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Article

Electrical Performance of Current Commercial Supercapacitors and Their Future Applications

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Abstract: From the first patent of supercapacitors, the industry has experienced the commercialization of supercapacitors happening rapidly after the year 2000. Within the last 5 years, the electronics industry has gained access to at least four different types of commercially available supercapacitor families, namely, electrochemical double layer capacitors (EDLCs), hybrid supercapacitors, battery capacitors and pseudo capacitors. Over the same period after year 2000, there has been huge developments in the electrochemistry of supercapacitors based on new materials such as graphene and mechanisms such as tailoring pore sizes for electrolyte ion exchange to increase volumetric energy density. This paper compares the characteristics of three different types of supercapacitors for large energy applications and how supercapacitors can be useful in future DC-DC converters in renewable and micro-grid applications.

Keywords: supercapacitors; batteries; energy storage devices; renewable energy

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1. Introduction

Electrochemical capacitors (ECs) often describe electrical double-layer capacitors (EDLCs), supercapacitors, ultracapacitors, pseudo capacitances, gold capacitors, power capacitors or power caches [1]. In terms of power and energy densities, ECs lie in-between batteries and conventional dielectric capacitors. This is depicted in the Ragone plot in Figure 1. Electrical energy is stored in batteries indirectly as chemical energy resulting from Faradic oxidation and the reduction of the electrochemically active reagents to release charges that flow between two electrodes of differing potentials. In contrast, capacitors utilize the non-Faradic process of storing energy electrostatically as negative and positive charges on its plates. Capacitors benefit from having no chemical and phase changes during charging and discharging, providing unlimited cyclability. However, this results in capacitors having very low energy density. Charged electrode/solution interfaces contain double layers offering capacitances of 16 to 50 μFcm^{-2}, resulting in very large capacitances with large accessible electrode areas afforded by high area carbon powders, felts and aerogels [2]. The surface area of the porous electrodes has been recorded to be as large as 1000–2000 m^2/cm^3.

General Electric company first patented the electrochemical capacitor in 1957, after a German physicist named Hermann von Helmholtz introduced the concept of double-layer capacitance in 1853 [3]. The first patented electrochemical capacitor consisted of porous carbon electrodes with a double-layer capacitance. In the climate-conscious era, there is ever more push to move into renewable energy sources to power civilization. While this is cause for celebration, there is the inherent fault of intermittency of these energy sources to completely sustain our energy needs. Better energy storage systems are required for the complete replacement of polluting energy sources. For electro-chemical energy storage, all rechargeable batteries have limited calendar lifetimes as well as charge–discharge cycles typically in the thousands, varying with the depth of discharge (DoD). Supercapacitors (SCs) have excellent life-cycling, high power density and excellent safety, but lower energy density compared with electrochemical batteries [4–8]. These qualities have led to the steady ramp up of supercapacitor development to provide higher power and energy densities for the ever-increasing demands of better energy storage devices. These include dominant research in aqueous electrolytes, due to their low cost and safety requirements for handling, to organic electrolytes, used in the commercial space due to their higher operating voltage ranges of 2.5–2.8 V [9]. Research into various electrode materials including, but not limited to, graphene, transition metal oxide and transition metal selenides and combinations of SC electrodes with battery electrodes have also been explored. This paper will explore the charge mechanisms of the supercapacitors while also exploring performance characteristics of existing commercial devices.

