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view

# Supercapacitors technical requirements for new applications

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## Abstract

The supercapacitors (SCs), also called ultracapacitors or electrochemical capacitors, are devices with a very high specific power and high capacitance, available for a long period of time with negligible deterioration, that have been historically proposed in small applications (memory back-up in consumer electronics, storage systems for micro solar power generators) and now are proposed for high power/energy applications, such as hybrid and electric vehicles, power quality systems and smart grids. The advancements in new materials and the rapid growth of more demanding storage systems in a variety of applications have created a lack of universally accepted definitions of these devices and, consequently, a real difficulty in describing developments and progress in the SC field.

This paper contains a brief survey of the history of the SC development, which is strongly related to the evolution of the SC technologies, tentatively classified in symmetric, asymmetric and hybrid. A short presentation of key parameters has been given to introduce the description of new applications with large SC devices, covering transport, industrial and electric utility sectors, with some reflections about the foreseen impacts on the future market more than quadrupled in 5 years up to almost \$877 million worldwide.

**Keywords:** supercapacitors, designs, classifications, performances, new applications, technical requirements.

## 1 Introduction

The need to improve efficiency and sustainability of energy systems in all the aspects from generation up to the end uses is motivating the research and development of new storage systems and methods. The variety of existing or projected applications ranging from consumer electronics, electric and hybrid vehicles up to large power generation plants and electricity distribution grids with improved power quality and larger introduction of renewable energy sources requires storage systems with extremely varying performance characteristics.

No ideal energy storage device and method are insofar available to meet all technical and economical requirements from a growing spectrum of applications. Electrochemical batteries, SMES (superconducting magnetic energy storage), pumped hydro, flywheels, CAES (compressed air energy storage) and hydrogen storage are alternative and/or competitive solutions for storing energy usually proposed.

The supercapacitors (SCs), also called ultracapacitors or electrochemical capacitors, are devices with a very high specific power and high capacitance, available for a long period of time with negligible deterioration, that have been initially proposed in small applications (memory back-up, cold start assist of thermal engines, storage systems for micro solar power generators) and now are proposed for high power/energy applications, such as hybrid and electric vehicles, power quality systems and smart grids. Since their initial discovery in the middle 1960's, SCs have received increasing interest and stimulus to progress by the growing demand of new specialized energy storage systems with high specific characteristics and long cycle life [1, 2, 3].

The advancements in new materials and the rapid growth of more demanding storage systems in a variety of applications have created a lack of universally accepted definitions of these devices and, consequently, a real difficulty in describing developments and progress in the SC field. In the last few years, many novel configurations of SCs have been investigated often mixing up battery and SC components with different behaviors and performance characteristics, all aimed at modifying specific technical parameters to better meet the technical, and even economical, requirements for the various applications.

The different types of SCs and the large extent of new applications have been demanding for suitable definitions and performance measurements that require the development of specific standards and procedures. Basic parameters are well known and are mostly based on a simplification approach that represents the SC with an equivalent electrical circuit model with defined electrical components. Unfortunately, the progress in configurations has somehow modified the real behavior of the various SCs, by asking for an experimental effort to harmonize and make comparable the key parameters of the different SC types.

The various applications of SCs, alone or in combinations with batteries or other energy source, are also addressing design issues: micro-systems as those of watches or memory back-ups look at very low energy

1  
2  
3 content but for a very long time, while large energy/power storage systems, such as those in transport means  
4 (hybrid vehicles with thermal engines or fuel cell generators) are more interested in SC devices with very high  
5 power capability in charge and discharge, lasting thousands of cycles.

6 This paper contains a brief survey of the history of the SC development, which is strongly related to the  
7 evolution of the types and related definitions. In the second part, an attempt is made to classify the various  
8 categories of present SC and to give some definitions to divide the recent scientific and technological  
9 advancements in identifiable groups. In the third part, the basic performance parameters are defined with a rough  
10 analysis of the existing testing procedures and standards to measure them. The fourth part gives some examples  
11 of the major and most interesting applications with description of technical requirements for some of them: the  
12 major emphasis is given to vehicle applications, which are receiving specific attention in recent years. Finally, in  
13 the fifth part, the market prospects that are positively seen by various companies are reported for the coming  
14 years.

## 15 16 2 Historical hints

17 The start of the SC technology is surely based on the work of Helmholtz, who first in 1853 recognized that  
18 the electrical charge could be stored not only on the surface of a conductor but also at “double-layer” interface  
19 between an electrode and an electrolyte [1,4]. Subsequently, almost one century later at GE (General Electric), in  
20 a not completely clear way, and at Sohio (The Standard Oil Company, then BP America, a subsidiary of the  
21 British Petroleum), first potential products were studied and patented. These initial claims were mainly the by-  
22 products of research work on carbon electrodes for fuel cells and novel batteries. The chief result at that time  
23 was the discovery of extraordinary high specific capacitances in high-surface-area carbons in molten salts or,  
24 preferably, in aqueous electrolytes. In practice, the “double-layer” capacitance at the most electrode-electrolyte  
25 interfaces, in the range of 5-50 microfarads/cm<sup>2</sup>, was greatly improved by the high specific surface areas (up to  
26 about 1,500 m<sup>2</sup>/g) of activated carbons. As a consequence, it was realized that capacitances of about some farads  
27 could be obtained in cells of 10-20 mL in volume: about 6 orders of magnitude with respect to the conventional  
28 capacitors. In the 1970's, there was a decade of enthusiasm and illusion in which different companies (Sohio,  
29 Corning Glass, NEC) tried to turn the electrochemical results of Sohio into a commercial product. Finally, in  
30 1979, NEC introduced on the market the first carbon-electrode SC with the brand name “Supercap”. Since then,  
31 with a growing interesting market, mostly covered by Japanese companies, the SC technologies continued to  
32 progress.

33 Alternative classes of SCs were, in parallel, researched and developed by trying to improve basic technical  
34 performances of commercial carbon-based SCs: the energy content, related to the low decomposition voltage of  
35 the electrolyte and/or to the low capacitance of the pure electrostatic charge transfer. At the beginning of 1980's,  
36 the investigation of the so called “*pseudocapacitors*” started: a novel device with the same technical features of  
37 an SC (as referred to specific capacitance), but working in a different way [1, 4 and 5]. The electrical charge was  
38 partially stored in the “double layer” and partially was the result of faradaic reactions (charge transfer of electron  
39 and protons) between electrode and electrolyte: the working mechanisms are moving from a conventional  
40 capacitor to a conventional electrochemical battery. These devices contain ceramic electrodes composed of  
41 transitional-metal oxides (e.g., iridium dioxide, ruthenium oxide and nickel oxide and a combination of these),  
42 deposited as thin coating on metallic substrates. Another class of SC, investigated and even marketed in 1970's,  
43 uses solid-state electrolytes, such as sodium-silver-iodide. These SCs were commercialized for a short time by  
44 Gould Ionics in a configuration having silver anodes and activated carbon cathodes with most charge storage at  
45 cathode-electrolyte interface: the low dissolution voltage (about 0.6 V) and the high cost of the cathode solid  
46 electrolyte material negatively impacted customer interest on this device, which was quickly withdrawn from the  
47 market.

