Supercapacitors vs. Lithium-ion Batteries: Properties and Applications

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Supercapacitors attract attention due to their superior values in the parameters like capacitance, discharge currents and cycle lifespan. Supercapacitors are designed and used in many applications where they partially or completely substitute conventional batteries. On the other side, supercapacitors are used in applications which are not so far suitable for these devices. To avoid wrong design and misuse of the supercapacitors it is necessary to correctly understand their properties, key advantages and disadvantages. Similar situation can be found in the field of lithium-ion batteries.

Keywords: Batteries, Energy storage, Hybrid energy storage system, Lithium-ion, Renewable energy, Supercapacitors

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1 Introduction

Supercapacitors and lithium-ion batteries, the right understanding of physics and operation principle of each device is crucial to ensure their correct and effective application. This paper contains summarized facts and aspects relating to both devices aiming to provide comprehensive point of view. It is necessary to realize how important and widely spread the energy storage devices are today. There are plenty of varying applications which requires energy storages. It is not only transportation as cars, busses, forklifts and small electric vehicles and portable consumer electronic devices. But there are the other growing markets like renewable energy storage, grid and industry. Each application has got its own special requirements and operation conditions which must be taken into account if the energy should be effectively utilised.

Both devices as lithium-ion batteries and supercapacitors undergone a long development during their know existence. In case of the batterie, we can start the at the turn of the 18th and 19th century with the voltaic pile, in case of capacitors we can start in the year 1745 by discover so called Leyden jar which represents first capacitor at all. During the years there were many types of batteries and capacitors, skip the other important types of batteries and capacitors which appeared during the development period and look at the present time. Today, the lithium-ion batteries and supercapacitors represent the most advanced, leading technology among batteries and capacitors. The development of rechargeable lithium-ion cells begins in the late 1970s with the discovery of reversible intercalation of lithium into graphite, along with the discovery of the positive electrode material $LiCoO_2$ (Lithium Cobalt Oxide). This was followed in the mid-1980s by the first experimental secondary cells where the negative electrode was made of graphite and the positive electrode $LiCoO_2$ only in 1991, SONY launched the first commercial secondary lithium-ion battery powering a portable camera. The development of supercapacitors ran in parallel with the development of lithium-ion batteries, but due to the success of these batteries, the development of supercapacitors was to some extent lagged behind. The first experiments with supercapacitors (in this time called ultracapacitors or late electrochemical capacitors) date from the 1950s to the 1970s by General Electric and Standard Oil of Ohio (SOHIO), the capacity of these supercapacitors was around 1 F [1–18].

The first commercial supercapacitors named "GoldCap" from Panasonic and "Supercapacitor" from Japanese Nippon Electric Company (NEC) companies were patented and introduced to commercial market in the 1970s. These first supercapacitors differed in used electrolyte where GoldCap use aprotic electrolyte and Supercapacitor use aqueous electrolyte, unfortunately both possessed high internal resistance. In the 1980s, the first supercapacitor with low internal resistance, manufactured for military purposes was introduced. In the early 1990s, Maxwell Laboratories launched the first commercial supercapacitor with capacitance 1 kF. This modern supercapacitor named

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"BoostCap" already had low internal resistance It can be considered as direct predecessor of present supercapacitors. Today, supercapacitors over 3 kF are commonly available [19–34].

