# Properties and applications of supercapacitors
# From the state-of-the-art to future trends

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## I. Abstract

Electrochemical double-layer capacitors, also known as supercapacitors or ultracapacitors, are electrical storage devices, which have a relatively high energy storage density simultaneously with a high power density. Recent developments in basic technology, materials and manufacturability have made supercapacitors an imperative tool for short-term energy storage in power electronics. With much higher energy density than today's capacitors and none of the problems associated with conventional battery technology, supercapacitors give an access to new power electronic and industrial storage applications.

The paper presents basic supercapacitor technology, component specific properties as well as state-of-the-art product applications. The problematic nature of supercapacitor series connection for higher voltage applications is touched on. The review also deals with an energy storage system, which is based on the hybridization of rechargeable batteries and supercapacitors, with a suitable designed electronic interfacing arrangement in order to obtain a very high energy density device with a high power performance and a long lifetime. Finally, an overview over future trends regarding the supercapacitor technology as well as application scenarios, mainly in the traction domain, is given.

## II. Introduction

Supercapacitors are energy storage devices with very high capacity and a low internal resistance. In a supercapacitor, the electrical energy is stored in an electrolytic double-layer. Therefore such energy storage devices are generally called electrochemical double-layer capacitors (EDLC). Helmholtz has discovered the storage process, based on the separation of charged species in an electrolytic double layer, in 1879. ECDLs or supercapacitors (i.e. supercaps) are also known as ultracapacitors, Boostcaps™, Bestcaps™ etc. Supercapacitors are attractive for their high energy and power densities, their long lifetime as well as their great cycle number. In addition to the high specific power the energy storage in supercapacitors is reversible in contrast to conventional batteries [1].

The electronic applications need passive components to store the electrical energy in volume and weight as small as possible. The choice of the storage device type depends in particularly on the speed of the storage process, in other words on the power required by the application.

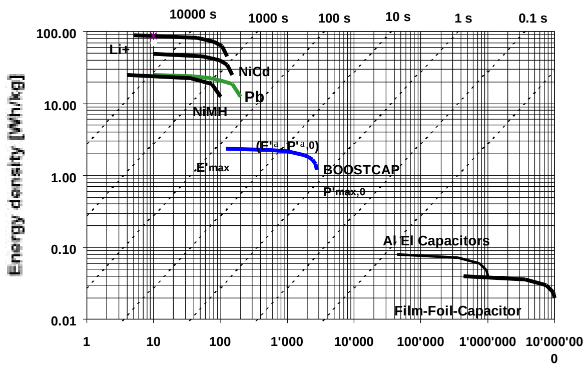



Figure 1: The Ragone plot shows the energy density vs. the power density

Actually, while the slower storage processes may be performed with batteries, the faster ones have to be done with capacitors. In general the electrical energy storage devices are of 3 types: faradaic batteries, electrostatic

capacitors and magnetic inductors. The situation may be well summarized by the following so-called Ragone plot (Figure 1). Detailed informations on the Ragone plot are given in chapter 4.The energy density in a battery may rise to 150 Wh/kg. This is about 10 times higher than the highest expected value of a supercapacitor. The power density in a battery has difficulty to reach 200 W/kg and is therefore about 20 times smaller than the expected supercapacitor performance. The batteries suffer from several weaknesses, which exhibit a rapid decrease of their performances. The origins may be the fast charge-discharge cycles or the cold environmental temperature. The batteries have also a limited lifetime and require expensive maintenance.
Through the different capacitor technology types, the EDLC presents the highest energy density. Dielectric and electrolytic capacitors, as well as ceramic capacitors show very high power densities but very low energy densities. Compared to batteries, capacitors reveal much longer lifetimes and cyclabilities. In terms of power and energy density the supercapacitor fills up the gap between the batteries and the classical capacitors, allowing new applications. The properties of the different energy storage devices are presented in Table 1.

| | Capacitors | EDLC | Batteries |
|---|---|---|---|
| Energy density [Wh/kg] | 0.1 | 3 | 100 |
| Power density [W/kg] | $10^7$ | 3'000 | 100 |
| Time of charge [s] | $10^{-3}$-$10^{-6}$ | 0.3-30 | >1'000 |
| Time of discharge [s] | $10^{-3}$-$10^{-6}$ | 0.3-30 | 1'000-10'000 |
| Cyclability [1] | $10^{10}$ | $10^6$ | 1'000 |
| Typical lifetime [years] | 30 | 30 | 5 |
| Efficiency [%] | >95 | 85-98 | 70-85 |