48 Finally, in the last two decades with the introduction of high-voltage decomposition electrolytes (e.g.,  
49 organic, ionic liquids) [6, 7 and 8], the improvement of activated carbon properties and the introduction of new  
50 configurations (increased combination of SC and batteries components) and the growth of market demand on  
51 specific high power devices, the classes and designs of SCs have significantly augmented with the creation of a  
52 sort of chaos [9] in the SC field with the proliferation of categories and definitions used for the description of  
53 these devices. Figure 1 briefly summarizes the chief milestones and the key dates for the progress of the SC  
54 technology in most chemistries and designs.

## 55 56 3 General classification

57 The SCs are basically working according to the same principles of conventional capacitors, both electrostatic  
58 and electrolytic, with much different technical properties: an SC has specific capacitance and energy 10 times  
59 greater than that of an electrolytic capacitor and 100 times than that of an electrostatic capacitor. SCs are the  
60 scientific and technological evolution of conventional capacitors towards electrochemical batteries with clear  
fundamental differences: the main one is that in the batteries the energy is stored by means of chemical reactions,  
while in SCs the energy can be stored by simply electrostatic charge transfer. In practice, the differences between

conventional and batteries are not so sharp, because the last SCs are trying to use properties and performance characteristics of both devices.

The rapid evolution and developments of these devices have been creating serious difficulties in identifying and agreeing upon an internationally accepted nomenclature. Different definitions and terms have been used over the years to classify SCs. Initially, it was accepted to indicate these devices as electrochemical capacitors, to better distinguish them from the conventional capacitors, but this definition was hardly accepted by some companies for commercial reasons: the term electrochemical could be disqualifying for more conventional capacitors. Other terms for SC have been ultracapacitors, pseudocapacitors (or “Batcaps”), and even brand names from leading producing companies have been used. In the last two decades, the classification of the SC has been more related to the specific designs, the use of specific materials in the electrolyte (organic, aqueous, ionic liquids, solid) and/or in the electrodes (activated carbons, electronically conducting polymers, ceramic oxides, battery-like components).

An exemplary case of the ambiguity existing in the SC terminology is represented by the interpretation of the acronym EDLC, which was initially used to describe carbon-based SC: they are purely capacitive devices in which the charge and discharge processes are very rapid, due to the simple *electric* charge orientation of the double layer at the electrode-electrolyte interface. In reality, EDLC acronym is equally used for two different definitions: 1) Electric Double Layer Capacitor; or 2) Electrochemical Double Layer Capacitor. The former surely represents the more correct operation way for these types of SC, while the latter generates confusion in the attempt to introduce in the same device the concept of “pseudocapacitance”, which is typical of SC devices with faradic processes, or to emphasize the fact that the charge reorientation happens at the electrochemical double layer [2, 4, 8]. This double meaning is currently used in the scientific and technological literature [8, 9] and even in international standards [10, 11].

For sake of simplification in the attempt to more clearly classify the different types of SCs, an adaptation of existing taxonomy is here proposed. All the existing commercial and under development SCs can be divided in three main categories:

1. Symmetric SC
2. Asymmetric SC
3. Hybrid SC

With respect to the existing approaches, the three terms are more related to the cell designs, electrode materials and the fundamental operating principles (physical or chemical processes, or a combination of the two). With significant adaptation from [2, 4, 12], Figure 2 presents the three possible categories of the current and under development SCs.

### 3.1 Symmetric SC

Symmetric SCs are basically the historical EDLC (electric double-layer). The term “symmetric” stands for the use of electrodes made with the same material (for example, activated carbon as in the EDLC) with the same design and, practically, the same mass loading on both electrodes. The prevailing charge storage principle effectively working (either physical or chemical or a combination of the two) must be the same on both electrodes.

Two major SC types (or classes) can be included in the symmetric category: 1) EDLC; and 2) pseudocapacitors.

#### Electric double-layer capacitors

The electrical charge is only physically stored in the double-layer, naturally formed at electrode-electrolyte interface under voltage. These devices are highly reversible and can guarantee the longer cycle life, because no chemical reactions, and then material transformations, happen during charge and discharge cycles (pure electrostatic charge storage). The large increase in basic properties (capacitance and internal resistance) with respect to conventional capacitors is mostly due to the use of the double-layer charge storage at both electrodes, normally using high-surface-area materials such as activated carbons, with a much higher surface area (in the order of hundreds of  $\text{m}^2/\text{g}$ ) and much smaller thickness of double layers (in the range of  $10^{-10}$  m), compared to the electrode distance in conventional capacitors. Alternative materials, or carbon formulations, can be used for this type of SC, all based on double-layer non-faradic capacitance, with different electrolytes (aqueous, organic, ionic liquids) and different electrode (activated carbons, carbon aerogels, carbon nanotubes).

#### Pseudocapacitors

A second class of symmetric SC is represented by supercapacitors. Such devices are composed by electrodes using active materials that work differently from EDLC to store electrical charge and, then, energy. In fact, only part of the charge storage is assured by the double layer between electrode and electrolyte, while a greater amount of charge transfer and storage is due to faradic mechanisms (electrosorption, redox reactions, and intercalation). The latter process is able to more than double the energy density than that of EDLC. From the original ceramic materials (iridium dioxide, ruthenium dioxide, nickel oxide and their combinations), new materials with pseudocapacitive characteristics have been investigated in recent years, such as electronically conducting polymers and other metal oxides (vanadium oxide, manganese dioxide) [1, 13, 14, 15]. These devices

1  
2  
3 have had in the past significant drawback in the use of previous metals, which made expensive their application.  
4 Conducting polymers (for example, by negatively and positively doping electrodes) may improve their economic  
5 attractiveness, while applications requiring limited cycle number may take advantage of the significant higher  
6 energy density of any type of pseudocapacitor.  
7