2 EDLC Supercapacitor and lithium-Ion Battery

2.1 EDLC Supercapacitor and Lithium-Ion Battery Operation Principles

To understand operation principle of each device is necessary to understand the way which each device use for storing of electric charge. First it is necessary to define the major electrical quantities which describe both devices. The supercapacitors can be characterised by the electric potential marked by symbol V or φ measured by joule per coulomb ($J\,C^{-1}$) or more common in volts (V). The difference between electric potential points, in case of supercapacitors it is between two electrodes, we call electric potential difference, commonly called as voltage that is symbolised by U or V and having the same unit volt (V). In case of lithium-ion batteries, we work with electromotive force abbreviated as *EMF* or Greek letter ε, sometimes denoted as E, to avoid confusion with energy symbolized by E and having unit joule (J) the Greek letter ε is preferred. Same as in supercapacitor, the *EMF* measured between two battery electrodes is called electromotive force difference and as in the supercapacitors, this difference is named as voltage symbolised as U or V and having the same unit volt (V). Here is very important to realise that whereas electric potential or sometimes called electrostatic potential is extensive physical quantity, i.e., in our cases depends on the amount of the charge stored, the EMF is intensive physical property linked with energy of the reaction and molecule bond, i.e., does not depend on the amount of the charge stored. This is important physical distinction that determines electrical characteristics and behaviour of each device.

Another electrical quantity is the ability to store electric charge. The charge capacity of supercapacitors is expressed by the capacitance quantity marked by C with farad (F) unit. The lithium-ion batteries have got electric charge capacity or most common just capacity with symbol Q and unit coulomb (C) or most usual ampere-hour (Ah). As in the case of supercapacitor and lithium-ion battery, the capacitance and capacity property, both are extensive physical quantities depending on the amount of electric charge [35–38].

2.2 Supercapacitors

There are few types of supercapacitors such as an electric double layer (EDLC) supercapacitor, pseudo-supercapacitor, and a hybrid supercapacitor. Each type differs by the electrode material symmetry along with the mechanism which it uses to store energy, resp. electric charge. On the commercial market, the EDLC supercapacitors share the waste majority. There are a few pseudo-supercapacitor models which are not well known and spread, and the hybrid supercapacitors are currently limited only to the research area.

The EDLC supercapacitors are symmetric supercapacitors where both electrodes are made from the same material. EDLC supercapacitors use as electrode material amorphous carbon, often named as carbon, black or activated carbon coated on aluminium collector see Fig. 1. This amorphous carbon is not an expensive and well conductive material. As the most important property of the amorphous carbon can be considered the large specific surface area that reaches up to $10\,000\,m^2g^{-1}$. This is a key property that allows EDLC supercapacitors get such high capacitance. The electrolyte is an essential part of EDLC supercapacitor. There are three basic properties of the electrolyte that strongly affects its parameters, it is a potential window, dielectric strength, and the electrolyte resistance. As there is no solid-state diffusion, the total resistance of EDLC supercapacitors is given only by the resistance of the electrolyte so-called equivalent series resistance R_{ESR} (Ω). The R_{ESR} parameter limits the power which the EDLC supercapacitor can provide. Another important property of the electrolyte is its dielectric strength, commercial supercapacitors possess apparent low maximal voltage, but the most common EDLC technology provides $U = 2.7$ V. Is seems to be a lower voltage than in the case of lithium-on batteries, but there is necessary to realize that the energy of EDLC supercapacitor is stored in a very thin dielectric-polarized layer (film) on electrode-electrolyte interface. This thin film called the Helmholtz layer has got the thickness ranging from 0.1 to 10 nm. If we compare this thickness of Helmholtz dielectric layer with voltage, we get that the dielectric strength of this layer can be in $MV\,m^{-1}$ order, for comparison aluminum oxide Al_2O_3 that works as a dielectric layer in electrolytic capacitors has got the dielectric strength around $8\,MV\,m^{-1}$ [38–46].

2.3 Lithium-Ion Batteries

In contrast to EDLC supercapacitors, lithium-ion batteries use a different mechanism and operation principle to storage electric energy (charge). The lithium-ion batteries dominate the commercial market as the electrochemical system with the highest energy density of all. There are few variants of lithium-ion batteries which differ from each other by cathode or anode material, but the operation principle is the same as depicted in Fig. 2. The lithium-ion batteries are based on the intercalation principle where the host (active electrode material) accommodates or releases lithium ions moving between the electrodes during charge and discharge. This operation principle is also known as "rocking chair"