Table 1: Storage component property comparisons

## III. Technological aspects of supercapacitors

### 3.1 Cell construction

A supercapacitor cell basically consists of two electrodes, a separator, and an electrolyte (Figure 2). The electrodes are made up of a metallic collector, which is the high conducting part, and of an active material, which is the high surface area part. The two electrodes are separated by a membrane, the separator, which allows the mobility of the charged ions but forbids the electronic conductance. This composite is subsequently rolled or folded into a cylindrical or rectangular shape and stacked in a container. Then the system is impregnated with an electrolyte. The electrolyte may be of solid state, organic or aqueous type, depending on the application power requirement. The working voltage of supercapacitor is determined by the decomposition voltage of the electrolyte and depends mainly on the environmental temperature, the current intensity and the required lifetime. The capacitance of an EDLC can be very large, e.g. several thousands of Farads, thanks to the very small distance which separates the opposite charges at the interfaces between the electrolyte and the electrodes and thanks to the very huge surface of the electrodes.

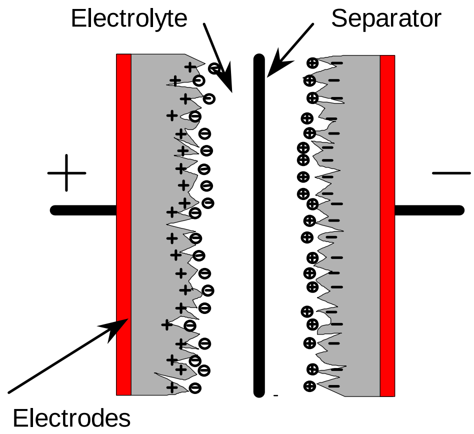



Figure 2: Supercapacitor sketch

In the following, the different materials used in supercapacitor are discussed more in detail.

#### 3.1.1 Electrode

Since the capacitance is proportional to the surface area, electrochemical inert materials with the highest specific surface area are utilized for supercapacitor electrodes in order to form a double layer with a maximum number of electrolyte ions. As high surface active materials, metal oxides, carbon and graphite are the most interesting. The main difficulties are to find cheap materials, which are chemically and electrically compatible with the electrolyte. Capacitors for high energy applications require electrodes made of high surface area activated carbon with appropriate surface and pore geometry. Carbonaceous materials commonly are activated carbon fibers, carbon black, active carbon, carbon fibers, carbon gel, skeleton carbon, mesocarbon as well as microbeads. The best carbon electrodes have surfaces as high as 3'000 $m^2$ per gram of material. The electrode capacitance increases linearly with the carbon surface area and may reach a capacitance of 250 F/g. They are usually prepared from high surface area carbon powders or fibers. The powders are applied, e.g. as a paste on the metallic current collector. Such an arrangement, however, leads to a considerable contact resistance between grains and between the grains and the support. In order to overcome these problems, pressure has to be applied or the carbon powder has to be mixed with metal fibers or powders in order to increase conductivity.

Recently several capacitors using high surface area electrodes composed of $RuO_2$ based composites have been introduced [14]. Such devices have e.g. the size of a credit card and have a capacitance of 200-300 mF at 4-8 V. The RC time constant is about 5 ms.

### 3.1.2 Electrolyte

As mentioned above the electrolyte may be of the solid state, organic or aqueous type. Organic electrolytes are produced by dissolving quaternary salts in organic solvents. Their dissociation voltage may be greater than 2.5 V. Aqueous electrolytes are typically KOH or $H_2SO_4$, presenting a dissociation voltage of only 1.23 V. The energy density is thus about 4 times bigger for an organic electrolyte. As a consequence of the quadratic dependence of the energy density of the capacitor on the capacitor's voltage use of an organic electrolyte would be desirable. However, if power density is important, the increase in the internal resistance (ESR) due to the lower electrolyte conductivity has to be considered as well. The electrolyte solution should therefore provide high conductivity and adequate electrochemical stability to allow the capacitor being operated at the highest possible voltages.