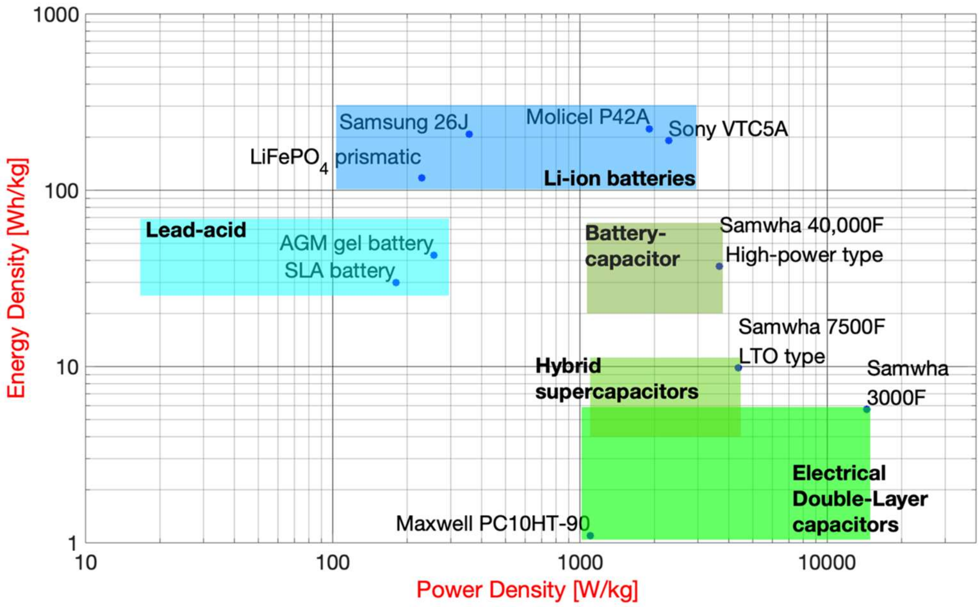


Figure 1. Ragone plot. Adapted from [10].

2. Supercapacitors as an Energy Storage Device

With continuous development in supercapacitor technologies, it is possible to use them as short term ESDs (Energy Storage Devices) in electronic systems that allow for extended life cycling, low maintenance and a low constant equivalent series resistance (ESR). Table 1 shows a comparison of properties between SCs and batteries.

Table 1. Comparison between electrochemical batteries and SCs (Adapted from [8]).

Item	Supercapacitors	Batteries
Charge time	1–60 s	1–5 h
Discharge time	0.1–30 min	0.3–3 h
Energy density, Wh/kg	1–20	20–100
Power density, W/kg	2000–10,000	50–200
Cycle time	50,000–1,000,000	500–2000
Charge/discharge efficiency	Near 100%	70–85%
Internal resistance or ESR	Fractional mΩ to several mΩ (Constant with DoD)	From 50 mΩ to few Ω (increases with DoD)

Supercapacitors can be categorized according to their charge mechanisms as EDLC, pseudo-capacitance and battery type behaviors, as shown in Figure 2. The physical process of accumulating charges on an electrode surface governs the behavior of EDLCs, resulting in good reversibility with a long cycle life. EDLCs utilize reversible adsorption/desorption of ions at the electrode/electrolyte interface. Active carbon is normally used as the electrode. High performance EDLC design requires electrode materials with high specific surface area, large porosity and proper pore distribution, as its performance depends on the electrochemical activity and kinetics of the electrodes [11]. Pseudo-capacitance is based on Faradic redox reactions, intercalation and electrosorption [12,13]. Surface redox pseudo-capacitance relates to the Faradaic charge transfer between electrode and electroactive ions of the electrolyte at the electrolyte–electrode interface. The second pseudo-capacitance mechanism involves reversible intercalation/deintercalation of ions into the crystal structure of the electrode material. The Faradaic reactions result in the formation of a reversible monolayer on the surface of the electrode [14–17]. Pseudocapacitance is also achieved when a monolayer is formed from the cations on the electrode surface, known as under-potential deposition [18]. It is important to note that no material phase change occurs in pseudo-capacitance mechanisms [7]. Metal oxides such as RuO_2 and MnO_2 are conventionally used as pseudo-capacitive materials [11,19], but also include metal hydroxides, transition-metal chalcogenides, transition-metal nitrides, conductive polymers, perovskites, polyoxometalates, transition-metal oxides and transition-metal selenides [20,21].