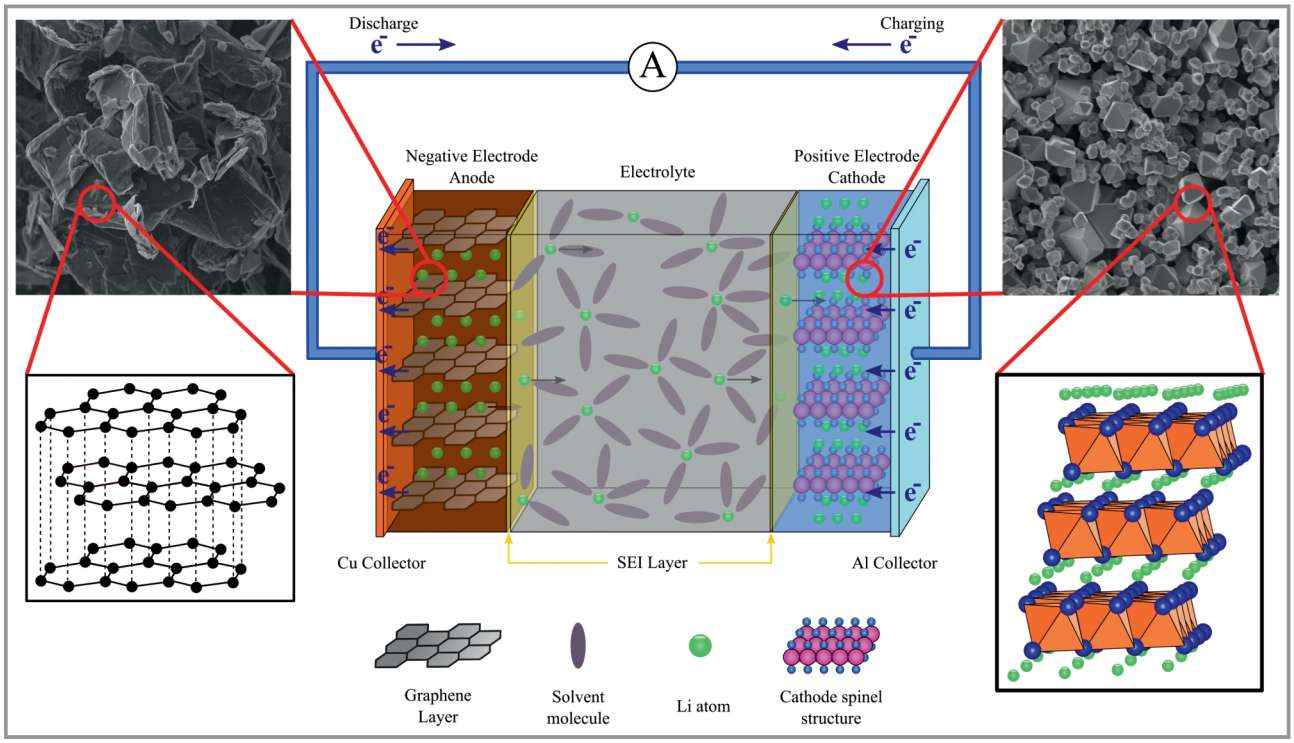

Figure 1. The representation of lithium-ion battery where negative electrode (anode) is made from graphite and positive electrode (cathode) is formed from lithium cobalt oxide – $LiCoO_2$.