Earlier work [2] indicated TEATFB in acetonitrile as the best performing organic electrolyte system for EDLC applications. Depending on the molarity conductivities up to 60 mS/cm are possible. Covalent Associates introduced novel electrolytes known as ionic liquids. The advantage of these electrolytes are manifold, they are non-corrosive, the typical conductance is about 8 mS/cm, and the electrolytes can be used up to high temperatures of about 150 °C. Blending with acetonitrile results in a conductance of 60 mS/cm.

### 3.1.3 Separator

Many of the commercial available separators are designed for battery use mainly. Hence an accurate evaluation of the separator is essential to achieve the exceptional performance of EDLCs. If organic electrolytes are used, polymer (typically PP) or paper separators are applied. With aqueous electrolytes glass fiber separators as well as ceramic separators are possible. The separator allows the transfer of the charged ions but forbids the electronic contact between the electrodes.

The basic principles to obtain a competitive EDLC is to collect all the following performances: high ionic electrolyte conductance, high ionic separator conductance, high electronic separator resistance, high electrode electronic conductance, large electrode surface, low separator and electrodes thickness.

In Table 2 an overview over material specifications for best performance EDLCs using an organic electrolyte are given (based on model calculations).

| | |
|---|---|
| Active layer thickness | 100 µm |
| Volumetric Capacitance | 100 F/cm$^3$ |
| Electrolyte | 0.05 S/cm, |
| Cell Voltage | 2.5 V |
| Current Collector Thickness | 25 µm |
| Separator Porosity | 50 % |
| Separator Thickness | 25 µm |
| Distributed Resistance in Pores | 10 x electrolyte |

Table 2: EDLC best performance parameters

### 3.1.4 Material research

Most of the recently published works [3-6] deal with developing and testing of new electrode materials on laboratory scale devices. Carbonaceous materials in their various forms have been studied as electrodes for the construction of EDLC energy storage devices. Activated carbon composites and fibers [7] with surfaces up to 3'000 $m^2/g$, measured by gas adsorption, as well as carbon aerogels [8] with surface areas up to 850 $m^2/g$ have been investigated. Unfortunately a significant part of the surface area resides micropores (<2nm) which are not accessible to the electrolyte ions. The remaining surface area electrochemically accessible (meso and macropores) reveals a capacitance well below the estimated values. Therefore the pore size distribution together with the surface area are important for the determination of the double layer capacitance.

Since Iijima's original work [9], nanostructured materials such as carbon nanotubes have been recognized as a material with promising applications in chemistry and physics. Several methods were developed to synthesize nanotubes as arc-discharge process [10, 11], chemical vapor deposition (CVD) i.e. pyrolisis of hydrocarbons [12], laser ablation and a variety of combinations of the above mentioned methods [13]. Several requirements still remain to be fulfilled before the development of a nanotube-based technology, in particular the production of macroscopic quantities of nanotubes can be achieved. Recently Emmenegger et al. [11] have realized EDLC electrodes with well aligned carbon nanotubes films synthesized with a pyrolytic method on a thin aluminum substrate (Figure 3).

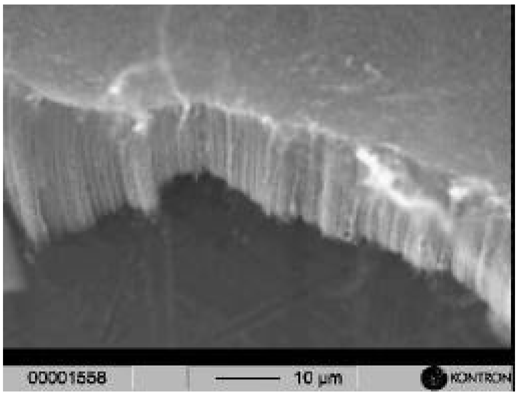



Figure 3: Carbon nanotube electrode [11]

### 3.2 Devices

Two construction types of supercapacitor devices are generally used: the monopolar cell design and the bipolar cell design.

