



# Principles and applications of electrochemical capacitors

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## Abstract

Electrochemical capacitors (EC) also called ‘supercapacitors’ or ‘ultracapacitors’ store the energy in the electric field of the electrochemical double-layer. Use of high surface-area electrodes result in extremely large capacitance. Single cell voltage of ECs is typically limited to 1–3 V depending on the electrolyte used. Small electrochemical capacitors for low-voltage electronic applications have been commercially available for many years. Different applications demanding large ECs with high voltage and improved energy and power density are under discussion. Fundamental principles, performance, characteristics, present and future applications of electrochemical capacitors are presented in this communication. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Capacitors which store the energy within the electrochemical double-layer at the electrode/electrolyte interface are known under various names which are trade marks or established colloquial names such as ‘double-layer capacitors’, ‘supercapacitors’, ‘ultracapacitors’, ‘power capacitors’, ‘gold capacitors’ or ‘power cache’. ‘Electrochemical double-layer capacitor’ is the name that describes the fundamental charge storage principle of such capacitors. However, due to the fact that there are in general additional contributions to the capacitance other than double layer effects, we will call these capacitors electrochemical capacitors (EC) throughout this paper.

Electrochemical capacitors have been known since many years. First patents date back to 1957 where a capacitor based on high surface area carbon was described by Becker [1]. Later in 1969 first attempts to

market such devices were undertaken by SOHIO [2].

However, only in the nineties electrochemical capacitors became famous in the context of hybrid electric vehicles. A DOE ultracapacitor development program was initiated in 1989, and short term as well as long term goals were defined for 1998–2003 and after 2003, respectively [3]. The EC was supposed to boost the battery or the fuel cell in the hybrid electric vehicle to provide the necessary power for acceleration, and additionally allow for recuperation of brake energy. Today several companies such as Maxwell Technologies, Siemens Matsushita (now EPCOS), NEC, Panasonic, ELNA, TOKIN, and several others invest in electrochemical capacitor development. The applications envisaged are principally boost components supporting batteries or replacing batteries primarily in electric vehicles. In addition alternative applications of EC not competing with batteries but with conventional capacitors are coming up and show considerable market potential. Such applications will also be discussed in detail in the second part of the paper.

The reason why electrochemical capacitors were able to raise considerable attention are visualized in Fig. 1

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where typical energy storage and conversion devices are presented in the so called ‘Ragone plot’ in terms of their specific energy and specific power. Electrochemical capacitors fill in the gap between batteries and conventional capacitors such as electrolytic capacitors or metallized film capacitors. In terms of specific energy as well as in terms of specific power this gap covers several orders of magnitude.

Batteries and low temperature fuel cells are typical low power devices whereas conventional capacitors may have a power density of  $>10^6$  watts per  $\text{dm}^3$  at very low energy density. Thus, electrochemical capacitors may improve battery performance in terms of power density or may improve capacitor performance in terms of energy density when combined with the respective device. In addition, electrochemical capacitors are expected to have a much longer cycle life than batteries because no or negligibly small chemical charge transfer reactions are involved. A monograph volume on electrochemical capacitors was recently published by Conway [4].

In the following the basic principal of electrochemical capacitors, the different types of ECs, some theoretical considerations as to the performance of ECs, and some applications will be discussed.

## 2. Principle of energy storage

Electrochemical capacitors store the electric energy in an electrochemical double layer (Helmholtz Layer) formed at a solid/electrolyte interface. Positive and negative ionic charges within the electrolyte accumulate

at the surface of the solid electrode and compensate for the electronic charge at the electrode surface. The thickness of the double layer depends on the concentration of the electrolyte and on the size of the ions and is in the order of 5–10 Å for concentrated electrolytes. The double layer capacitance is about 10–20  $\mu\text{F}/\text{cm}^2$  for a smooth electrode in concentrated electrolyte solution and can be estimated according to equation Eq. (1)

$$C/A = \varepsilon_0^* \varepsilon_r / d \quad (1)$$

assuming a relative dielectric constant  $\varepsilon_r$  of 10 for water in the double layer [5].  $d$  being the thickness of the double-layer with surface area  $A$ . The corresponding electric field in the electrochemical double layer is very high and assumes values of up to  $10^6$  V/cm easily. Compared to conventional capacitors where a total capacitance of pF and  $\mu\text{F}$  is typical, the capacitance of and the energy density stored in the electrochemical double layer is rather high per se and the idea to build a capacitor based on this effect is tempting.

