High Energy Density Supercapacitors for Space Applications: A Leap Forward in Space Exploration Energy Systems

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ABSTRACT

High energy density supercapacitors constitute a leap forward in creating hybridized energy storage systems that boost traditional batteries by offering faster recharge, longer cycles, and enhanced efficiency in the demanding conditions in space applications. This paper aims to present a quantitative characterization of a novel Lithium free high energy density hybrid supercapacitor, highlighting their applications and potential in space.

We propose a Lithium free hybrid supercapacitor, superior in energy density (60 Wh/kg) and cell voltage (3.3 V) to conventional supercapacitors, that utilizes environmentally friendly electrolytes and demonstrates resilience up to 85 °C—outperforming conventional solutions. This innovation promises to enhance power systems by offering high power, minimizing payload, thermal runaway and safety risks. We developed an electrochemical double layer capacitor (EDLC), enduring over 100,000 cycles with minimal performance decline (less than 14 % capacitance decline and 73 % increase in DC ESR- equivalent series resistance), alongside a high-energy hybrid supercapacitor tested for 60,000 cycles (20 % capacitance decrease and 61 % increase in DC ESR), which exemplify significant advancements towards robust, high-efficiency space applications, where they can reduce the mass and volume of power systems significantly compared to conventional batteries, offering a substantial advantage in payload optimization.

INTRODUCTION

The use of supercapacitors has been investigated in order to advance energy systems for space exploration, providing critical support for fluctuating power demands and enhancing operational efficiency, for example in stabilizing power supply fluctuations by peak shaving in geostationary Earth orbit (GEO) subsystems, including power bus voltage regulation in GEO subsystems, peak power supply for electro-mechanical thrust vector actuation, pyrotechnic mechanisms and many more [1], [2]. With the rapid progression in aerospace technology, the demand for energy storage solutions that offer both high power density and reliability in harsh environments has significantly increased. For such applications that require a significant power in a short amount of time, current energy storage solutions face several limitations: (1) low power density which restricts the charge and discharge currents that can be safely applied and (2) degradation both at low and high temperatures. These limit their use during eclipses when they are expected to support the entire load, which leads to oversized battery capacities, which can unnecessarily increase the volume and complexity of the system, working at reduced efficiencies. These constraints highlight the need for advancements in battery technology or alternative solutions like hybridization with supercapacitors that can operate more efficiently under the broad range of conditions encountered in space exploration.

In response to these needs, several European Space Agency (ESA) initiatives [1], [3], [4] have rigorously tested a variety of electrochemical double layer capacitors (EDLCs) employing diverse technologies and assembly configurations. The results from these tests have been promising, with supercapacitors achieving energy densities surpassing 7 Wh/kg and power densities up to 100 kW/kg [3]. These performance metrics underscore the potential for integrating hybrid systems that leverage both the high energy storage capacity of batteries and the superior power delivery and cycling capabilities of supercapacitors, in order to achieve more efficient and robust power management systems for next-generation spacecrafts [1].

The current challenge remains the relatively low energy densities of supercapacitors, which hinders their broader application in space technology [1]. Advancements in supercapacitor technology are essential for providing sustainable, efficient and powerful energy solutions, crucial for the demanding operations of future space missions.

The proposed electrochemical energy storage solutions comprehend double layer capacitors (EDLC) also known as supercapacitors, Fig. 1a), batteries, Fig. 1c) and hybrid capacitors Fig. 1b). Batteries, such as lithium-ion, are capable of storing large amounts of energy over extended periods. However, they often suffer from slower charge/discharge rates and shorter cycle life, particularly under high rate cycling conditions. EDLCs, on the other hand, can deliver rapid bursts of power and have an extremely long cycle life. The differences come from the underlying principles depicted in Fig. 1, namely batteries store energy via redox reactions that involve electron transfer across electrodes, leading to chemical changes, while supercapacitors store energy through electrostatic charge accumulation at the electrode-electrolyte interface. Hybrid supercapacitors combine these approaches: one electrode operates through redox reactions similar to a battery, while the other accumulates charge electrostatically.