### 8 **3.2 Asymmetric SC**

9 Asymmetric SCs are included in the most controversial category. Different views are described in literature  
10 about the term of asymmetric configurations, as a result of the significant developments in SC technology over  
11 the last 20 years. A first definition issued in 2002 clearly showed the uncertainty on how to classify new SC  
12 devices: *the "asymmetric" supercapacitor is the supercapacitor, on polar electrodes of which processes different*  
13 *in their nature are carried out* [16]. As a representative example of this category of SCs, a redox reaction on one  
14 of the electrodes and charge-discharge of electrostatic charge storage in the electric double layer on another was  
15 then mentioned. In the same period, the term "hybrid" has been alternatively used to name such SCs. In order to  
16 improve clarity in the increasing variety of SC designs and chemistries, a clear distinction of the two terms  
17 "asymmetric" and "hybrid" might be advisable. This classification effort may be functional in practical selection  
18 and applications of these devices, but also useful in specifying technical characteristics, measuring procedures  
19 definition of standards and SC modeling. In this simplification approach, there is also the intention to take into  
20 account the recent advancements in electrolyte materials (such as non-aqueous, ionic liquids), whose  
21 applications can be further improved by optimizing the different maximum potential excursions achievable,  
22 separately, at the negative and positive electrodes [17]. In this category, it is thus possible to include all the  
23 modified symmetric SCs, in which there are changes in the electrolyte compositions and in the mass loading and  
24 geometry of the electrodes, without changing the active materials and the operating processes (physical or  
25 chemical).  
26

### 27 **3.3 Hybrid SC**

28 Hybrid SCs are the most innovative solution to combine the better performances of different SC  
29 configurations. The basic idea is to substantially improve technical characteristics, and even reduce costs, of  
30 more conventional SCs by using the best geometry and materials for each component. In practice, the recent  
31 research and development activities have shown multiple combinations of positive and negative electrodes  
32 coming from various technologies, even from conventional electrolytic capacitors: the major technological  
33 challenge is to reduce the performance gap between SC and electrochemical batteries by using an electrode from  
34 one technology and the other electrode from the other technology. The basic design of a hybrid SC uses two  
35 electrodes made of different materials and, eventually, using different operating processes (faradaic and non-  
36 faradaic). The investigated combinations are aimed at maintaining the long cycle life of EDLC and power  
37 capability of conventional capacitors, reduce the cost constraints of pseudocapacitors and try to increase specific  
38 performances (e.g., energy density) to get closer to those of batteries. Three main types can be considered in this  
39 category: 1) Hybrid electrolytic capacitors; 2) Composite; 3) Battery-like.

#### 40 **Hybrid electrolytic capacitors**

41 A pseudocapacitive electrode, as those based on metal oxides, can be combined with the electrode of a  
42 conventional electrolytic capacitor. In this way, the high power characteristic of electrolytic capacitors is still  
43 saved, but the addition of the pseudocapacitance on one electrode substantially augments the specific capacitance  
44 of the device.

#### 45 **Composite**

46 A second class of hybrid SC is represented by devices, combining the electrode of an EDLC with a  
47 composite electrode, using carbon-based material (for example, carbon nanotubes) that incorporates either a  
48 conducting polymers or a metal oxide [6, 18, 19]. Such devices are also called asymmetric hybrid SC.

#### 49 **Battery-type**

50 These SCs put in the same device two completely different electrodes, coming from two different storage  
51 technologies: an SC electrode is then coupled with a battery electrode. Recent research has investigated different  
52 combinations of SC electrodes with electrodes derived from batteries: lead acid (lead oxides), alkaline (nickel  
53 oxides), lithium (titanate, manganese oxide and others) [20, 21, 22, 23]. These devices are considered extremely  
54 interesting even if more research is required to reduce the main disadvantages related to the need to overcome  
55 battery-related limitations.  
56

## 57 **4 Basic performance definitions and measurements**

58 The use of SCs is growing with more demanding technical performances to better meet specific requirements  
59 from applications varying from very small sizes, with limited energy content, up to the level of hundreds of kW  
60 in various vehicles (hybrid passenger cars, hybrid buses and trains) and for electric utility services. The variety  
of applications has also determined the need for clearly measuring the SC properties, which may differ when  
they are used in different operating conditions. It is well know that technical properties of SCs are from being

ideal and may be greatly affected by frequency, temperature, current and, in same case, by the category (symmetric, asymmetric and hybrid may have different reactions to the various working conditions).

International standards have been already defined [10, 11] for measuring and determining the key technical properties of SCs, but these standards are referred to small-size applications in electronic equipment, such as, back up memories for consumer products. In addition, the current standards consider only EDLCs.

In parallel, testing procedures have been also developed over the years to respond to more specific demands of SC testing for automotive applications [24, 25, 26] and, more recently, related standards are under preparation.

An ideal SC can be represented with a first-order electric equivalent circuit, as described in Figure 1. It is comprised of four ideal circuit elements, which include a capacitor C, a series resistor  $R_s$ , a parallel resistor  $R_p$ , and a series inductor L.  $R_s$  represents the equivalent series resistance (ESR) and accounts for the power loss during charge and discharge.  $R_p$  is the parallel resistance responsible for the energy loss due to capacitor self-discharge. This model is the simplest one and also the most adequate for low and medium power applications. In high power applications the non-ideal behavior of electrochemical capacitors cannot be neglected, depending on temperature, current, power, frequency, in case of alternate current systems, and also on SC category. The charge-discharge curve for the SC, represented by the circuit in Figure 3, is presented in Figure 4.

where,

$V_R$  is the rated voltage (V)

$V_1$  is the start voltage (V) for calculation

$V_2$  is the end voltage (V) for calculation

$\Delta U_3$  is the voltage drop (V)

$T_{CV}$  is the constant voltage charging duration (s)

$t_1$  is the time elapsed from start to reach voltage  $V_1$

$t_2$  is the time elapsed from start to reach voltage  $V_2$

Figure 4 assumes that the charge and discharge behavior of an ideal SC is practically linear. In reality, the charge and discharge curves are nonlinear and are normally dependent on the current and the rated voltage. Consequently, most SC performance parameters must be measured according to the working conditions. Looking at the applications, it is also apparent that only some performances must be necessarily known and measured to be able to design the SC system and incorporate it in the final application.

The basic SC performance data to be necessarily known in any application are: capacitance, ESR and cycle life. Other technical performances are more useful in certain applications, particularly when large amount of energy and power is involved: self-discharge, mass and volumetric energy and power density and efficiency.

It is important to outline that for medium to high power applications, the basic performances are measured and calculated during charge phase, and not only during discharge, because the SC behavior changes and may affect the design and functioning of the system.