In order to achieve a higher capacitance the electrode surface area is additionally increased by using porous electrodes with an extremely large internal effective surface. Combination of two such electrodes gives an electrochemical capacitor of rather high capacitance.

Fig. 2 shows a schematic diagram of an electrochemical double-layer capacitor consisting of a single cell with a high surface-area electrode material, which is loaded with electrolyte. The electrodes are separated by a porous separator, containing the same electrolyte as the active material. The potential drop across the cell is also shown in Fig. 2.

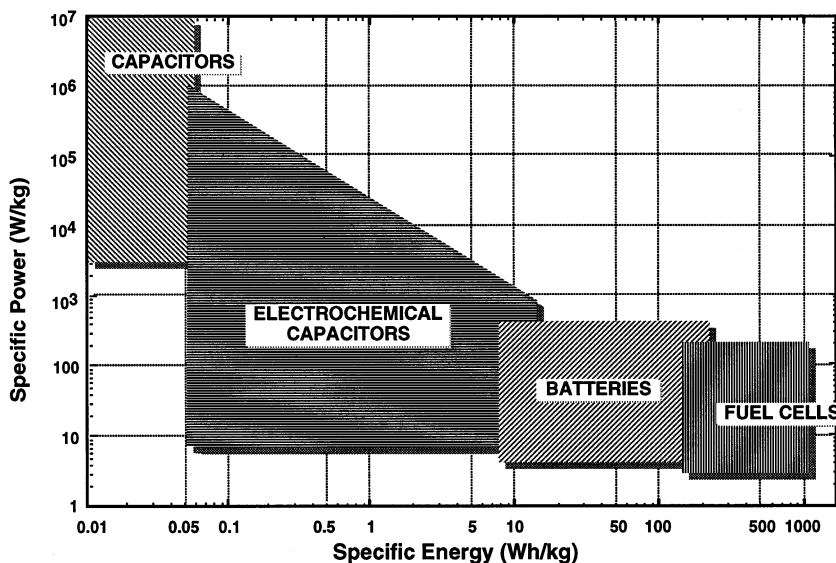


Fig. 1. Sketch of Ragone plot for various energy storage and conversion devices. The indicated areas are rough guide lines.

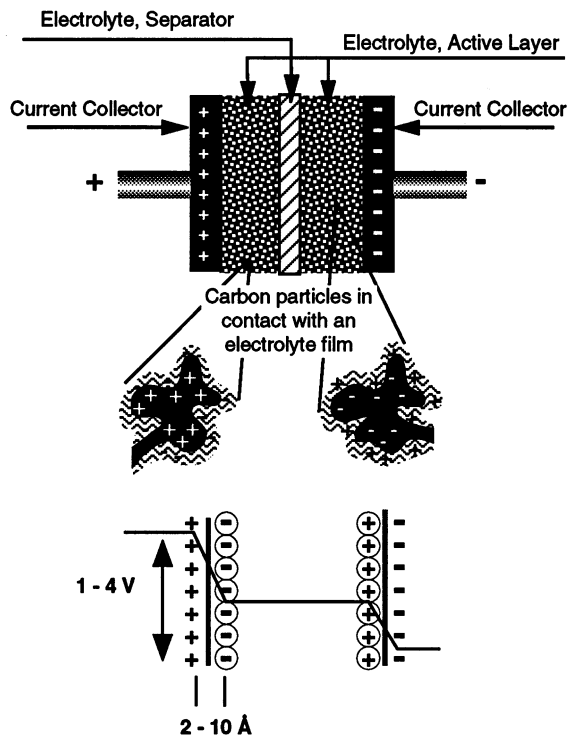


Fig. 2. Principle of a single-cell double-layer capacitor and illustration of the potential drop at the electrode/electrolyte interface

The capacitance of a single electrode can be estimated by assuming a high surface area carbon with  $1000 \text{ m}^2/\text{g}$  and a double layer capacitance of  $10 \text{ }\mu\text{F}/\text{cm}^2$ . This leads to a specific capacitance of  $100 \text{ F/g}$  for one electrode.