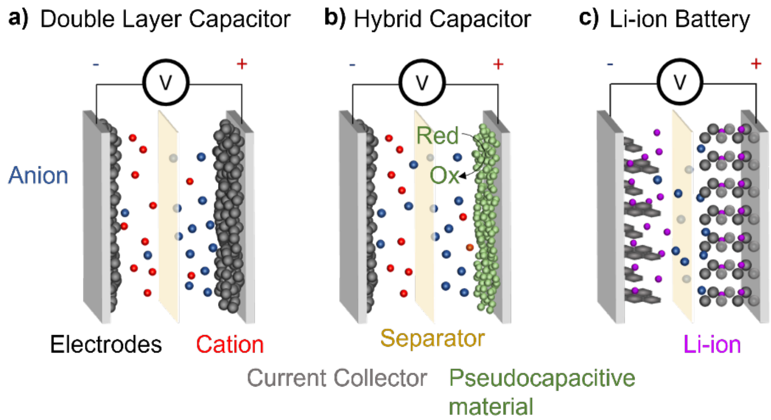

Fig. 1. Representation of electrochemical devices for energy storage. a) Symmetrical electrochemical double layer capacitor. b) Redox enhanced hybrid electrochemical double layer capacitor. c) Lithium-ion battery.

These technologies have various energy and power trade-offs. As it is well known, batteries are an excellent choice for long term independent energy storage due to their high energy density, in contrast, they have lower power density, as illustrated in Fig. 2. Furthermore, when they are subjected to short, high-rate pulses, their efficiency decreases significantly, and the resistances of the electrodes pose significant challenges to fast charging. High-rate pulses caused immediate voltage changes, with the maximum current limited to around 10 C for cathodes and 3–5 C for anodes before risking lithium plating. Sustaining high-rate pulses shows that the anodes are limited by lithium diffusion, with high resistances, leading to lithium deposits which compromises the safety of the full system [5]. Supercapacitors are a viable option to handle high power demands and avoid battery damage [6].

To achieve optimal performance in supercapacitors, they must possess high specific capacitance, a wide operating voltage range, and low equivalent series resistance (ESR). Nevertheless, surpassing an energy density of 10 Wh/kg while maintaining low production costs and using environmentally friendly materials remains a significant challenge for material scientists and researchers worldwide [7], [8]. A common strategy to increase energy density is to incorporate redox enhanced materials and metal oxides are most frequently employed. This strategy is effective, but the power density and lifetime are significantly reduced [9]. Another important strategy towards improving energy density are Lithium-ion capacitors (LICs), which are a combination of Li-Ion batteries and supercapacitors which were shown to improve the energy density by bridging the gap between these two devices, Fig. 2. Developing LICs with high energy density presents significant challenges, primarily due to the kinetic mismatch between the capacitor-type cathode and the battery-type anode [10]. Moreover, there is a growing preference for metal-free LICs over those that use costly and unsustainable metal-based electrode materials. Identifying suitable metal-free cathode and anode materials that combine high capacity with exceptional rate performance is crucial for advancing supercapacitors for commercial applications. A crucial drawback for applications is the reduced power density of LiCs when compared to EDLCs, limiting the capabilities of handling high current peaks, which are essential for the targeted applications [11].

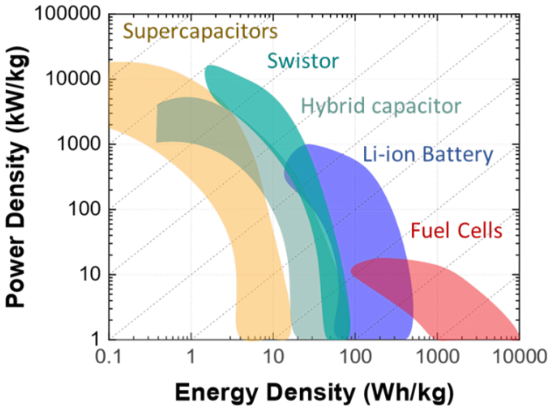

Fig. 2. Ragone plot showing the trade-offs between energy density and power density for the different electrochemical energy storage devices including Swistor capacitors.