The monopolar device shows very high capacitance due to a high surface area. The devices are assembled by winding or stacking in parallel identical electrodes, separator and collector foils. The voltage of the device is identical to that of the single cell. It is also possible to produce asymmetric devices with one supercapacitor electrode and one battery electrode such as NiOx or MnO2 [14]. The idea is to double the capacitance of the device because only the supercapacitor-electrode determines the capacitance now. In addition the cell voltage is higher due to the redox potential of the battery electrode. As an advantage the voltage of such supercapacitors during discharge decreases only slightly. Energy densities of up to 20 Wh/kg and power densities of up to 5 kW/kg are possible. Another type of asymmetric device is the hybrid capacitor by Evans [15]. He uses $RuO_2$ for a high capacitance electrode and a Ta electrolytic capacitor electrode. This device was made for military applications and resisted several thousand g acceleration.

A high productivity is obtained by winding the different monopolar cell components with a precise control of all the parameters.

The bipolar devices allow a high voltage, low resistance and low capacitance [16]. Such supercapacitors are built up by stacking several single cells in series into one case. The sealing of such devices is very sophisticated, as the electrolyte must be prevented from contacting one cell with another.

### 3.3 The winding technology

Many production and deposition methods exist to produce supercapacitor electrodes. The extrusion of charged polymers, produced by mixing activated carbon in a polymer matrice, is a possible way to produce good performance and low cost carbon electrodes for supercapacitors. The advantages of this process are a continued fabrication process resulting in a high productivity and therefore in low costs. The extruded carbon foil is very homogeneous, can be produced in variable sizes and is self-supporting.

Different processes are applied to assemble the electrodes, the separator and the current collector layers.

Advantages of the winding technology are a very reliable process, a high productivity and therefore low costs. The winding technology allows variable sizes and designs of the devices as the composite is subsequently rolled or folded into a cylindrical or credit card shape. Due to a good control of the foil tensions during the winding, it is possible to achieve a low internal resistance ESR.

Figure 5: Montena metal winding machine

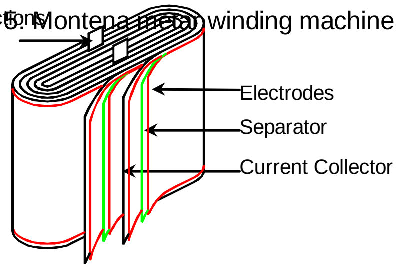



Figure 4: Supercapacitor flat winding

## IV. Properties of supercapacitors

### 4.1 Capacitor equivalent circuit

The capacitor may be modelized by the electrical circuit presented in Figure 6. The equivalent series resistance ESR limits the current and is responsible for the electrical losses. To get high power, it is absolutely necessary to have a low series resistance. The parallel resistance $R_P$ is responsible for the capacitor self discharge time. Its value must be as high as possible to limit the leakage current. The time constant $\tau$ of the self-discharge is $\tau = R_P C$.

### 4.2 Ragone plot

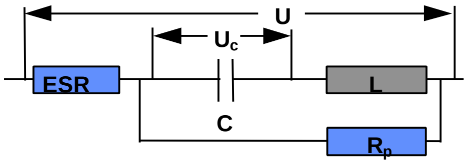



Figure 6: Supercapacitor equivalent circuit

The Ragone plot is a chart, which gives the relation between the energy density and the power density of a storage system. It is used to compare the performances of the different storage types like batteries, supercapacitors and conventional capacitors.

Before to give the equation of the Ragone curve let us define

**C** the capacitance [F]
**$u_c$** the voltage on the theoretical capacitor [V]
**$R_S$** the capacitor internal resistance ESR [Ω]
**$R_L$** the load resistance [Ω]
**P** the power [W]
**$P_0$** the initial power during a discharge at constant **$R_L$**
**$P_{max,0}$** the initial maximum power [W]
**M** the capacitor mass
$t_0$ the technology time constant: $\tau_0 = R_S C$
t the application time constant: $\tau = (R_L + R_S) C$
**i** the current: $i(t) = C\, du_c/dt$
**u** the voltage on the physical cap. $u(t) = u_c(t) - R_S i(t)$
**$E_{max}$** the max. energy stored in the cap. $E_{max} = C U_o^2 / 2$