For a capacitor two electrodes are needed with doubled weight and half the total capacitance ( $1/C = 1/C_1 + 1/C_2$ ) resulting in  $25 \text{ F/g}$  of active capacitor mass for this example.

The difference between single electrode values and specifications given for the complete capacitor is of significant importance. Whenever specifications of an EC are given, one should indicate whether the values correspond to single electrode measurement or are calculated for a complete capacitor. The difference between these two situations is a factor of four and therefore of significant importance.

The maximum energy stored in such a capacitor is given by

$$W = 1/2 C U_0^2 \quad (2)$$

With a cell voltage  $U_0$  of  $1 \text{ V}$  (aqueous electrolyte) one obtains a specific energy of about  $3.5 \text{ Wh/kg}$  of active mass. Using an organic electrolyte with a typical cell voltage of  $2.3 \text{ V}$  one obtains about  $18 \text{ Wh/kg}$  of active mass. These values are considerably lower than

those obtained for available batteries but much higher than for conventional capacitors. It should be mentioned that the above values depend on the double layer capacitance, the specific surface area of the respective electrode material, the wetting behavior of the pores, and on the nominal cell voltage.

### 3. Classification of electrochemical capacitors

Electrochemical capacitors may be distinguished by several criteria such as the electrode material utilized, the electrolyte, or the cell design. With respect to electrode materials there are three main categories: carbon based, metal oxides and polymeric materials. A comprehensive review of possible electrode materials suitable for ECs is given by Sarangapani [6].

#### 3.1. Electrode material

##### 3.1.1. Carbon

Carbon in various modifications is the electrode material used most frequently for electrodes of electrochemical capacitors. Reasons for using carbon are manifold such as (i) low cost, (ii) high surface area, (iii) availability, and last but not least (iv) established electrode production technologies. Carbons are available with a specific surface area of up to  $2500 \text{ m}^2/\text{g}$  as powders, woven cloths, felts, or fibers.

Charge storage on carbon electrodes is predominantly capacitive in the electrochemical double layer. Carbon based electrochemical capacitors come close to what one would call an electrochemical double layer capacitor. There are however contributions from surface functional groups which are in general present on activated carbons and which can be charged and discharged giving rise to pseudocapacitance.

A typical cyclic voltammogram (CV) for an activated glassy carbon electrode is reproduced in Fig. 3 for electrochemically activated glassy carbon in aqueous and non-aqueous electrolyte [7,8]. The rectangular shape expected for an ideal capacitor is best approached in organic electrolyte, while the redox peak around  $0.4 \text{ V}_{\text{sc}}$  in aqueous electrolyte illustrates the contribution from surface functional groups. This corresponding pseudocapacitance is significantly reduced in organic electrolyte because protons are not available. The effect of surface functional groups containing oxygen on the stability of carbon electrodes in EC using organic electrolyte was investigated by Nakamura et al. [9]. These authors found that the stability of the activated carbon increases with the oxygen content when the carbon is used for the anode and decreases when used for the cathode. In general one can observe that both the stability and conductivity of the activated high surface area carbon decrease with increasing surface area [10].