Swistor technology employs the combination of high-surface-area nanostructured carbon with specifically enhanced redox-active species. This innovative approach is optimized for high-energy performance at elevated voltages, ensuring superior energy density and efficiency while maintaining high power density, as observed in Fig 2. Swistor supercapacitors, are designed with a focus on sustainability, adhering to environmentally renewable targets and avoiding the use of critical raw materials, addressing the growing need for green technology solutions in energy storage. The materials and techniques used are optimized to maximize the energy density performance of the supercapacitor while minimizing their cost and environmental impact.

EXPERIMENTAL

We have leveraged our expertise in microtechnology and nanostructured materials to enhance the performance of miniaturized supercapacitors. Our innovative approach includes the development of porous systems and innovative formulations that allow for scalable and efficient supercapacitor cells. Utilizing proprietary technology, we have fabricated electrodes with optimized interfaces between cell components, as depicted in Fig. 3, resulting in superior performance in both miniaturized and scalable designs.

At the core of our development is the strategic use of high surface area nanostructured carbon materials, which effectively accommodate ions from high voltage electrolytes. This optimization of interfaces between the carbon materials, redox-enhanced species, and electrolytes significantly improves energy and power density.

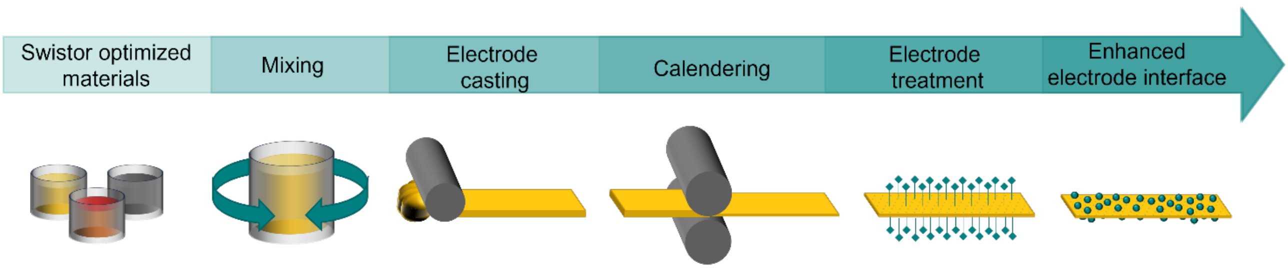

Fig. 3. Process flow for electrode manufacturing. Starting from raw materials, the electrode components are mixed, and the electrode is cast into a foil that is later densified by calendering. After this step the electrodes are subjected to a specific treatment to improve the interface with the electrolyte.

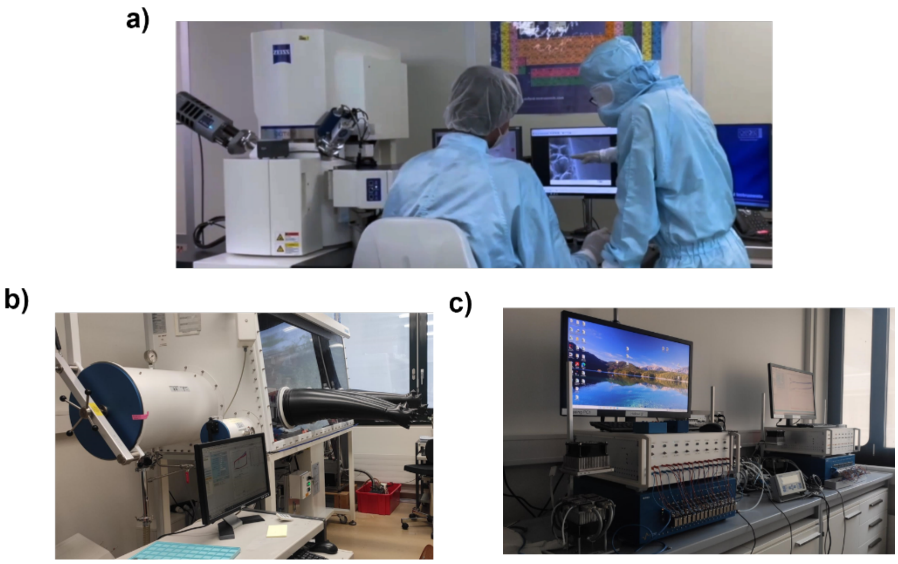

Fig. 4. Equipment for material development, cell manufacturing and testing. a) Scanning electrode microscope, b) glove box and c) electrochemical testing racks.