#### 4.2.1 Ragone plot coordinates

The parameter of the Ragone plot is actually the load resistance **$R_L$**. It does mean that the plot shows the energy and the power, which can be dissipated for the different values of the load resistance. To simplify the relations we introduce the parameter $\alpha$ defined by the relation $\tau = \alpha \tau_0$, $R_L + R_S = \alpha R_S$. If **$R_L$** is constant, the initial peak power at time t=0 may be written as

$$P_{\alpha,o} = U_o^2 (\alpha - 1) / \alpha^2 / R_s$$

The maximum peak power $P_{max,0}$ is available at time t=0 when **$R_S = R_L$**, and it is equal to

$$\mathbf{P_{max,o} = E_{max} / 2}\ t_o = U_o^2 / 4 R_s$$

Only a part of the stored energy is available for the load. The amount is equal to the load power integration from t = 0 to t = ∞.

$$\mathbf{E_a = E_{max} (a - 1) / a}$$

The Ragone plot coordinates for a given $\mathbf{R_L}$ are consequently

$$E'_a = E_a / M = E_{max} (a - 1) / a / M$$

$$P'_{a,o} = P_{a,o} / M = 2 E_{max} (a - 1) / a^2 / t_o / M = 4 P_{max,o} (a - 1) / a^2 / M$$

The numerical values of these coordinates are usually given per unit of component weight.

#### 4.2.2 Available power

When the load resistance is smaller than the internal resistance, the current will be higher, but the voltage drop on the load is strongly reduced. The consequence is that a smaller power may be delivered to the load.

On the right side of the Ragone plot (Figure 1), the curve is interrupted on a point of maximum power density $P'_{max,0}$ corresponding to a load resistance equal to the capacitor internal resistance. On the left side, in the "low" power range the load resistance is much bigger than the capacitor internal resistance.

#### 4.2.3 Available energy

The first observation, which may be done, is that at the maximum power rate, only half of the stored energy is available. The second half is dissipated in the capacitor internal resistance. In this high power condition, the current is very important and the losses in the capacitor are proportional to the internal resistance time the square of the current.

The second observation is that in the "low" power condition almost all the energy $E'_{max}$ is available for the load. The losses are very small because for the same capacitor internal resistance, the current is very small.
All the above remarks are valid for the primary and secondary batteries.
The losses inside the capacitor are

$$E_{p\alpha} = E_{max} / a$$

$$P_{p\alpha,o} = 2 E_{max} / a^2 / t_o$$

The efficiency $\eta$, which is the ratio between the energy used in the load to the total energy content, is equal to $\eta = 1 ? 1 / \alpha = R_L / (R_L + R_S)$

### 4.3 Performance of supercapacitors

In Table 3 the performances of selected supercapacitors available today is given.

| Companies | Voltage [V] | Capacity [F] | Energy [Wh/kg] | Power [W/kg] |
|---|---|---|---|---|
| Asahi Glass (J) | 2.5 | 3000 | 7 | 0.4 |
| Econd (R) | 500 | | 0.3 | 56 |
| Elna Comp. (J) | 5.5 | 1 | | |
| Epcos (D) | 2.3 | 2700 | 2.5 | 2.7 |
| Evans (US) | 100 | 200 | 1.1 | |
| Matsushita (J) | 2.3 | 470 | 1.1 | 0.35 |
| Maxwell (US) | 2.3 | 2700 | 2.5 | 2.7 |
| Montena (CH) | 2.5 | 800 | 2.4 | 2.8 |
| Nec (Tokin) (J) | 5.5 | | 1.3 | 0.5 |
| Polystor (USA) | 2.5 | 7 | | 4 |

Table 3 : Performance of supercapacitors [17]

The actual detailed performance of the montena Boostcap ultracapacitors are given in Table 4.

| | | BCAP0005 | BCAP0007 |
|---|---|---|---|
| Rated voltage | [V] | 2.5 | 2.5 |
| Max. voltage | [V] | 2.8 | 2.8 |
| Capacitance | [F] | 800 | 1'400 |
| DC serial resistance | [mW] | 2.4 | 1.6 |
| Time constant | [s] | < 2 | < 2 |
| DC parallel res. (24h, 25°C) | [W] | > 2'000 | > 2'000 |
| Self discharge current | [mA] | < 2 | < 2 |
| Spec. energy (@ 2.5V) | [Wh/kg] | 2.4 | 4.3 |
| Spec. peak power (@ 2.5V) | [W/kg] | 2'200 | 3'450 |
| Weight | [g] | 290 | 280 |
| Volume | [l] | 0.255 | 0.255 |
| Operating temperature | [°C] | - 35 to 65 | - 35 to 65 |
| Storage temperature | [°C] | -35 to 65 | -35 to 65 |

Table 4 : Performance of montena Boostcap™ ultracapacitor

#### 4.3.1 Performance in future

The EDLC goal is to reach the highest energy and power densities to get the smallest component volume and weight for a given application. Concretely the goals of montena have been fixed to 5 Wh/kg for the energy density and to 5 kW/kg for the power density.