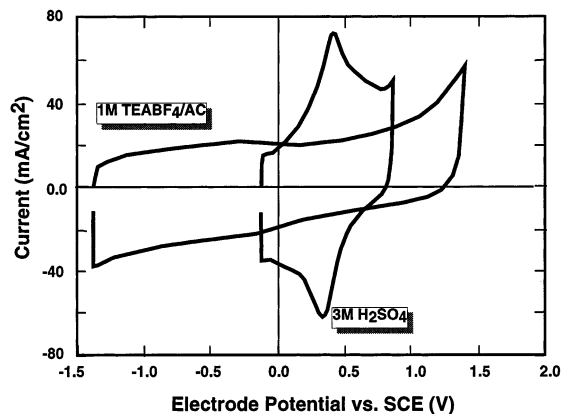


Fig. 3. Cyclic voltammograms of activated glassy carbon electrodes at 100 mV/s in 3M H<sub>2</sub>SO<sub>4</sub> (aq.) and in 1 M TEABF<sub>4</sub> in acetonitrile. Both electrodes received the same electrochemical activation.

### 3.1.2. Metal oxides

The cyclic voltammogram of RuO<sub>2</sub> (and also IrO<sub>2</sub>) electrodes have an almost rectangular shape and exhibit good capacitor behavior [11,12]. However, the shape of the CV is not a consequence of pure double layer charging, but of a sequence of redox reactions occurring in the metallic oxide. The valence state of Ru may change from III to VI within a potential window of slightly > 1 V. The ratio of surface charging to bulk processes was nicely separated by Trasatti [11]. In aqueous acid electrolytes the fundamental charge storage process is proton insertion into the bulk material.

Very high specific capacitance of up to 750 F/g was reported for RuO<sub>2</sub> prepared at relatively low temperatures [13]. Conducting metal oxides like RuO<sub>2</sub> or IrO<sub>2</sub> were the favored electrode materials in early ECs used for space or military applications [14]. The high specific capacitance in combination with low resistance resulted in very high specific powers. These capacitors, however, turned out to be too expensive. A rough calculation of the capacitor cost showed that 90% of the cost resides in the electrode material. In addition, these capacitor materials are only suitable for aqueous electrolytes, thus limiting the nominal cell voltage to 1 V.

Several attempts were undertaken to keep the advantage of the material properties of such metal oxides at reduced cost. The dilution of the costly noble metal by forming perovskites was investigated by Guther et al. [15]. Other forms of metal compounds such as nitrides were investigated by Liu et al. [16]. However, these materials are far from being commercially used in ECs.

### 3.1.3. Polymers

Polymeric materials, such as *p*- and *n*-dopable poly(3-arylthiophene), *p*-doped poly(pyrrole), poly(3-methylthiophene), or poly(1,5-diaminoanthraquinone)

have been suggested by several authors [17–19] as electrodes for electrochemical capacitors. The typical cyclic voltammogram of a polymer however is in general not of rectangular shape, as is expected for a typical capacitor, but exhibits a current peak at the respective redox potential of the polymer. In order to be able to use one and the same electrode material on both capacitor electrodes polymers with a cathodic and an anodic redox process were utilized recently [19].

Using a polymeric material for electrochemical capacitor electrodes gives rise to a debate as to whether such devices should still be called capacitors or whether they are better described as batteries. In terms of the voltage transient during charge and discharge and with respect to the CV they are batteries. Compared to metallic oxides, however, the term capacitor is justified. The difference being only that the metallic oxides exhibit a series of redox potentials giving rise to an almost rectangular CV while the polymer typically has only one redox peak.

For such capacitors rather high energy density and power density have been reported [19]. The long-term stability during cycling, however, may be a problem. Swelling and shrinking of electroactive polymers is well known and may lead to degradation during cycling.

## 3.2. Electrolyte

Another criteria to classify different electrochemical capacitors is the electrolyte used. Most of the presently available capacitors use an organic electrolyte.

### 3.2.1. Organic

The advantage of an organic electrolyte is the higher achievable voltage. According to Eq. (2) the square of the unit-cell voltage determines the maximum stored energy. Organic electrolytes allow for a unit cell voltage above 2 V. Typically the cell float voltage is 2.3 V with the possibility to increase the voltage for a short time to 2.7 V. The cell voltage is most probably limited by the water content of the electrolyte. In order to achieve higher voltage, some companies plan to go up to a float voltage of 3.2 V, extreme purification procedures of special electrolyte have to be applied and the corrosion of the carbon electrodes has to be reduced by special protective coatings [20]. However, similar problems concerning the potential window of organic electrolyte are known from Li-ion battery production and can be overcome.