#### 4.1 Capacitance

The capacitance of an SC is an intrinsic constant property, measured in Farad (F), and is related to the amount of electrical charge Q (in coulomb) effectively stored in the SC, when it is at the rated voltage  $V_R$ , according to the following equation:

$$C = \frac{Q}{V_R} \quad (1)$$

The standardized method proposed to measure the capacitance is called “constant current discharge method” and is based on the discharge curve in Figure 3. With this method, the capacitance is calculated with the following equation:

$$C = \frac{I \times (t_2 - t_1)}{V_1 - V_2} \quad (2)$$

where I (in A) is the discharge current. This method has been mostly based on the assumption that the discharge behavior of the SC remains linear. The values of  $V_1$  and  $V_2$  can differ from various procedures and standards and can be stated as a fixed quotient of the rated voltage. In current standards for electronic equipment,  $V_1 = 0.8 V_R$  and  $V_2 = 0.4 V_R$ , while in testing procedures for electric vehicles,  $V_1 = 0.6 V_R$  and  $V_2 = 0.4 V_R$ .

An alternative method can be applied in order to minimize the potential voltage differences due to non linearity of the discharge curve. The “energy conversion capacitance method” is then suggested to calculate the SC capacitance and is based on the energy equation:

$$C = 2 \frac{E}{V_2^2 - V_1^2} \quad (3)$$

where E, in Joule (J), represents the amount of energy discharged effectively when the SC voltage changes from  $V_1$  to  $V_2$ , also in this case these voltages can be fixed values of the rated voltage.

## 4.2 ESR

The internal series resistance, also called Equivalent Series Resistance (ESR), is the value of the element  $R_s$  in the first-order circuit, as described in Figure 3. Different methods have been applied until now and new ones have been proposed for measuring the ESR. It corresponds to ohmic resistance associated with the voltage drop in the discharge curve represented in Figure 4. The ESR value does not depend on the voltage at which the SC is charged or discharged. The most common measuring method is called “*current interrupt*”: the variation of voltage due to the sudden change in current is measured. The ESR is calculated with the following formula:

$$ESR = \frac{V_f - V_i}{I} \quad (4)$$

where ESR, in ohm, represents the ohmic resistance of the SC when the SC voltage changes from  $V_i$  to  $V_f$ , with a quick variation of current I.

## 4.3 Cycle life

It is generally believed that SCs do not show appreciable deterioration over a long period of time and under hundreds of thousands of charge and discharge cycles, even if it is fully discharged at a voltage near to zero. In reality this is true for the EDLC, but it is not the case for SC, in which faradaic processes are implied to store charge. The ageing of SCs is related to a variety of processes, which depend on the SC design and the operating conditions, then, from the applications. A critical aspect in the cycle life determination is the definition of the end of life criteria: some characteristics, such as capacitance, ESR and rated voltage, of the SC changes significantly and can be used to state the end of the life.

Cycle life test procedures are normally based on a *constant current profile*. The SC are charged and discharged at constant current between the rated voltage and a defined end-of-discharge voltage arbitrary selected, as a percentage of the rated voltage (normally, one half or one-third of the rated voltage). Periodically, after a defined number of complete charge and discharge cycles, the basic characteristics of the SC are measured and the variations are estimated. The measurement is terminated whenever the capacitance (or the energy) decreases for at least 20 or 30 % with respect of the initial one [24, 25, 26].

## 4.4 Peak power

The high power capacity is one of the peculiar features of the SCs and must be clearly defined and accurately measured or calculated. It is out of the scope of this paper to examine all the possible definitions of peak power, which are normally used. There are anyhow some definitions, which are normally presented in product data sheets or even in analyzing application requirements. One common approach to calculate the peak power of an SC is based on the concept of maximum power transfer: considering the simplified circuit of Figure 3, it represents the condition where a load with a resistance equal to the ESR ( $R_s$ ), then called matched load, is attached to the SC. Then, the initial peak power  $P_{peak}$  delivered to the load is calculated from the following equation:

$$P_{peak} = \frac{V_R^2}{4 ESR} \quad (5)$$

Unfortunately, this maximum power is transferred to the matched load with only 50% of power transfer efficiency, and, then one-half of the stored energy in the SC is dissipated as heat within the SC. Alternative methods for measuring peak power consider the maximum power achievable in 5 sec to discharge an SC from  $V_R$  up to  $V_R/3$  [26], or the maximum power associated with the maximum current at a given voltage, according to the equation:

$$P_{peak} = I_{MAX} \cdot V \quad (6)$$

where  $I_{MAX}$  is selected in a way to guarantee an energy efficiency of 95%, both in charge and discharge. For such case, the peak power is given by:



$$P_{Peak} = \frac{9}{16} \cdot (1-EF) \cdot \frac{V_R^2}{ESR} \quad (7)$$

where EF is the energy efficiency and  $V_R$  is the rated voltage.

#### 4.5 Specific energy and efficiency

The ideal value of the electrical energy stored in an SC is calculated by:

$$E_{Max} = \frac{1}{2} \cdot C \cdot V_R^2 \quad (8)$$

where C is the capacitance and  $V_R$  is the rated voltage. In practical uses, the complete discharge up to a voltage equal to zero is impossible and, consequently, a useable energy content is defined, which considers the energy delivered when the SC is discharged in a defined manner (e.g. at constant current or at constant power) from the

rated voltage  $V_R$  up to  $\frac{1}{2} V_R$ . For most application, the maximum discharged energy is given by:

$$E_{Max} = \frac{3}{8} \cdot C \cdot V_R^2 \quad (9)$$

The energy efficiency is defined according to the definition of delivered energy as the ratio in percent of the energy delivered by an SC to the energy that was supplied to it during a defined cycle.

The specific values of energy and power can be easily obtained by dividing the measured or calculated values of energy and power with the overall weight of the SC.

## 5 SC new applications areas

At beginning of its commercial history, about three decades ago, SCs were mainly produced in limited sizes for small, in capacitance and voltage, applications. The preferred uses over the years still remain the prevailing applications in consumer electronics with SC devices containing a few unit cells with a total voltage below 11 V and an overall capacitance up to a Farad. The main function in low voltage, power and capacitance applications is to protect memories and simply CMOS circuits in video and audio systems, in electronic toys and watches, in security and alarm systems, in PC motherboards, in home telephones, and in smoke detectors. The technical requirements for such applications are from 50 mF up to 1 F with an overall voltage of about 5,5 V [8].

The growing demand of high performance power devices with enabling the development is open up the SC application to new industrial sectors with brand new market areas, with much larger SC systems: industrial and residential applications, transportation and conventional and renewable electricity grids. The demanding technical and economical requirements for these new application areas have fostered the variety of scientific and technological breakthroughs in the SC technology with a large spectrum of technical characteristics [27]. Table 1 gives an update view of the state-of-the-art of current SC commercially available and under development, practically covering all the categories [28]. These applications normally require large or very large SC devices with technical requirements which are application-specific and, often, may greatly vary in size and performances in the same application area.