To meet these values, it is necessary to increase capacitance density, to reduce the ESR and to increase the cell operating voltage. The efforts are concentrated on the study of the electrode surface and accessibility, the grain to grain and grain to support contacts, the separator materials, and the electrolytic decomposition voltage.

## V. Applications

Today small size supercapacitors as for example gold caps from Tokin are widely used as maintenance-free power sources for IC memories and microcomputers [18]. Among newly proposed applications for large size supercapacitors are load leveling in electric and hybrid vehicles as well as in the traction domain, the starting of engines, applications in the telecommunication and power quality and reliability requirements for uninterruptable power supply (UPS) installations. In general supercapacitors may be adapted to the following two application domains.

The first one corresponds to the high power applications, where the batteries have no representative access. The EDLCs, thanks to their high power capability, will allow new opportunities for power electronics. All applications where short time power peaks are required can be provided by these capacitors. Typical examples where a big current is required during a short time are the fast energy management in hybrid vehicles or the starting of heavy diesel engines

The second one corresponds to the low power applications, where the batteries could be more suitable but are at the origin of maintenance problems or of insufficient lifetime performance. The supercapacitors, even if they are much bigger, bring enough advantages to substitute the batteries. In this field, the UPS as well as security installations are the most representative examples.

### 5.1 Typical applications

The ECDL capacitors may be used wherever high power delivery or electrical storage is required. The following examples give an overview over typical supercapacitor applications.

#### 5.1.1 Starter

Today the energy that is required to crank a small or big engine is stored in either Pb or Ni-Cd batteries. Because of their high internal resistance, which limits the initial peak current, they have to be oversized. The fast battery discharging and the cold environmental temperature affect heavily their properties. The supercapacitors have a better power behavior and a better environmental acceptance.

#### 5.1.2 Hybrid vehicle

The mean power of a small car is about 30 kW and its peak power should be about 60 kW. The supercapacitors may supply the power to the electrical vehicle required to meet the city road traffic conditions. Nevertheless in most of the cases there is a need for an additional battery to insure a certain amount of autonomy and to reach the range requirement.

Since 1991 in the department of electrical engineering of the HTA Lucerne (University of applied Science of Central Switzerland) concepts for hybrid vehicles have been developed and realized [19]. In April 1997, as one of the first vehicles in the world, the « Blue-Angel » prototype-vehicle was able to recuperate energy by means of supercapacitors in a so-called SAM (Super Accumulator Module) (Figure 7 and 8).

Figure 7: Blue-Angel of the HTA Lucerne pulling an 85t ADtranz locomotive [19]


ECN Netherlands is active in a fuel cell/supercapacitor project for an electric scooter. The fuel cell has a power of 1.2 kW and is mounted in a trailer pulled by the scooter. The supercapacitor has a 15 kWs energy. The supercapacitors were mounted on the scooter replacing the former battery. The feasibility of the fuel cell plus supercapacitor concept is demonstrated in this project. Honda announced at the vehicle conference 2000 of Geneva that the first fuel cell vehicles will be introduced on the market in 2003.

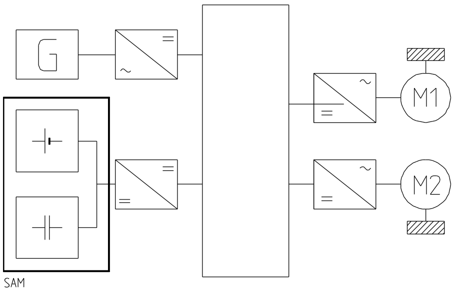



Figure 8: Hybrid vehicle sketch

#### 5.1.3 UPS

The Uninterruptable Power Supplies (UPS) may find some economical interests by using the ECDL capacitors, thanks to the suppression of an inverter and to the suppression of the maintenance. The energy supply during a limited time, at a voltage much higher than that of batteries, is easier to perform with these capacitors.