On the other hand organic electrolytes have a significantly higher specific resistance. Compared to a concentrated aqueous electrolyte the resistance increases by a factor of at least 20, typically by a factor of 50. The higher electrolyte resistance also affects the equivalent distributed resistance of the porous layer and consequently reduces the maximum usable power, which is calculated according to

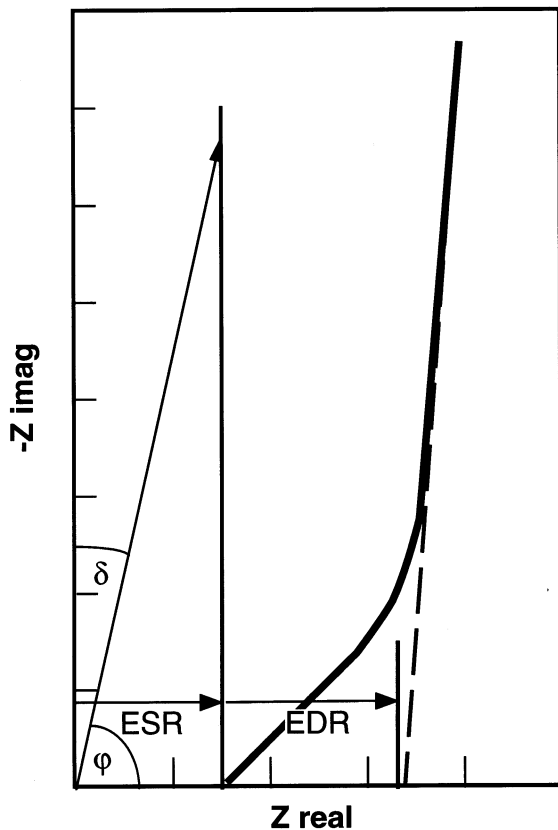


Fig. 4. Schematic representation of the Nyquist impedance plot of an ideal capacitor (vertical thin line) and an electrochemical capacitor with porous electrodes (thick line).

$$P = U^2/4R \quad (3)$$

where  $R$  represents the total effective series resistance (ESR). However, part of the reduction in power is compensated by the higher cell voltage achievable with an organic electrolyte. A listing of potential organic electrolytes for electrochemical capacitors is provided in [21].

### 3.2.2. Aqueous

Aqueous electrolytes limit the unit cell voltage of the EC to typically 1 V, thus reducing the available energy significantly compared to organic electrolytes. Advantages of the aqueous electrolyte are the higher conductance (0.8 S/cm for  $H_2SO_4$ ) and the fact that purification and drying processes during production are less stringent. In addition cost of aqueous electrolytes are usually much lower than for suitable organic electrolytes. Capacitors build by NEC [22] and ECONDO use aqueous electrolyte. Aiming at high power density, the glassy carbon based capacitor developed in our laboratories also uses an aqueous electrolyte [23]. It should be pointed out that the capacitor has to be

developed for one or the other electrolyte, not only because of material aspects but also the porous structure of the electrode has to be tailored for the size and the properties of the respective electrolyte.

In order to avoid electrolyte depletion problems during charging of the EC, the electrolyte concentration has to be high. If the electrolyte reservoir is too small compared to the huge surface area of the electrodes, performance of the capacitor is reduced. This problem is particularly important for organic electrolytes where the solubility of the salts may be low. Zheng and Jow found, however, that concentrations higher than 0.2 molar are sufficient [24].

## 4. Electrochemical capacitor performance

The performance characteristics of electrochemical capacitors differ somewhat from those of conventional capacitors. In Fig. 4 the impedance plane representation (Nyquist plot) of an ideal capacitor and a simplified electrochemical capacitor, both having the same ESR (equivalent series resistance at 1 kHz), are compared. While the ideal capacitor exhibits a vertical line, the electrochemical capacitor starts with a 45° impedance line and approaching an almost vertical line only at low frequencies.