Currently, the use of large SCs is really promising with many prototypes and demonstration projects, seconded by a lot of simulation analyses covering applications from tens of watts up to tens of kW. The major concern is now of economical nature with the high cost of SC devices that cannot be clearly recovered with the interesting savings and advantages associated with their applications.

Anyhow, new applications areas for large SCs entail the following sectors:

- Industrial applications;
- Electric utility applications
- Automotive applications

In each of these sectors, different uses can be envisaged with promising potentialities for SCs. Most of these applications require high power storage systems which may be eventually coupled with a high energy storage system. The basic idea is to use the most appropriate technology for each function to be performed, considering both technical and economical aspects. Each applications analysis needs to clearly identify technical requirements and costs for design evaluation.

## 5.1 Industrial applications

In the industrial, residential and business building sectors, there are increasing demands for storage systems for back-up needs and for improving energy efficiency of systems aimed at carrying and elevating masses. The most interesting applications are the uninterruptible power supply systems (UPS) and the integration of storage systems in civil and industrial movers, such as elevators and cranes.

### 5.1.1 UPS

The use of electronic devices, the large diffusion of computers rooms and even the extended use of software controlled industrial processes are sensitive loads, all requiring back-up devices in case of emergency and fault conditions. The UPS with battery energy storage are devices very well developed and applied to sensitive loads and in critical events. The need of power quality improvement and number loads requires uninterruptible supply and is rapidly growing, due to the significant economical losses, due to lack of continuity and quality in power supply. The battery is the source of energy which is delivered to load usually, but the power capability of electrochemical batteries is not comparable with that of SCs. Depending on the specific operating conditions and failure risks the UPS are addressing, two different designs are now proposed [29]: 1) *Combined SC and battery UPS*. By combining an SC with a battery-based UPS system, the life of the batteries can be extended. The SC gives power during short-duration interruptions and voltage sags. The batteries provide energy and power only during the longer interruptions. This reduces the cycling duty on the battery and extends its life. 2) *Only SC UPS*. For sensitive loads needing only a few seconds or tens of seconds of ride-through, an UC system with no batteries is feasible and should have very low maintenance costs.

The technical specifications of SCs in UPS are consistent with existing technologies, because in this application the SC device has to provide power for a few seconds. About the cost, this strongly depends on the associated benefits and the power quality requirements.

### 5.1.2 Elevators and cranes

In principle, elevators and cranes are devices that vertically move masses by consuming electrical energy. In general, conventional elevator and crane systems are not capable of recuperating energy during downward motion for further use, even if, theoretically, with exclusion of friction losses, most of the energy spent for elevating masses can be recovered during descending phase. These devices cause huge energy losses and very high acceleration currents. SC may store large amounts of energy in a very short period of time and to release high currents on demand: exactly the key functions required by these applications. Many studies and demonstrations have been performed outlining the advantages of using SC in such systems [30, 31, 32]. SC devices with power between 20 and 100 kW (for a discharge time up to 50 s) have been designed and even used with interesting practical and economical implications. In the practical use in a gantry crane for ship unloading, the integration of an SC bank (100 kW for 42 s) with a diesel generator has resulted in an overall fuel reduction per unit time of 38%, a yearly consumption reduction of \$ 24k, and an yearly reduction of polluting emissions of 40%.

## 5.2 Electric utility applications

Progress in SC systems has made them suitable for high-power applications with growing interest from electric utilities, which are looking to these devices for performance improvement and reliability in a variety of areas, with much higher power levels and with voltage up to 600 V. The key peculiar features of SC are extremely appealing for a variety of applications in electricity grids: fast response time in millisecond, high energy efficiency (more than 95%), high power density and long calendar and cycle life. Various functions can be then performed by SC devices in electric grids, such as, for example [33, 34]:

1. *Transmission line stability*. The stability of a transmission system by adding energy storage. This serves to dampen oscillation through the successive generation and absorption of real (as opposed to reactive) power. There is also transient stability — the stability required after a utility event (loss of substation or major line). During a transient event, achieving stability requires a substantial capability to absorb energy quickly. This is somewhat analogous to “dynamic braking” because generator turbines must be slowed. A typical specification is 100MW with 500 MJ (< 5 sec).
2. *Spinning reserve*. This is the generation capacity that a utility holds in reserve to prevent service interruptions if a generator fails. An ultracapacitor system can be built to supply power during the interruption, until quick-start diesels begin to supply power. A typical specification is 20MW to 100MW and 300 MJ to 1500 MJ.
3. *Area and frequency control*. The lack of matching between electrical energy production and energy consumption (including losses) appears as a frequency variation. An SC system, thanks to its fast response time, would be considerably more effective than a generating plant in supplying frequency regulation. A system based on SCs can absorb or supply energy as required, freeing other generation sources from frequency regulation or tie-line control duties. A typical specification is 100 MW to 1000 MW and 0.1 MWh to 10 MWh.

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4. *Voltage regulation.* Voltage regulation is the ability of the grid to maintain stable the voltage in any point of a transmission line within 5%. Voltage control devices are capable of regulating local-area voltage or regulating power flow without a significant amount of energy storage. The need for voltage regulation and power flow control is site-specific and is compatible with SC properties.

### 5.2.1 Smart grids

“A smart grid uses digital technology to improve reliability, security, and efficiency (both economic and energy) of the electric system from large generation, through the delivery systems to electricity consumers and a growing number of distributed-generation and storage resources” [35, 36]. The integration of renewable energy source and the overall regulation of the electric system can be aided by using energy storage devices. There are some functions in the smart grids particularly suitable for the features of SC systems. Table 2 summarizes the key requirements and the most suitable storage systems, associated with the main functions.

## 5.3 Automotive applications

In the transport sector, the use of SC devices has been proposed for a variety of vehicles and transport systems from small ones (light-duty commercial and passenger cars) up to heavy-duty systems, such as, trucks, buses, trams up to trains. The proposed applications for these devices range from very low energy content for very high power services (engine starts) up to more energy-intensive service in hybrid vehicle configurations combining conventional thermal engines and, even, more advanced electrical generators, such as the fuel cells. Even in these applications, the SC systems can be act alone or combined with a battery. The advantages to use SC devices are many: the availability of more power; the drivetrain efficiency is substantially increased because of the higher share of regenerative braking energy; the smoothing action during charge and discharge can be beneficial for the battery because reduces stress and improve cycle life. The potential positive effects of SC systems have stimulated efforts in public research program and industries. Technical requirements, at least for road transport applications, have been, in some cases, already defined and represent the current frontier for SC development. Table 3 summarizes the technical and economical requirements, defined in the FreedomCar Program in the USA, for the use of SC in 3 different modes: mild-hybrid (only start-stop function) at 12V and 42V and power-assist operation in hybrid vehicles.

