of cylindrical cells the performance of the cells, as well as the energy and power densities with be improved. Moreover, the connection of the cells would be more efficient leading to higher capacitance, lower resistances, leakage current and self-discharge.

AKNOWLEDGEMENT

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