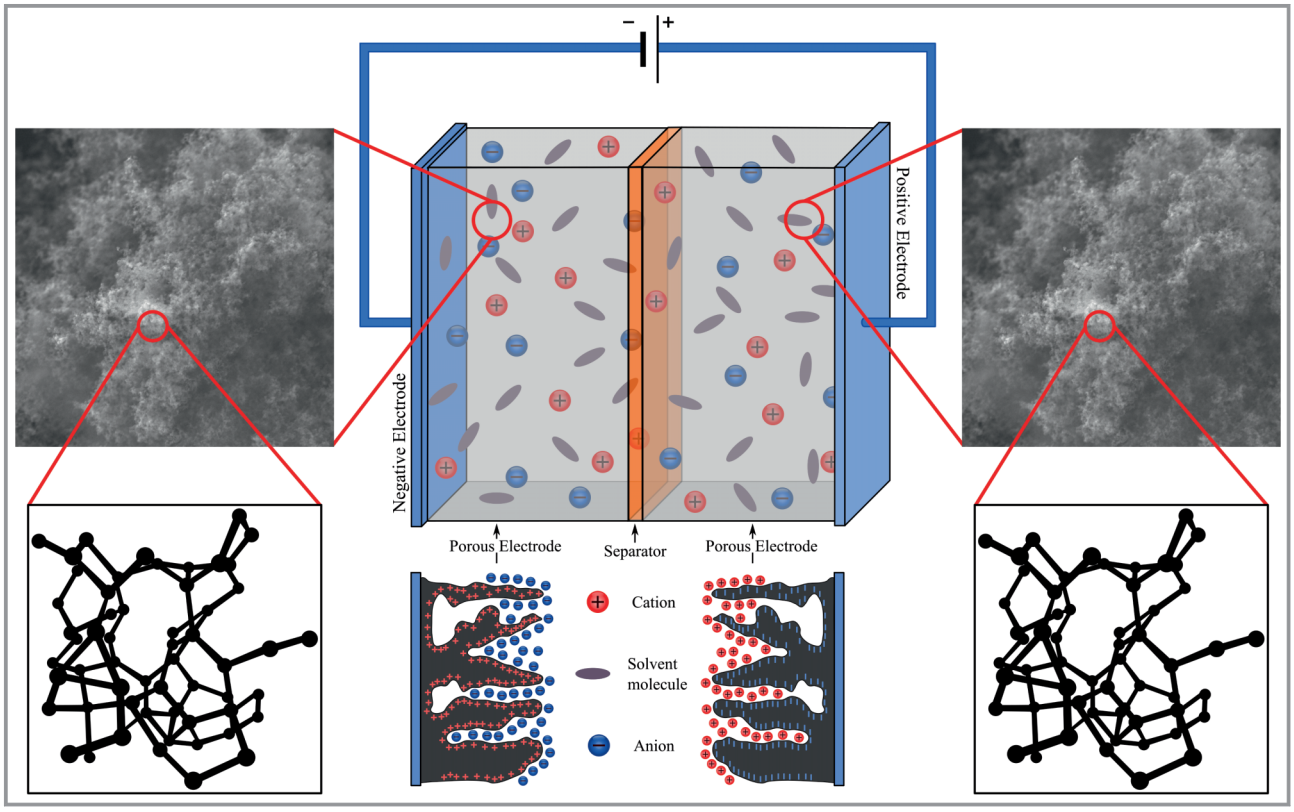

Figure 2. Schematic representation of the symmetric EDLC supercapacitor. The electrodes are made from amorphous carbon.

principle. There are three main variations of lithium-ion batteries on the commercial market determined by the electrode material. The most common variation is the combination lithium cobalt oxide (LCO) as the positive electrode material coated on aluminium collector and graphite with negative electrode material coated on copper collector which provide voltage U = 3.6 V. The second most widely spread variant is similar to the previous one with one different positive electrode material being made from lithium iron phosphate (LFP) material. This battery provides lower voltage around U = 3.2 V but offers better stability, safety, and higher rate capability. The last and most rare variation of lithium-ion batteries on the commercial market is the combination of lithium cobalt oxide (LCO) as a positive electrode material and lithium titanate oxide (LTO) as a negative electrode material. This variation offers the lowest voltage U = 2.3 V but exhibits excellent stability and cycle durability over 10 000 charge-discharge cycles [47–51].