We fabricate the full devices in house, Fig. 4b), from material development and optimization and advanced metrology, Fig. 4a) and we perform a full electrochemical characterization and durability tests, Fig. 4c).

We manufactured and fully characterized supercapacitors tailored to precise specifications, producing coin cell formats, Fig. 5a), with capacitances ranging from 0.2 to 2 Farads and pouch cell formats of 5 Farads, Fig. 5b). Coin cells are used to validate the performance capabilities of materials and integrate into small-scale devices due to their compact size and compatibility with existing formats. Conversely, pouch cells are selected for their lightweight properties and adaptability in space-constrained environments, making them ideal for applications where form factor and weight are critical considerations.

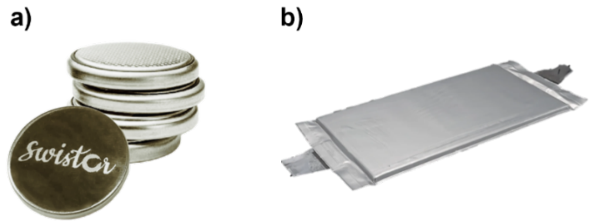

Fig. 5. a) Coin cell format with capacitance from 0.2 to 2 F. b) Pouch cell with capacitances up to 5 F.

The materials and supercapacitor cells here presented are tested employing electrochemical measurements, 2-electrode (full supercapacitor cells). Cells are characterized using cyclic voltammetry, constant current charge-discharge, long-term continuous cycling to evaluate the performance and durability of supercapacitors in a controlled temperature environment.

We calculate the capacitance, energy density and power density from the performance at constant current charge-discharge following the guideless for material characterization expressed in ref [12]. The resistance (DC ESR) is calculated from the voltage drop occurring at the first 10 ms of discharge from galvanostatic discharge characterization.

RESULTS: ACHIEVING HIGH ENERGY DENSITY SUPERCAPACITORS

We have developed and performed a full electrochemical characterization on 2 types of supercapacitors. First an EDLC was developed, tailored to the requirements of a dual dynamic system, charging and discharging with high efficiency