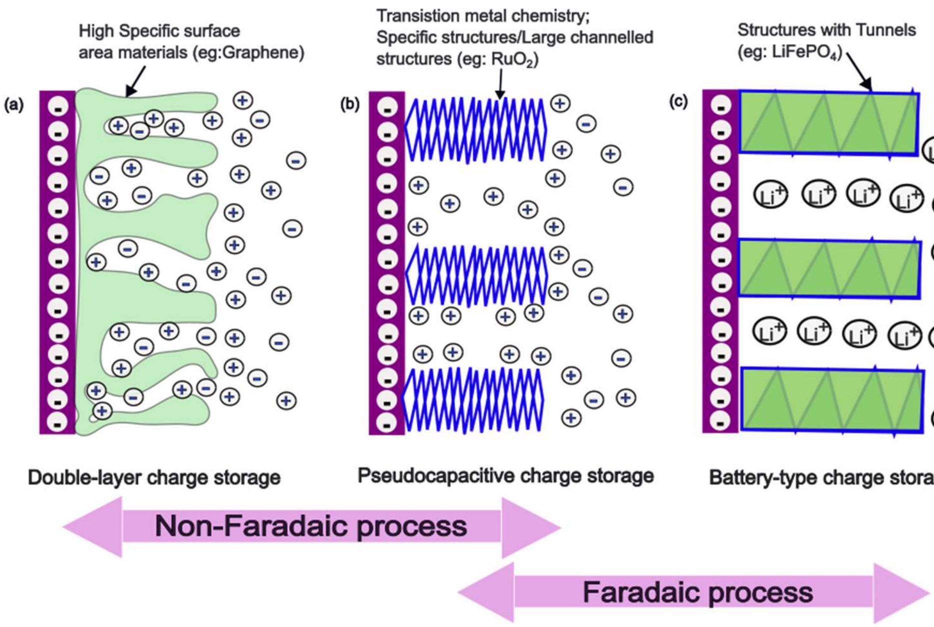


Figure 2. Electrode processes in: (**a**) electrical double layer, (**b**) pseudocapacitive, (**c**) Faradaic electrodes.

Battery type behavior is when ion intercalation during a charge/discharge electrochemical process results in a phase change. Battery type provides high energy capacity but with low power due to the slow phase transformations [22]. Battery type materials with specially designed nanostructures can provide high specific areas, creating more active sites for redox reactions and, when combined with capacitive electrodes, such as active carbon, result in hybrid supercapacitors with high energy and power density. Battery type materials sometimes have pseudo-capacitive behavior, exhibiting high electric conductivity and high specific surface to allow electron transportation and suppress phase transformations. They are combined with EDLC-based carbon materials and organic electrolytes containing Li^+ or Na^+ to create Li-ion or Na-ion supercapacitors or with aqueous electrolytes to form hybrid supercapacitors [7].

Hybrid supercapacitors consist of a combination of EDLCs and pseudocapacitive behavior, resulting in improved power and energy densities. They are divided into composite, asymmetric and battery type supercapacitors. The electrodes in composite supercapacitors consist of both carbon, providing high surface area and high conductivity, and pseudocapacitive material, allowing for EDLC formation and Faradaic reactions [23–26]. An asymmetric supercapacitor, as the name suggests, uses one electrode made of EDLC material while the other is from a pseudocapacitive material, allowing high operating voltages equating to high energy density compared with [26–30]. Battery type supercapacitors combine a supercapacitor electrode, providing enhanced power density, with a battery type electrode, increasing energy density [31–37].

Research is still being undertaken to increase the energy density of supercapacitors. The increased surface area of electrodes results in increased gravimetric capacitance. Studies include using variations of graphene for increased surface area and achieving an energy density close to 88.1 Wh/L [38,39]. Graphene is increasingly seen as important for the world of electronics due to the high mobility afforded by its charge carriers. Since Si-based semiconductors are reaching their limits, graphene is seen to deliver great features. Graphene powder is proposed to be used in future electric batteries, where graphite is used extensively. Graphene proves large surface to volume ratio and high conductivity [40]. The charge carriers in graphene mimic relativistic particles and are described using the Dirac equation. More information of the Dirac equation can be found in [41]. In the pursuit of more surface area, a new material type known as Covalent organic frameworks (COFs) are also under research, as they have low density and high chemical stability [42].

Over the last decade, supercapacitors have improved in performance and there are now three to four different families of devices commercially available. SAMWHA^{TM} CAPACITOR manufactures the EDLC supercapacitor, hybrid capacitor, high-energy type battery capacitor and high-power type battery capacitor, shown in Figure 3a. Recent development has allowed the proliferation of battery-type hybrid SCs (battery capacitors) to have large power and energy density, leading the path in replacing lead–acid batteries. Table 2 refers to a comparison of parameters of commercially available SC families. Although battery capacitors offer reduced cycle life and power density compared with the EDLCs, they offer much higher power density and cycle time than lead–acid batteries [8]. Parameters of batteries and supercapacitors are presented in Table 3, showcasing their benefits and tradeoffs.