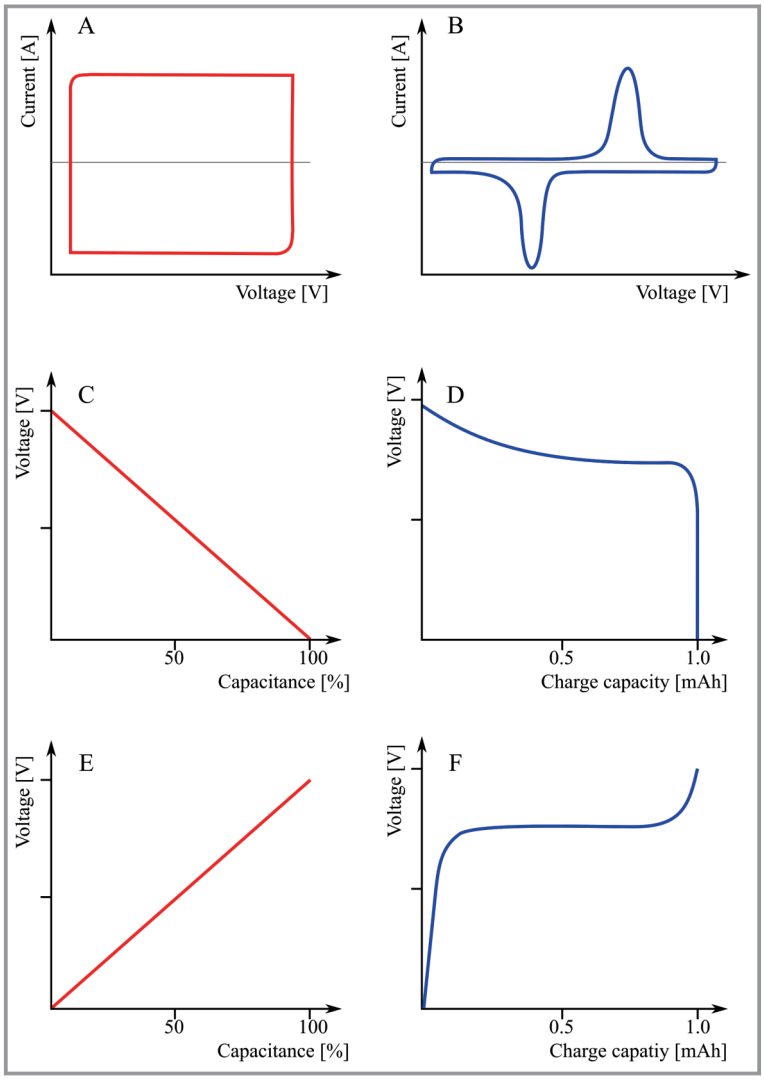

Figure 3. Curves representing basic electrochemical behaviour, the symmetric EDLC supercapacitors (red) and lithium-ion battery (blue). A) Cyclic voltammetry (CV) of an ideal EDLC supercapacitor, C) and E) discharging and charging of EDLC supercapacitor respectively. B) CV of an ideal lithium-ion battery with significant oxidation and reduction peaks. D) discharging and F) charging od lithium-ion battery.

2.4 Characteristics

As the most important thing that defines both devices is the principle and mechanism by which their store and hold electric charge. In case of EDLC supercapacitors the charge carriers move through the electrolyte toward electrodes where adsorb on the electrode's surface to create dielectric-polarized (Helmholtz) layer. This process is very fast and key role plays only the resistance of the electrolyte as stated above. In the case of lithium-ion battery the charge carries (lithium cations) move toward the electrodes where penetrate (insert) inside of the bulk of active electrode material, here the redox reaction take a place. This process of penetration and moving of lithium cations into and inside the bulk of active electrode material is called solid state diffusion. The solid-state diffusion process is very slow in contrast to diffusion of charge carries in the electrolyte. This diffusion difference between EDLC supercapacitor and lithium-ion battery is the key which governs rate and charge-discharge characteristics of each device. It is necessary to realise that each system is as fast as its slowest process. The Fig. 3 presents elementary characteristics of EDLC supercapacitor and lithium-ion battery [52–56].