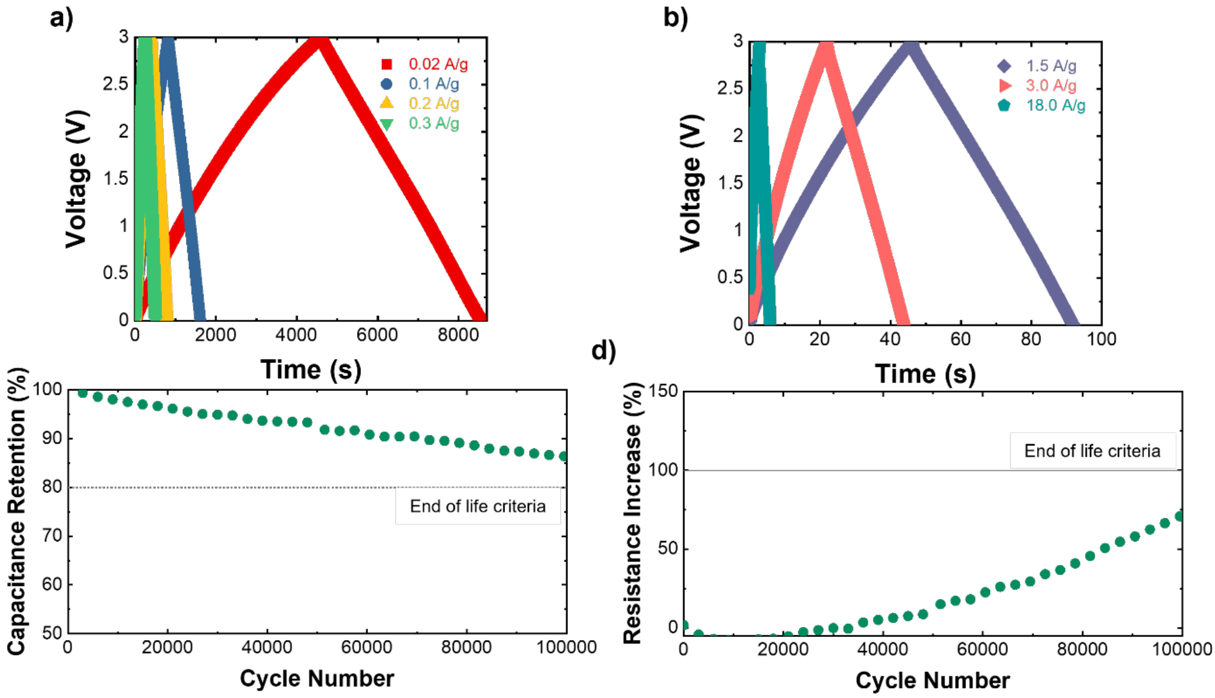

Fig. 6. Performance for small coin cell EDLC supercapacitors of 0.15 F at 3V at different current ranges densities normalized by electrode mass. a) Charge-discharge curves for low current densities, b) Charge-discharge curves for high currents densities. Durability upon continuous cycling at 3 V indicating c) capacitance retention and d) resistance increased.

(> 95 %) both at low currents (20 mA/g) and at high currents (18.0 A/g - limited by our small cell size and measurement set-up capabilities, we expect reaching current densities up to 100 A/g with process and cells scaling), as illustrated in Fig. 6a),b). This capability is crucial for space missions where variable power loads are common, and reliability under diverse operational conditions is mandatory. This ensures that energy captured during periods of low demand can be stored efficiently and then deployed quickly when high-power outputs are needed, offering enhanced efficiency and adaptability for a wide range of applications.

We characterized the cell up to the maximum voltage of 3.6 V and performed a durability test up to 3 V, demonstrating a consistent long-lasting performance, considering an end-of-life criteria based on a capacitance retention of less than 80 % and a resistance increase lower than 100 %. We obtain less than 14 % capacitance decline and 73 % increase in resistance after 100,000 continuous cycles as shown in Fig. 6c),d), highlighting the supercapacitor's robustness and reliability over extended use. The results show a viable and efficient solution for energy storage in space applications, where durability and long-term stability in harsh conditions are as crucial as energy density and power delivery.

We have also developed a redox enhanced supercapacitor achieving a high energy density of 60 Wh/kg that outperforms competitors, while employing no Lithium, but instead abundant and cheap materials. Figures 7a),b) illustrate the robust performance of Swistor cell high energy density supercapacitor, which operates at a rated voltage of 3.3 V across a broad current range, withstanding currents up to 160 mA. We obtain a maximum power of 50 kW/kg, demonstrating a significantly higher energy density while having a high power density, which is critical for the envisioned applications.

We have performed tests on 20 identical cells, cycling 75 % up to the nominal voltage 3.3 V. We obtain less than 80 % capacitance loss, and a resistance increase of less than 40 % as shown in Fig. 7c),d). We have also tested the durability of the supercapacitors on continuous cycling at 75 % energy at maximum voltage of 3 V (0.9 x rated voltage) demonstrating a lifetime of more than 100,000 cycles, Fig. 7c),d) similar to the EDLC counterpart.