(**a**) (**b**)

Figure 3. Commercially available supercapacitor families: (**a**) left to right different EDLCs, one hybrid and two battery capacitors; (**b**) 3000F EDLC (left) vs. 3300F battery capacitor (middle) vs. 360F EDLC (right), demonstrating how battery capacitors have improved their energy density with smaller canister sizes. [Source: Samwha Electric].

Table 2. Comparison of commercially available SCs (Adapted from [8] and and Samwha Electric, South Korea).

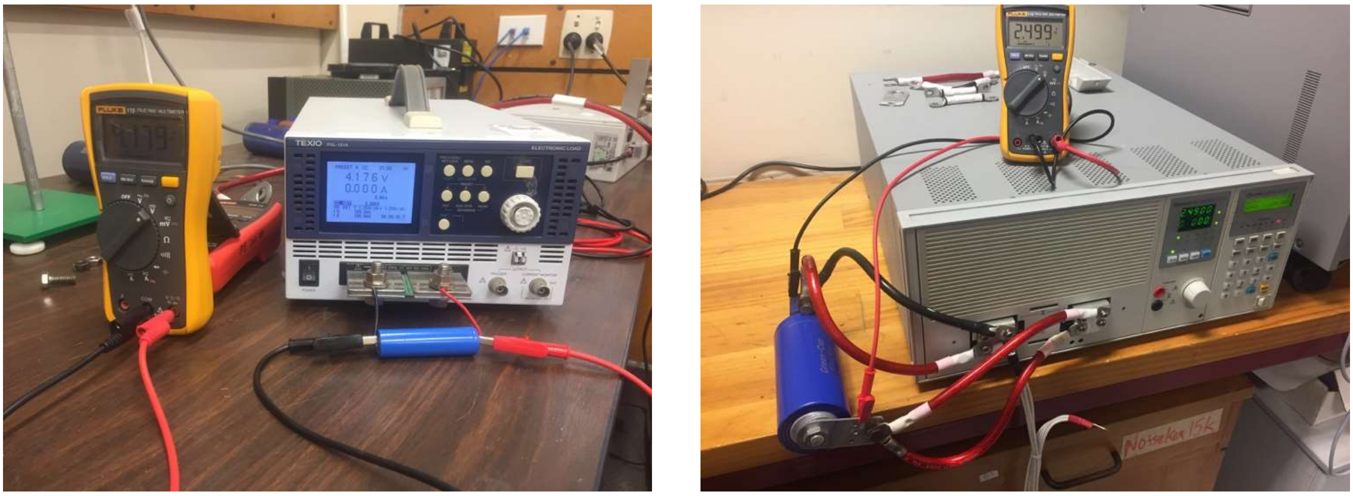
Parameter	EDLCs	Hybrid SCs	Battery Capacitors
Energy Density, Wh/L	5–8	10–14	50–120
Power Density, W/L	8000	2500–4000	1600–3200
Cycle Time, cycles	1,000,000	40,000–50,000	15,000–20,000
Rated Voltage, V	2.7–3.0	2.7-2.8	2.7
Capacitance, F	1–5000	200–7500	1000–100,000

Table 3. Parameters of Li-ion and EDLCs (Data from [18,43] and Samwha Electric, South Korea).

Energy Storage	Li-Ion Battery	Lead–Acid Battery	EDLC Supercapacitor	Hybrid Supercapacitor	Battery Capacitors
Specific Power (W/kg)	3000	250	14,000	5000	4000
Specific Energy (Wh/kg)	100–200	30–100	1–10	7–12	20–71.4
Life Cycle	250–1000	500–1000	500,000–1,000,000	40,000–50,000	15,000–20,000
Temperature Range	0 to 60 °C	0 to 40 °C	−40 to 60 °C	−20 to 60 °C	−20 to 60 °C

3. Performance Measurements

Two different DC loads were used to obtain the performance characteristics of the devices. To explore the high current capabilities of the supercapacitors, the 1200 W Chroma 6314 A, capable of up to 240 A, was used. A secondary 300 W capable TEXIO PXL-151 A, capable of handling 150 A, was used for the Li-ion battery due to its comparatively lower current capability. The experimental setup is shown in Figure 4.



(**a**) (**b**)

Figure 4. Experimental setup: (**a**) TEXIO PXL-151 A discharging a Li-ion cell; (**b**) Chroma 6314 A discharging a supercapacitor.