#### 5.1.4 Toy applications

Another domain are toy applications, where the total running time is typically not longer than 10 hours [20]. A supercapacitor designed for ten years or several 100'000 cycles is not optimized for such application, lower performance is thoroughly sufficient. For short terms the largest markets are for devices with < 12 V and only around 2004 the market for devices with > 48 V will have grown to the same size and will give opportunities for the supercapacitor market.

#### 5.1.5 GSM applications

During the short 0.5 ms pulse of 1 A, the battery voltage drops considerably. If it is below a certain limit, the phone is not longer operable. With a supercapacitor the voltage drop is reduced significantly and it takes much longer until the critical low voltage is reached during the pulse. In essence the operation time of the phone is extended.

#### 5.1.6 Other applications

There are a variety of other very interesting applications, which also emphasizes the economically interesting aspects of the supercapacitors for high-power density applications. Additional applications may be found in:

- elevators, cranes or pallet trucks in the electric transportation domain
- handtools or flashlights
- radars and torpedoes in the military domain
- defibrillators and cardiac pacemakers in the medicinal domain
- pulsed laser and welding in the industry
- memory supplies in phones or computers.

### 5.2 SAM

Most of the applications, where supercapacitors may be involved, need an additional battery to insure a certain amount of autonomy. Thanks to the great know-how of the HTA-Lucerne in applications with supercapacitors and their integrated intelligent electronic control management systems, montena components and the HTA-Lucerne became partners in developing the already mentioned SAM (Super Accumulator Module), consisting of the hybridization of supercapacitors and batteries with an intelligent control for universal applications (Figure 9) [19].
The parallel connection of the ECDL with a battery must be done in a clever way because batteries and capacitors have a fundamental different dynamic behavior. The batteries are faradaic (redox) storage devices. During their charging or discharging the voltage remains in principle constant. The capacitors are electrostatic storage devices. The voltage changes proportionally to the charge Q.

### 5.3 Voltage repartition

The main difficulty with the supercapacitors is their extreme low operating voltage. In the case

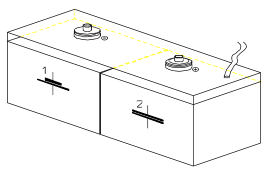



Figure 9: Supercapacitor and battery in a Super Accumulator Module (SAM) [18]

of organic electrolyte for example this voltage lays between 2 and 3 Volts (with some hope to 4 Volts in future). Contrarily most powerful applications need much higher voltages up to 700 V. The main reasons of these operating voltages are, on one side the current reduction which requires smaller and lighter conductors, and on the other side, the voltage drop in the semiconductors which is proportionally much less important in comparison to a 2.5 V application. To reach the required application voltage the super-capacitors are connected in series to form a "system".

2 electrodynamics laws govern the voltage repartition between the single cells. In continuous operation the voltage is distributed through the cells in function of their parallel resistance. Those, which have a higher resistance, are submitted to a higher voltage. A cell with a small resistance has a behavior which looks like a short. In transient operation the voltage is distributed through the cells in function of their capacitance. Those, which have a higher capacitance, need more time to change their voltage.

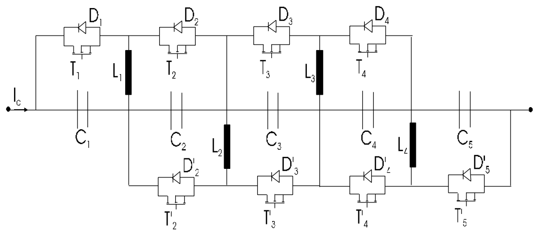
If all the cells had the same parallel resistance and the same capacitance, the voltage would be equal on each of them. It is actually not the case because several factors induce a scattering of the supercapacitor properties:

- the manufacturing process (5-10%)
- the temperature gradient in the system
- the cell aging

To prevent the decompostion of the electrolyte, which causes a supercapacitor failure, the voltage between the electrodes must be maintained under the electrolyte decomposition potential. This later depends on the electrolyte type, but also on the materials which are used for the electrodes, the conductors and the can. The voltage repartition is not only important for security reason but also to assure an equal aging of the cells. The problem is well known for electrolytic capacitor where the voltage repartition is generally controlled with resistors. It does mean finally that each supercapacitor cell must be controlled or protected.