### 5.3.1 Starting engines

Diesel fueled engines have problems to start at cold temperature (up to  $-40^{\circ}\text{C}$ ). The problem is mostly related to the viscosity of lubricating oil at low temperature that requires high cranking torque with decrease in temperature. Lead acid batteries are presently used in vehicles for starting engines, but at low temperature the power capability of these batteries is very low and with difficulties in supplying high discharge current necessary to crank a cold engine [37]. Furthermore, this poor performance at low temperature in lead acid battery is further reduced with age, strongly affecting the ability to sustain this current during extended engine start. To overcome this problem, an SC device has been proposed in conjunction with battery to supply cranking current at low temperatures.

### 5.3.2 Electric and hybrid vehicles

In case of electric and hybrid electric vehicles, SC devices can be usefully applied to carry out different functions: 1) peak power storage for acceleration and recovery of energy during braking/deceleration; 2) peak shaving of peak demands on batteries; 3) cost reduction of electricity generators, such as fuel cells, by optimal sharing of power size according to the duty cycles. The advantages of using SC are various: 1) the life of battery is less affected by transient operating conditions like acceleration and deceleration because battery cannot be charged or discharged at high rate, reducing battery replacement needs during vehicle life; 2) the energy efficiency of the vehicle may be improved because there is a better charge capacity of SC with respect to battery at high charge rates; 3) the cost per power unit of electrical generators, as fuel cells, is significantly higher than that of SC, allowing for a power downsizing and cost reduction in drivetrain production. As already indicated in Table 3, the technical and economical specifications for some of the possible applications of SC devices in vehicles have been already stated [27]. In general, for such applications, the overall energy content and power for SC devices may vary from 50 Wh up to 2000 Wh, depending on the configuration with or without batteries and the size of the vehicle.

#### Fuel cell hybrid vehicles

In 2000 Honda showcased a prototype fuel-cell vehicle FCXV3 with high-pressure hydrogen tank and SC power bank. The lay-out of the FCX is in Figure 5. The SC bank supports acceleration and regenerative braking.

The definition of the application requirements for the developed SCs according to determined duty cycles and the possible role and impact of SCs in FCVs have been also investigated by means of mathematical models [38]. A reference van, named NEO (No Emission Outfit) has been used. It is a series-hybrid electric prototype, developed by Micro-vett (Italy), of the ‘range extender’ type, with a storage battery able to supply the traction power, while a FC system recharges the battery and extends the vehicle range, well beyond that available with

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3 the battery alone. The FC system power is lower than that required for moving the vehicle, with 30-kW  
4 continuous power and a 60-kW peak power (for 2 minutes). The rated powertrain voltage is 280 V,  
5 corresponding to the voltage of the 64Ah Zebra (Na-NiCl<sub>2</sub>) battery system. The simulation work has been  
6 concentrated on simulating a modified vehicle configuration with the addition of the SC systems in order to  
7 reduce maximum current and peak power and extend cycle life of the battery system. Table 4 clearly presents the  
8 possible hydrogen savings under different duty cycles by using an SC integration in the NEO van.  
9

### 10 5.3.3 Heavy duty and large transport systems

11 SC applications have been also proposed in very large transport system as hybrid transit buses, trams and  
12 trains.

#### 13 Hybrid buses, trolley buses and trams

14 ISE Corporation produced a hybrid bus with a 360 V SC device to support a 225 kW electric motor,  
15 propelled by alternative generators (gasoline and diesel engines and even fuel cells). The small energy storage  
16 SC unit with about 0.5 kWh assists only acceleration of the vehicle. More than 100 ISE buses have been  
17 produced and are in normal daily service in USA.

18 SC units have been also proposed for trolley buses and trams in order to improve energy efficiency and  
19 minimize braking failure in both cases with or without feeding lines. Vossloh Kiepe in Germany has developed a  
20 trolleybus with an SC unit (Figure 6). The SC bank supports acceleration and regenerative braking. It operates  
21 without contact wires for 500 m. The SC unit is composed of 288 cells, has a capacitance of 2600 F and a total  
22 energy content of 648 Wh. The energy saving achieved with the SC unit is between 23-34 % with respect to the  
23 same vehicle without SC unit.

24 A similar concept of using trolleybuses with periodic service without feeding contacts has been proposed in  
25 Italy with the project "ZeroFilobus": SC units onboard of are charged during idle time at stop stations with fast  
26 charge schemes. A 24% of energy savings is estimated for this application.

27 Finally, an onboard SC storage unit is considered to be a promising tool for railway rolling stock. Electric  
28 trains can run without feeding lines and diesel electric trains can absorb and use regenerative power. In case of  
29 electric trains with feeding lines, energy storage devices are useful to prevent regenerative energy failure at  
30 braking [39].  
31

## 32 6 Market prospects

33 Today, commercial SCs are available from a number of countries, such as Australia, France, Japan, Russia,  
34 South Korea and Russia. The interesting market prospects envisaged for the new application areas are partially  
35 negatively counterbalanced by the high cost of the SC, which has delayed widespread diffusion. Nevertheless,  
36 the progress in the technologies and the manufacturer increased efforts are going to reduce cost and extend  
37 technical performances to a larger number of applications.

38 Table 5 presents the average trend of the SC costs, that clearly shows the specific cost per unit capacitance  
39 has been greatly reduced in 15 years (about 150 times) as well as the cost per energy unit (about 220 times  
40 smaller).  
41

42 The SC market has been steeply growing in the last 20 years, even if it is still remained a few percents of the  
43 overall capacitor market. In 1989 about 75 million units were commercialized with total revenue of about \$40  
44 million. In 1999, about 201 million units were produced with a total value of about \$ 115 million, while in 2004  
45 there was a further increase until 660 million units with a related value of \$ 276 million. The prevailing share (>  
46 95%) of these markets has been for small SCs, but recent forecasts are quite optimistic with prospects of  
47 significant surge in the next almost 5 years. The expectations are to get close to about \$877 million of worldwide  
48 sales by 2014 with a large share of sales represented by large SC applications, as those in transport and electric  
49 utilities, estimated to reach about \$ 330 million.  
50

## 51 7 Conclusions

52 The story and the recent developments of SCs have been thoroughly analyzed with the scope to understand  
53 and simplify classifications and sometimes misleading nomenclature. The significant progress in material  
54 science and in electrochemistry has made possible the realization of electrochemical capacitors with promising  
55 technical and economical properties suitable for a continuously increasing number of applications. SCs are now  
56 available in multiple designs that can be almost covering all the performance range existing between  
57 conventional capacitors and electrochemical batteries.