3.1. EDLC Supercapacitor

The constant current discharge of a SAMWHA^{TM} 3000F EDLC is shown in Figure 5. It uses activated carbon as its electrodes and utilizes electrostatic charge storage. This non-Faradic process allows for a high cycle life in the millions without degradation. It has an operational range of 3.0–0 V. During constant current discharge, it follows a linear voltage drop down to zero, like the common electrolytic capacitor. The discharge capacity of the supercapacitor can be calculated from Equation (1),

$$Dischargecapacity[\mathrm{Ah}] = C\Delta V \times \frac{1}{3600} \quad (1)$$

where C = capacitance in Farads and ΔV = change in voltage. For the 3000F EDLC, theoretical discharge capacity is 2.5 Ah. It is important to consider that commercial supercapacitors come with a tolerance of usually 10% (but it can be as high as 30%) of stated capacitance. When this is accounted for, it gives a discharge capacity within 2.25–2.75 Ah, which is line with the data collected.

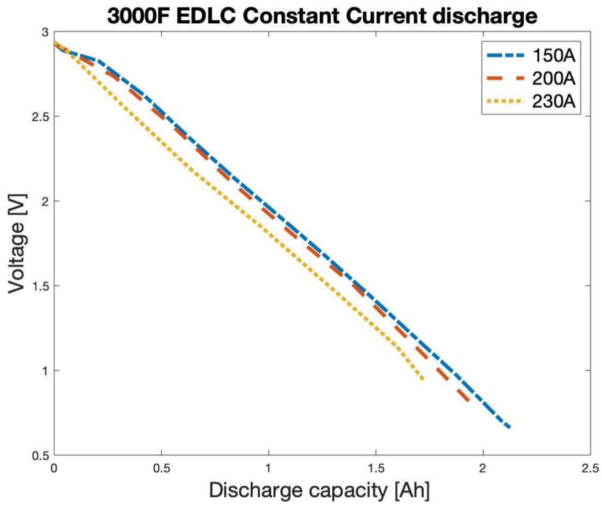


Figure 5. The 3000F EDLC constant current discharge.

3.2. Hybrid Asymmetric Supercapacitor

The constant current discharge of a SAMWHA$^{\mathrm{TM}}$ 7500F hybrid capacitor is shown in Figure 6. This is an asymmetrical supercapacitor consisting of a Lithium Titanium Oxide (LTO) or Lithium Manganese Oxide LMO anode and an activated carbon cathode. The energy storage is achieved with a mixture of a Li^+ intercalation–deintercalation process and an electrostatic absorbing process due to the electric double layer. As a result, the energy density has increased compared with an EDLC supercapacitor but has a lower life charge–discharge life cycle. It has an operational range of 2.8–1.6 V. The cutoff region of 1.6 V, according to the manufacturer, is due to the operational voltage of the LTO electrode being 1.55 V. Here as well, we have the 10% tolerance of capacitance and the discharge capacity varying from 2.25 to 2.75 Ah, which can be approximated by Equation (1).

3.3. Battery Capacitor

The constant current discharge of a SAMWHA$^{\mathrm{TM}}$ 40,000F and 70,000F battery capacitor is shown in Figure 7. This is an asymmetrical supercapacitor utilizing a Li transition metal oxide (LiM_xO_x) anode and an LTO ($Li_4Ti_5O_{12}$) cathode achieving energy storage via a Li^+ intercalation–deintercalation process. As a result, the energy density has increased compared with a hybrid supercapacitor while slightly diminishing its cycle life. It has an operational range of 2.7–1.6 V. The LTO electrode becomes unstable below 1.55 V, where permanent damage to the device occurs.