The different methods, which are used to equilibrate the voltage through the cells, are either based on external parallel resistances, on Zener diodes or on an active power electronic [21]. In the case of the external resistance, they have to be about typically 10 time less resistive then the internal parallel resistances in order to dominate them. The losses are therefore much more important. The typical system efficiency may be estimated to 16%. In the case of Zener diodes, the principle is that the diode start to be conducting when the voltage exceed the redact voltage. This method may be considered as a cell protection. When the system is working at voltage lower then the nominal one, the cell voltage distribution is not corrected. The aging will be different from one cell to the other. The efficiency is improved to 90%. With the active electronic (Figure 10), the system efficiency may rise to 97%. The losses are due to the transistor resistance.

Figure 10 : Electronic schema and setup of the active voltage sharing with Boostcaps™ [21]




The costs of the system are strongly related to the electronic components choice, especially to the current they have to manage. This later depends on the level of the cell properties unbalancing. Performant manufacturing processes and a good temperature repartition in the system is very important to reduce costs.

To determine the electronic components size it is necessary to analyze the type of voltage stresses in the application. Generally steady state and transient stresses are superposed. The parallel resistance distribution is important for capacitors, which are permanently charged. The time constant to reach a steady state behavior is given by T = Rp C which is typically equal to about 500 hours.

## VI. Conclusions

Supercapacitors may be used wherever high power delivery or electrical energy storage is required. Therefore numerous applications are possible. The use of supercapacitors allows a complementation of normal batteries. In combination with batteries the supercapacitors improve the maximum instantaneous output power as well as the battery lifetime. In order to increase the voltage across a supercapacitor device, a series connection is needed. An active voltage repartition device has been defined which ensures no over-voltage over any supercapacitor and an optimal efficiency.

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## VIII. References

[1] A. Schneuwly, R. Gallay, Proc. Power Conversion PCIM 1999
[2] D. Ue, K. Ida, S. Mori, J. Electrochem. Soc. **141**, 1994, 2989
[3] A. Yoshida, S. Nonaka, I. Aoki, A. Nishino, J. Power Sources **60**, 1996, 213
[4] Y. Kibi, T. Saito, M. Kurata, J. Tabuchi, A. Ochi, J. Power Sources, **60**, 1996, 219
[5] H. Shi, Electroch. Acta, **41**, 1996, 1633
[6] L. Diederich, P. Milani, A. Schneuwly, R. Gallay, Applied Physics Letters **75**, Nr 17, 1999, 2662
[7] I. Tanahashi, A. Yoshida, A. Nishino, J. Electrochem. Soc. **137**, 1990, 3052
[8] S.T. Mayer, R.W. Pekala, J.L. Kasch-mitter, J. Electrochem. Soc. **140**, 1993, 446
[9] S. Iijima, Nature **354**, 1991, 56
[10] T.W. Ebbesen, Nature **358**, 1992, 220
[11] C. Emmenegger, A. Züttel, L. Schlapbach, A. Schneuwly, R. Gallay, Applied Surface Science, to be printed
[12] M.Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, H.W. Kroto, J. Phys. Chem. Solids **54**, 1993, 1841
[13] P.L. McEwen, Nature **39**3, 1998, 16
[14] A. Beliakov, ELIT company, 9$^{th}$ Seminar ECDL Deerfield Beach FL, 1999
[15] D. Evans, 9$^{th}$ Seminar ECDL Deerfield Beach FL, 1999
[16] R. Kötz, Proc. 7$^{th}$ Seminar ECDL Deerfield Beach FL, 1994
[17] Proc. 7$^{th}$ - 9$^{th}$ Seminar ECDL Deerfield Beach FL, 1997-1999
[18] O. Haas and E.J. Cairns, Annu. Rep. Prog. Chem., Sect. C, **95**, 1999, 163
[19] V. Härri, SEV/VSE **1**, 1999, 25
[20] J. Nickerson, Fullpower Technologies, 9$^{th}$ Seminar ECDL Deerfield Beach FL, 1999
[21] P. Barrade, S. Pittet, A. Rufer, Proc. Power Conversion PCIM 1999