58 After the large applications in consumer electronics, in this article new interesting applications have been  
59 analyzed with the description of the targeted technical requirements and the relevant energetic and economical  
60 impacts. The described new applications areas refer mainly to large capacitance, power and energy SC systems  
and cover various energy-intensive sectors: industrial, transport and electricity grids. Various examples and  
demonstration project have been described to support this trend in SC applications.

The outlook for larger diffusion of SC devices in these new application areas is also confirmed by market studies, forecasting an average yearly growth rate of about 27% up to 2014, with a largely increasing share (up to about 40%) of SC devices in large system applications.

These overall prospects and the associated advantages of using SC devices in new applications will be surely power near term and future efforts in research, development and, even, in production processes to further improve technical performances for a larger spectrum of applications and significantly reduce costs.

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## 9 Figure Caption

- 10 Fig. 1 Key milestones in the development of SC technologies.  
11 Fig. 2 Classification of SC categories and classes. ...  
12 Fig. 3 The first-order electric equivalent circuit of a capacitor.  
13 Fig. 4 The typical charge-discharge curve for an EDLC.  
14 Fig. 5 Honda FCX prototype.  
15 Fig. 6 SC unit in the Vossloh trolleybus.  
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## Tables

Table 1 Technical performances of some present SCs [28].

Device or producer	Rated voltage $V_R$ (V)	C (F)	ESR (mOhm)	Specific Energy (Wh/kg) (1)	Specific Power (W/kg) (95%) (2)	Specific Power (W/kg) Matched Load	Weight (kg)	Volume (L)
Maxwell*	2.7	2885	.375	4.2	994	8836	.55	.414
Maxwell	2.7	605	.90	2.35	1139	9597	.20	.211
ApowerCap**	2.7	55	4	5.5	5695	50625	.009	---
Apowercap**	2.7	450	1.4	5.89	2574	24595	.057	.045
Ness	2.7	1800	.55	3.6	975	8674	.38	.277
Ness	2.7	3640	.30	4.2	928	8010	.65	.514
Ness (cyl.)	2.7	3160	.4	4.4	982	8728	.522	.38
Asahi Glass (propylene carbonate)	2.7	1375	2.5	4.9	390	3471	.210 (estimated)	.151
Panasonic (propylene carbonate)	2.5	1200	1.0	2.3	514	4596	.34	.245
LS Cable	2.8	3200	.25	3.7	1400	12400	.63	.47
BatScap	2.7	2680	.20	4.2	2050	18225	.50	.572
Power Sys. (activated carbon, propylene carbonate) **	2.7	1350	1.5	4.9	650	5785	.21	.151
Power Sys. (graphitic carbon, propylene carbonate) **	3.3 3.3	1800 1500	3.0 1.7	8.0 6.0	486 776	4320 6903	.21 .23	.15 .15
Fuji Heavy Industry-hybrid (AC/graphitic Carbon) **	3.8	1800	1.5	9.2	1025	10375	.232	.143
JSR Micro (AC/graphitic carbon)**	3.8	1000 2000	4 1.9	11.2 12.1	900 1038	7987 9223	.113 .206	.073 .132

(1) Energy density at 400 W/kg constant power,  $V_R - 1/2 V_R$

(2) Power based on  $P_{MAX}=9/16*(1-EF)*V^2/ESR$ ,  $EF$ =efficiency of discharge

\* Except where noted, all the devices use acetonitrile as the electrolyte.

\*\* all devices except those with \*\* are packaged in metal containers, these devices are in laminated pouches.

Table 2. Technical characteristics of some key functions in smart grids.

Time scale	Target	Storage requirements	Preferred energy storage type
Very fast (ms)	Power quality control, load smoothing, renewable integration	Very fast, very high cycle life, power demand changes	SC, SMES*
Fast (s)	Power quality control, load smoothing, renewable integration	Very fast, very high cycle life, power demand changes	SC, SMES*, flywheels
Medium fast (min)	Power quality control, load smoothing, renewable integration	Fast, high cycle life, power demand changes	SC, SMES*, flywheels, batteries

\* SMES = Superconducting Magnet Energy Storage



Table 3. United States Advanced Battery Consortium - FreedomCar Program. SC Requirements at the end of life for 3 different services.

System Attributes	12V Start-Stop (TSS)		42V Start-Stop (FSS)		42V Transient Power Assist (TPA)	
Discharge Pulse	4.2 kW	2s	6 kW	2s	13 kW	2s
Regenerative Pulse	N/A		N/A		8 kW	2s
Cold Cranking Pulse @ -30°C	4.2 kW	7 V Min.	8 kW	21 V Min.	8 kW	21 V Min.
Available Energy (CP @1kW)	15 Wh		30 Wh		60 Wh	
Recharge Rate (kW)	0.4 kW		2.4 kW		2.6 kW	
Cycle Life / Equiv. Road Miles	750k / 150,000 miles		750k / 150,000 miles		750k / 150,000 miles	
Cycle Life and Efficiency Load Profile	UC10		UC10		UC10	
Calendar Life (Years)	15		15		15	
Energy Efficiency on UC10 Load Profile (%)	95		95%		95%	
Self Discharge (72hr from Max. V)	<4%		<4%		<4%	
Maximum Operating Voltage (Vdc)	17		48		48	
Minimum Operating Voltage (Vdc)	9		27		27	
Operating Temperature Range (°C)	-30 to +52		-30 to +52		-30 to +52	
Survival Temperature Range (°C)	-46 to +66		-46 to +66		-46 to +66	
Maximum System Weight (kg)	5		10		20	
Maximum System Volume (Liters)	4		8		16	
Selling Price (\$/system @ 100k/yr)	40		80		130	

Table 4. Hydrogen savings with the introduction of an SC device in the fuel cell van NEO by Micro-vett.