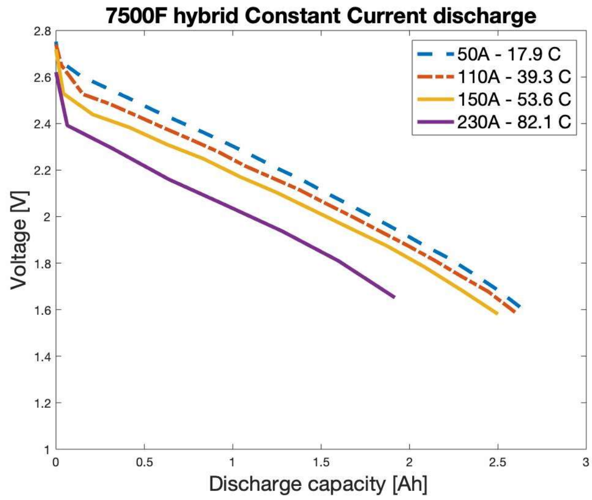
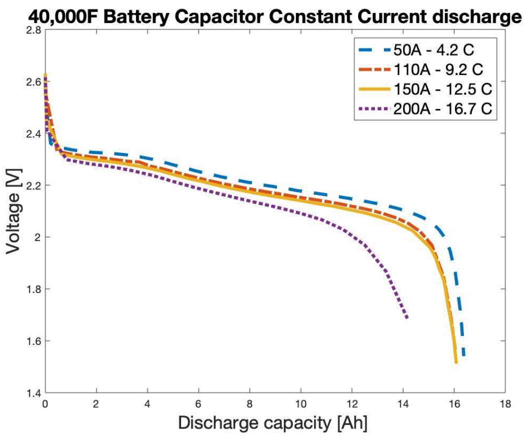
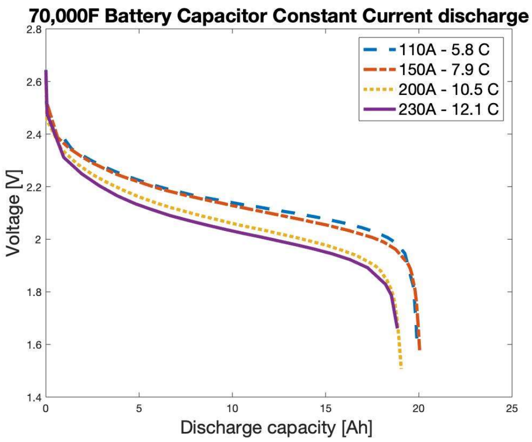


Figure 6. The 7500F hybrid constant current discharge curve.



(**a**)



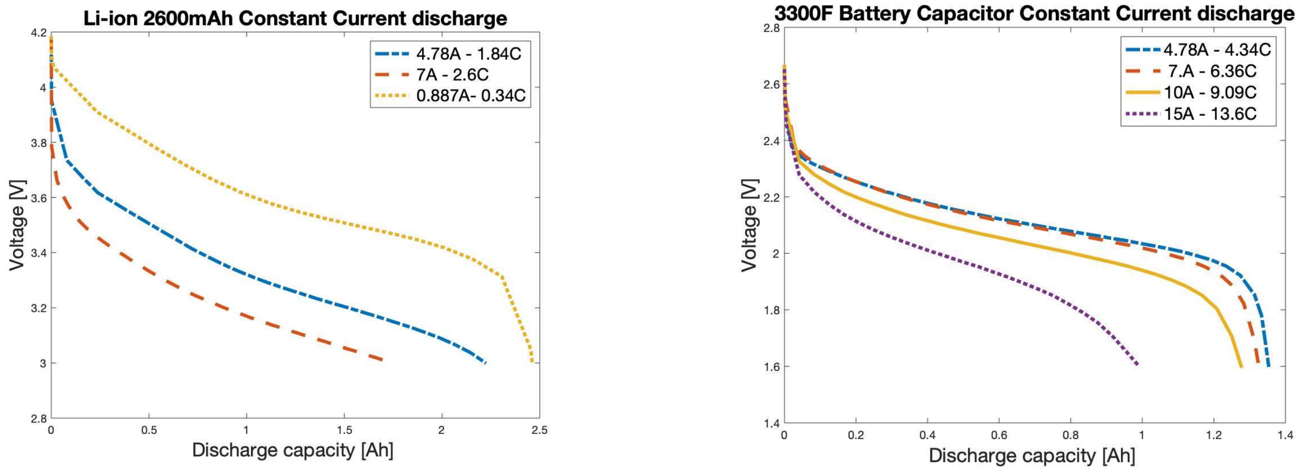
(**b**)

Figure 7. Battery capacitor discharge curve: (**a**) 40,000F (high power type); (**b**) 70,000F (high energy type).