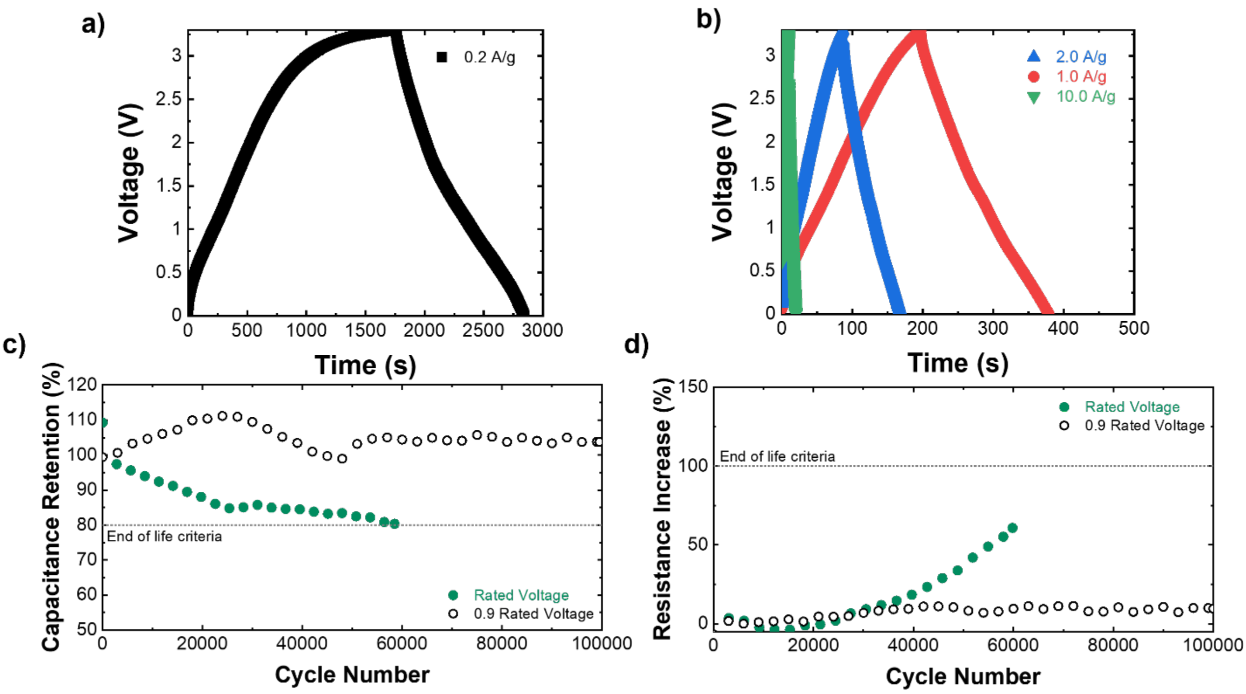

Fig. 7. Performance metric of a 0.2 F of a Swistor coin cell at different current ranges densities normalized by electrode mass. a) Charge-discharge curves for low current densities, b) charge-discharge curves for high currents densities. Lifetime performance at rated voltage of 3.3 V and 3 V (0.9 x rated voltage) following continuous cycling showing c) capacitance retention and d) resistance increase.

Our advancements in terms of ESR reduction are quantitatively demonstrated in Fig 8, which highlights the substantial progress made across different generations of our supercapacitors. By refining the electrode processing techniques and optimizing the interfaces between cell components, we have achieved an 80 % decrease in resistance from Generation 1 to Generation 2. This trend continued with a further 93 % reduction in resistance moving from Generation 2 to Generation 3, enhancing the overall performance of the supercapacitors.

These reductions in cell resistance not only improve the rapid charge-discharge capabilities, and high power peaks, but also enhance the longevity and reliability of the supercapacitors under high-load conditions. By continuously refining the microstructure of the electrodes and enhancing the conductivity pathways within the cell, we aim to set new benchmarks for what redox enhanced supercapacitors can achieve, driving forward their applicability in high-demand environments.

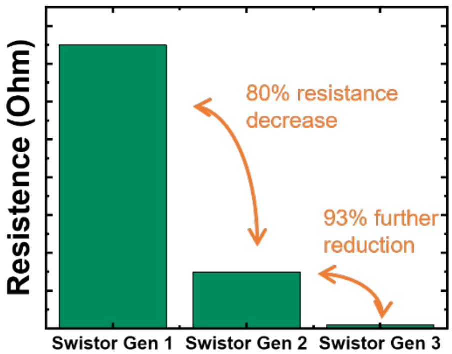

Fig. 8. Relative resistance improvement over the different cell generations.