Duty Cycle	H <sub>2</sub> savings (%)
Urban Ece 15	32.3
Real Micro-vett	4.0
Hyzem	13.6
Hyzem_70	19.6

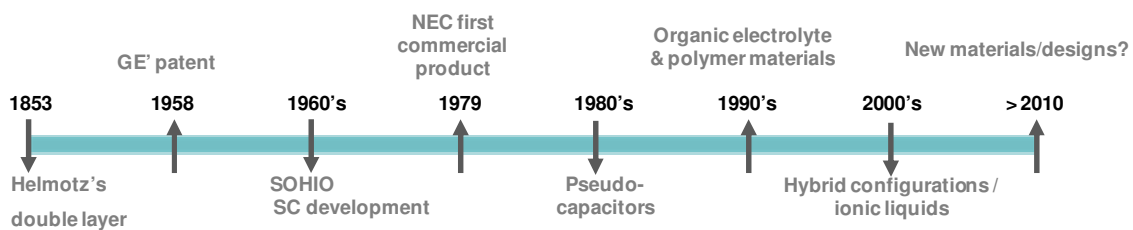
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Table 5. SC cost trend [40].

Year	Specific capacitance cost, \$/Farad	Specific energy cost, \$/kJ
1996	0,750	281,55
1998	0,400	151,23
2000	0,100	32,00
2002	0,023	7,51
2006	0,010	2,85
2010	0,005	1,28

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Figure 1



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Figure 2

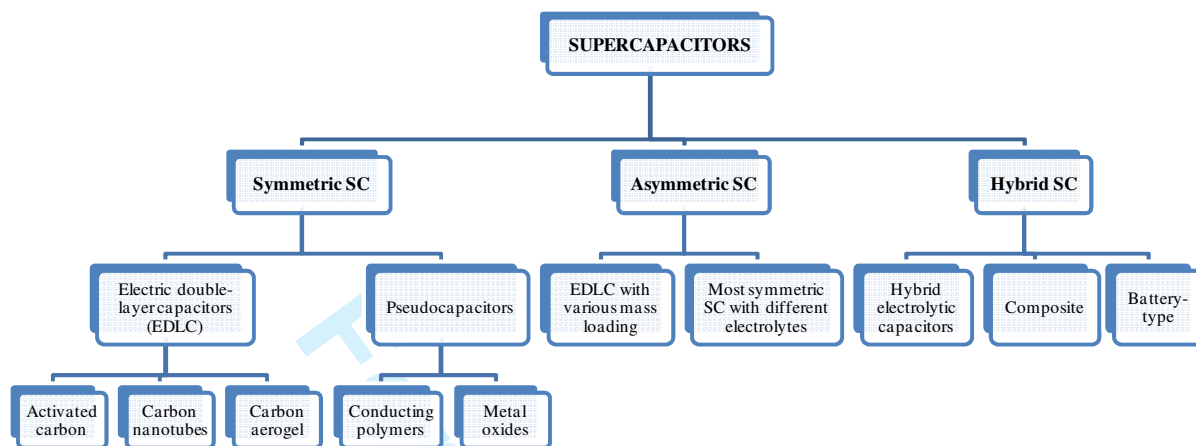
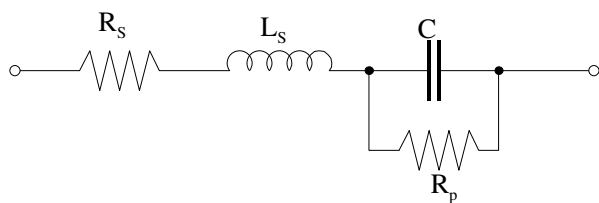
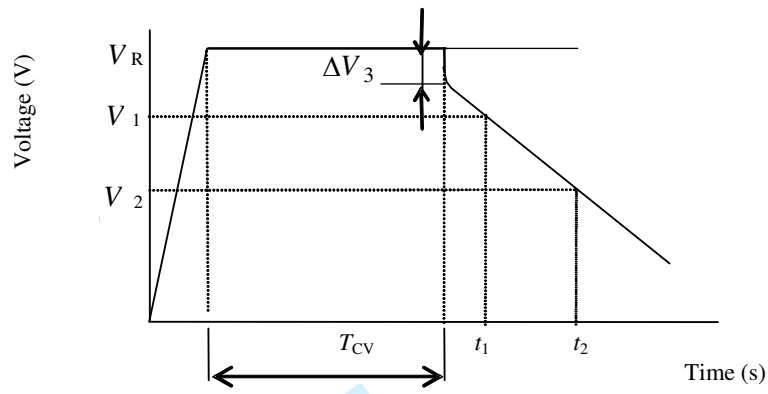


Figure 3



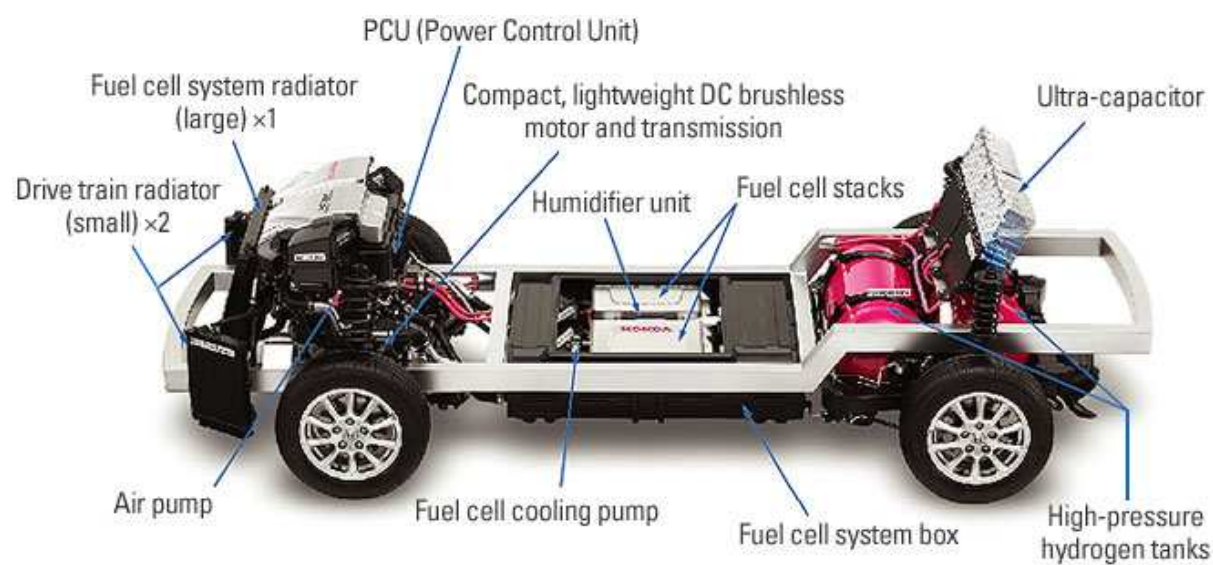
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Figure 4



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Figure 6.



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Figure 8.



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