3.4. Li-Ion Battery

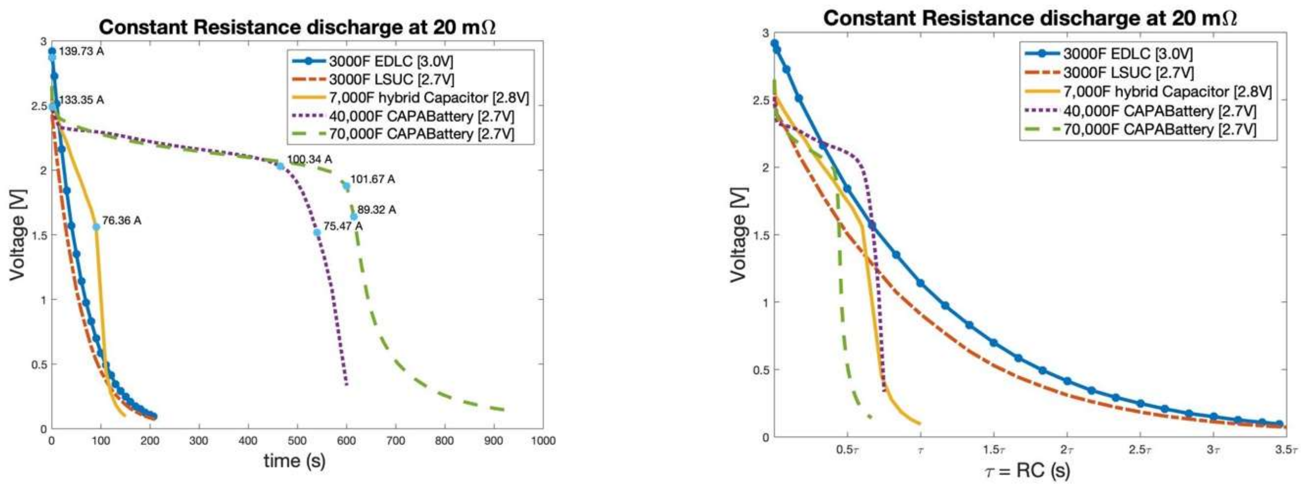
The performance of a 2600 mAh 18,650 Li-ion battery by Powertech^{TM} was compared with a 3300F battery capacitor, shown in Figure 8. From the discharge curves, we can infer that the hybrid and battery capacitor type supercapacitors follow a profile like that of Li-ion batteries. When the Li-ion battery discharges at higher C-rates, it loses capacity, while the battery capacitor remains closer to its specified 1.1 Ah capacity at a wider range of C-rates.

Figure 9 depicts the constant resistance discharge curves for different types of supercapacitors, with the horizontal axis units based on time constants. Time-constant-based graphs are used to compare the difference of behavior of each family, with different capacitance capabilities per unit volume of package.



(**a**) (**b**)

Figure 8. Constant current discharge curve (**a**) 18,650 Li-ion 2600 mAh; (**b**) 3300F battery capacitor.



(**a**) (**b**)

Figure 9. Constant resistance discharge curve: (**a**) with respect to time taken; (**b**) with respect to time constants.

4. Applications and Life Cycle Cost Comparison

Traditional applications of supercapacitors [44] (pp. 21–28) [45,46] include,

- BEVs, fuel cell vehicles and light trains;
- Cold starting trucks;
- Vehicle start–stop functions;
- Wind turbine pitch controls;
- Grid voltage stabilizers;
- Microgrids.

For many applications, supercapacitors are combined with other forms of energy storage to reap the benefits of cheap long-term storage with the ability to respond fast. They utilize so-called hybrid energy storage systems by connecting in passive, semi-active and fully active systems. A passive system is the connection of the supercapacitor and battery in parallel, allowing for the cheapest of the three systems. This ensures relatively low discharge of the battery along with a low C-rate, resulting in a longer lifetime as the supercapacitor does the heavy lifting. The passive system does have the disadvantage of the supercapacitor not operating at its full range due to it being tied to the small voltage variation of the battery.

Fully active systems control the power flow of both the battery and supercapacitor energy, resulting in even better performance enhancements and longevity [45]. However, the development of a battery capacitor with its high-power density and cycle life with comparable energy to lead–acid batteries could replace these systems.

The longer cycle life is also beneficial in the automotive industry, specifically for fleet vehicles. In the performance vehicle category, Lamborghini™ has developed a few limited hybrid models incorporating supercapacitors, even leading to a joint patent with The Massachusetts Institute of Technology (MIT) for supercapacitors based on "Metal-Organic Frameworks" [47,48].