The EDLC supercapacitors and lithium-ion batteries as devices designed to store electric energy (charge) have got few basic parameters such as voltage, capacity and energy. These parameters characterize each device and provide information about their ability to store and release electrical energy. The voltage provides, in both cases, the same information about the power that the device can potentially provide. The ability to store electric charge, in the case of lithium-ion batteries, is determined as a charge capacity or just capacity parameter denoted by Q (mAh or Coulomb). In the case of the EDLC supercapacitors, the parameter related to the ability to store electric charge is expressed by the capacitance parameter marked as C (F). These parameters, in both cases, represent the capability of the device to store a hold amount of electric charge. Due to the different nature of the mechanism which each device can use to store the charge, the parameters differ. Eq. (1) represent the relation between capacitance and capacity.

$$Ah = \frac{F\Delta V}{3600} \quad (1)$$

where Ah (ampere hour) is the unit of the lithium-ion battery capacity, F (Farad) is the unit of EDLC supercapacitor capacitance, and the ΔV is its voltage difference in volts. The EDLC supercapacitors can be fully discharged without any damage, thus in this case as ΔV the nominal voltage can be substituted. It is important to realise that 1 Ah is equal to 3600 Coulombs (C) and 1 F is equal to 1 C V^{-1}. In other words, one farad capacitor holding one coulomb of charge will be at a potential of one volt. As the third important determining parameter is the total energy which is stored inside the device. The energy is symbolised as *E* with joule unit (J). The energy stored in EDLC supercapacitor can be calculated by Eq. (2) where *C* is the capacitance, and the *U* is the nominal voltage. As can be seen, the energy stored in this device is directly proportional to amount of charge and the voltage under which the charge is hold.

$$E(J) = \frac{CU^2}{2} \quad (2)$$

The energy stored in lithium-ion battery can be calculated in a similar way, i.e., from the battery capacity *Q* in Ah and the nominal voltage *U* in volts, Eq. (3). It is necessary to realise that the watt-hour unit (Wh) can be expressed in joules, i.e., 1 Wh = 3600 J.

$$E(Wh) = QU \quad (3)$$

There can be seen an important consequence from the characteristics in Fig. 3 and Eqs. (2) and (3) above. As was stated, the energy of the device is directly proportional to the voltage which holds or drives the charge. As the voltage of the EDLC supercapacitor goes down (along discharging), the energy which supercapacitor store decrease as well with quadratic course curve (depends on the resistance of the load). It is in sharp contrast to lithium-ion batteries where during the discharge the voltage remains constant [57–62].

This constant voltage drives almost all charge stored in the battery, and all charge is driven with the same potential. It causes that the amount of energy stored in the battery is significantly higher than in the supercapacitor.

2.5 Parameters Comparison

All these characteristics of EDLC supercapacitors and lithium-ion batteries described above result in typical parameters. Two commercial samples of both devices were chosen and compared in Tab. 1 below.

As the typical representative of commercial production, the EDLC supercapacitor by Maxwell Technologies company with capacitance 3400 F was chosen. The EDLC supercapacitor has got a cylindrical format dimensioned as 60 mm diameter, 138 mm high. Lithium-ion battery representative, the 18 650 cylindrical cell (18 mm diameter, 65 mm high) by Panasonic company was picked out. The Tab. 1 shows a clear overview of the most important parameters coming from the commercial market. From the data can be seen an enormous energy density gap between both devices, where lithium-ion battery holds roughly 30 to 70 times more energy per weight and volume, respectively. What is significantly higher on the side of EDLC supercapacitor is its quick charging but has to be pointed out that in this very short time only a relative small amount of energy is stored. The self-discharge rate of the EDLC supercapacitor is very high, actually the EDLC supercapacitor lost its whole capacity within one month. In the case of EDLC supercapacitors and lithium-ion batteries, the self-discharge rate is strongly influenced by various parameters such as temperature, charge duration, discharge rate, or short-term history. There can be calculated other parameters, for example, the price per charge-discharge cycle, where the EDLC supercapacitor has a great advantage related to its high initial unit cost. However, the number of cycles which EDLC supercapacitor performs in the target application has to be taken into account as well.

As can be seen from the data listed above, the EDLC supercapacitors are not suitable for long-time energy storage and cannot be considered as an alternative to lithium-ion batteries.

3 Conclusions

Nowadays, many statements can be seen, followed by projects in which supercapacitors replace or alternate batteries.