We have conducted a thorough comparison between Swistor supercapacitors in coin cell format and 2 commercial off-the-shelf EDLC supercapacitors. The data is normalized based on electrode material mass (excluding current collectors). This analysis involved constant current charge-discharge characterization from 0 V to the specified nominal voltages of each supercapacitor. Our redox enhanced supercapacitors stand out by maintaining comparable or higher power densities to the of commercial devices while simultaneously achieving higher energy densities, as illustrated in a standard Ragone plot shown in Fig. 9a). These results are obtained while operating the cells at comparable current densities for all measured cells, Fig. 9b).

A key factor contributing to the enhanced performance is the operational voltage of our devices. Competitor products, such as those from Competitor 1 and Competitor 2, operate at lower voltages of 2.7 V and 2.1 V respectively. In contrast, Swistor technology is engineered to operate up to 3.3 V. This higher operational voltage allows for an increased energy storage capacity within the same physical limits, thereby enhancing the overall energy density without compromising power output. Moreover, this allows achieving higher voltages with less cells connected in series, minimizing the system and balancing complexity and size.

By optimizing the electrochemical properties and operational parameters of our supercapacitors, we provide a more robust and energy-efficient solution compared to standard market offerings, catering to applications that demand higher energy and power density.

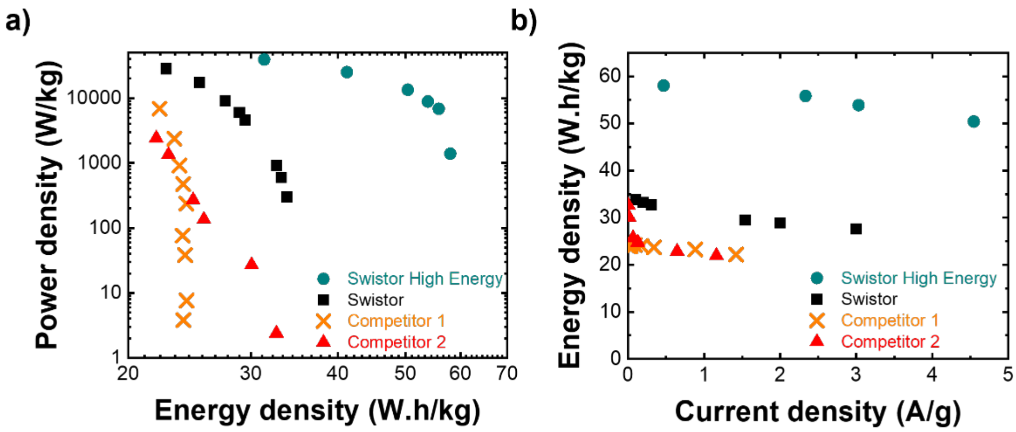

Fig. 9. Comparison plots normalized by electrode material. a) Ragone plot comparing energy and power density and b) energy density over current density for the two types of Swistor capacitors and two commercially available EDLC.

CONCLUSIONS AND FUTURE WORK

Our development of a redox-enhanced supercapacitor technology has successfully demonstrated a reliable performance at 3.3 V, a maximum voltage of 3.6 V, achieving an energy density of 60 Wh/kg while maintaining a power output over 1 kW/kg and a lifespan of over 60,000 cycles, outperforming competitors. Moreover, this has been accomplished using safe and non-critical raw materials. The demonstrated reliability, higher cell voltage, and superior energy density of our supercapacitors facilitate more efficient hybrid power supplies, crucial for long-duration space missions and complex satellite operations, optimizing overall mission effectiveness and payload efficiency.

Looking forward, we aim to expand our production capabilities to larger cell formats, namely pouch cells with capacities up to 10 F, and subsequently cylindrical cells of 20 F. This includes a focus on improving energy and power densities and refining our production processes to support the deployment of these technologies at a larger scale. Future initiatives will concentrate on rigorous testing to confirm compliance with space industry standards, continued material improvements, and maintaining a sustainable approach to production enabling devices that provide a robust solution to hybrid energy storage and management challenges, constituting a leap forward to space missions powered by reliable, high-performance energy systems.

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