Taking BEVs, Tesla model S 70D has a 70 kWh battery with an EPA range of 240 miles [49]. This accounts for 240,000 miles over the lifetime of a 1000 cycle -ion battery, which is more than adequate for a consumer. However, this is fractions compared with a commercial vehicle's lifetime mileage. For commercial EVs., an energy storage system with a long life cycle and high power is a necessity to avoid long downtimes for battery replacements and charging, and this is an area where the more energy-dense battery capacitor technology fits in.

The long-time constant circuits allowed by supercapacitors have resulted in the development of more non-traditional applications [10,50]. These new techniques are known as Supercapacitor-Assisted (SCA) techniques.

Supercapacitor-Assisted Low-Dropout regulator (SCALDO);
Supercapacitor-Assisted Surge Absorber (SCASA);
Supercapacitor-Assisted Temperature Modification Apparatus (SCATMA);
Supercapacitor-Assisted LED lighting (SCALED).

The supercapacitor families have low to moderate energy storage, but make up for it with high power capability, combined with their high cycle life compared with that of Li-ion batteries. It can be observed from Table 4 that the cost per kWh of all the supercapacitor families is very high compared with that of Li-ion batteries of USD 132/kWh in 2021, as mentioned in [51]. However, the advantage is seen in long-term cost savings. While Li-ion batteries have close to 1000 cycle times, different supercapacitor families have life cycles ranging from 15,000 to 1,000,000 cycles. By factoring this in, we obtain a cost per kWh that is much better than that of Li-ion batteries. If weight and space is not a restriction, for long running systems supercapacitors offer improved cost saving compared with that of Li-ion batteries.

$$Energy[\mathrm{Wh}] = \frac{1}{2} \times Capacitance \times \left[V_{initial}^2 - V_{final}^2\right] \times \frac{1}{3600} \tag{2}$$

$$\frac{\$}{\mathrm{kWh}} = \frac{Costperdevice[\$]}{Energy[\mathrm{Wh}]} \times 1000, \tag{3}$$

$$\frac{\frac{\$}{\mathrm{kWh}}}{1000cycles} = \frac{\$/\mathrm{kWh}}{totallifecycleofdevice}, \tag{4}$$

For grid-based applications, Skeleton Technologies™ offers the SKELGRID line, which provides Fast Frequency Response and frequency stabilization [52]. It is used in tandem with a flywheel to make sure the lifetime of the batteries is extended, while enabling 100% renewable energy in the Isle of Eigg, Scotland [53]. A system of 144 supercapacitor modules of 102 V 88F can provide 50 MW of power for 6.5 s.

Table 4. Cost analysis of commercial supercapacitor families.

Type	Capacity			Cost per Unit [USD]	Wh/kg	USD/kWh	Life Cycles	USD/kWh per 1000 Cycles
	[F]	[mAh]	[Wh]					
EDLC	3000	2200	3.04	51.85	5.7	17,055.92	1,000,000	0.02
Battery capacitor (High power type)	40,000	12,000	26.28	88.89	37.0	3382.42	20,000	169.12
Battery capacitor (High energy type)	3300	1100	2.17	7.41	40.1	3414.75	15,000	227.65
Battery capacitor (High energy type)	70,000	19,000	45.99	98.77	56.7	2147.64	15,000	143.18
Battery capacitor (High energy type)	100,000	28,000	65.69	104.94	71.4	1567.50	15,000	104.5
Li-ion batteries (Data collected from industry)						132 [51]	1000	132

5. Conclusions

The cost of Li-ion batteries was at USD 684/kWh in 2013 [51], but was reduced due to mass manufacturing and new manufacturers competing. The same could be expected in the supercapacitor markets, with large manufacturers increasing their investments in the supercapacitor space, along with improvements in energy density, leading to more areas of application. This experimental work demonstrates the development of commercial supercapacitor families within the last eight years and how they will be useful in future renewable energy systems to reduce the effective longer-term costs of renewable energy system building blocks. This work also demonstrates that hybrid supercapacitors are rapidly reaching the energy density of lead–acid batteries, which could be the potential longer-term competition to Li-ion families.

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Conflicts of Interest: The authors declare no conflict of interest.

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