Table 1. Comparison of selected parameters of commercial EDLC supercapacitor and lithium-ion battery.

Parameter	EDLC supercapacitor	Lithium-ion battery
Nominal voltage [V]	2.7	3.6
Charge capacity	3400 F / 3.4 Wh / 12.4 kJ	3.35 Ah / 12.1 Wh / 43.5 kJ
Energy density [Wh kg^{-1}]	7.1	248
Energy density [Wh L^{-1}]	9.2	677
Max. power [W]	7020	18
Charge time [s]	3.4	7200
Self discharge [% per month]	> 80*	< 1*
Price per kWh [US-$]	10 000*	140*
Cycle life (charge-discharge cycles)	> 1 000 000	> 500*

* values were additional calculated or estimated.

Supercapacitors possess interesting properties for which they are often popularized, but they also have significant limitations. There are advanced types of supercapacitors, which are under intensive research and development, for example pseudo-supercapacitors or currently advantaged hybrid-supercapacitors. These types of supercapacitors are trying to remove the limits of current commercial EDLC technology, with the help of new electrode materials which exhibit pseudo capacitance or even faradaic behaviour. These advanced types reach significant improving in energy density parameters. The wider look does not show only improving in energy density but on the other hand also demonstrates decreasing values in the specific power (current) parameter. The hybrid supercapacitors advanced in specific energy density thanks to the utilization of a graphite intercalation host, the same intercalation host in common lithium-ion batteries. Using graphite material decreased the specific power due to the nature of graphite as intercalation material. The fall of the specific power parameter is counted for solid state ion transport inside the graphite host, which is much slower in comparison with surface charge polarization.

The special lithium-ion batteries designed for high specific power applications can reach very similar parameters as these hybrid supercapacitors with enhanced specific energy density. It is obvious that advanced types of supercapacitors and lithium-on batteries are approaching very close and overlap in terms of specific power and energy density.

There is a question about the way of further development of these devices. More than 30 years have passed since the first true supercapacitors and lithium-ion batteries were launched on the commercial market. During that time, both technologies have undergone intensive development and research. It can be said that both technologies are probably already at the limit of their technological possibilities.

If there is a need to effectively store and reversely supply high current peaks (power) with a sufficient amount of energy (energy density), the most perspective solution seems to be the complementary combination of supercapacitors and lithium-ion batteries represented by the hybrid energy storage system (HESS). Utilization of HESS seems to be as the most promising solution that meets the energy and power density requirements along with long life cycle, response rate and other parameters. The main issue lays in the hybrid battery management system (HBMS) and its adaptation for a particular application where it has to ensure energy and process efficient operation.

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Symbols used

C	[F]	capacity
EMF, ε	[V]	electromotive force
E	[J]	energy
Q	[Ah, C]	electric charge
R_{ESR}	[Ω]	equivalent series resistance
U	[V]	electric potential difference
V, φ	[J C^{-1}, V]	electric potential

Abbreviations

EDLC	electric double layer capacitor
$LiCoO_2$	lithium-cobalt oxide
LCO	lithium-cobalt oxide
LFP	lithium iron phosphate
LTO	lithium titanate oxide
CV	cyclic voltammetry
HESS	hybrid energy storage system
HBMS	hybrid battery management system

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Supercapacitors vs. Lithium-ion Batteries: Properties and Applications

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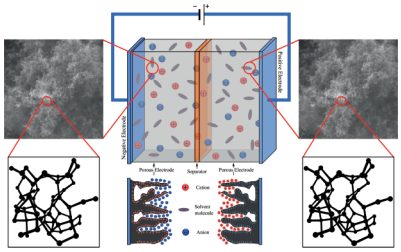

Review Article: The modern world faces many challenges, one of the biggest technology challenge of today is the accumulation and storage of electric energy. This issue is related with the use of renewable energy sources and the rapid development of electromobility. Theoretically, there are many ways to store electric energy, but in reality, these possibilities are limited to the battery and supercapacitor technology.