The non-vertical slope of the low frequency impedance of any real electrochemical capacitor can be easily reproduced in any model equation by replacing the capacitance expression with a constant phase element (CPE) expression. This amounts to replacing every  $j\omega$  expression with  $(j\omega)^p$ , where  $0 < p < 1$ , and where  $p = 1$  represents an ideal capacitor with no frequency dependence. This non-ideality is a typical feature of electrochemical charging processes, and may be interpreted as resulting from a distribution in macroscopic path lengths (non-uniform active layer thickness) [25] or a distribution in microscopic charge transfer rates [26], adsorption processes, or surface roughness.

The 45° region (Warburg region) is a consequence of the distributed resistance/capacitance in a porous electrode. At higher frequencies the resistance as well as the capacitance of a porous electrode decreases, because only part of the active porous layer is accessible at high frequencies. The electrochemical capacitor may thus be represented by an ideal capacitor with an ESR increased by the 'equivalent distributed resistance' EDR.

### 4.1. Porous electrode

The porous electrode is often described by a truncated RC-transmission line according to Fig. 5. The equivalent circuit of the pore of a porous electrode is approximated by a line of  $R$  and  $C$  elements representing the elemental double layer capacitance and the

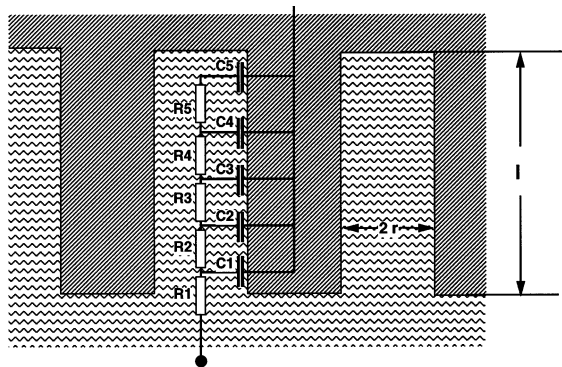


Fig. 5. Equivalent circuit representation of the distributed resistance and capacitance within a pore. Five-element transmission line.

respective electrolyte resistance at a particular depth of the pore. The resistance of the bulk material is assumed to be much smaller than the electrolyte resistance. At high frequencies the capacitors behave like small impedance elements ( $Z = 1/j\omega C$ ) and the current flows predominantly along  $R1$  and  $C1$  into the bulk material and almost no current flows deep down the pore. Consequently, resistance and double layer capacitance are reduced at high frequencies [27].

A more complete description of the porous electrode behavior was given by De Levie [28]. Assuming straight cylindrical pores with a radius  $r$  and length  $l$ , a double layer capacitance and an electrolyte conductivity  $\kappa$  one can calculate the impedance according to

$$Z(\omega) = \sqrt{\frac{R_w}{j\omega C}} \coth \sqrt{j\omega R_w C} \quad (4)$$

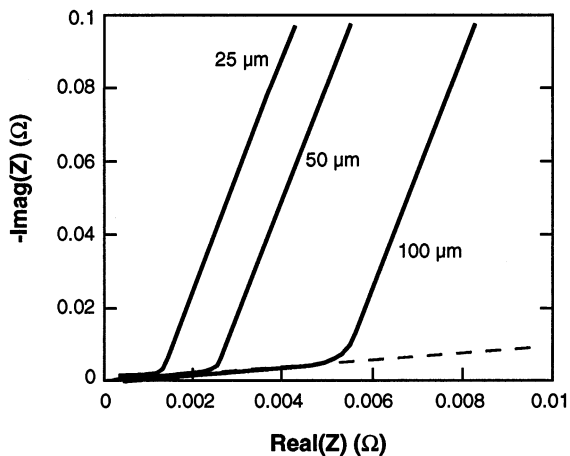


Fig. 6. Calculated impedance plots for porous electrodes with different thickness. Assumptions: Double layer capacitance:  $10 \mu\text{F}/\text{cm}^2$ ; pore diameter:  $3 \text{ nm}$ ; electrolyte conductivity  $0.8 \text{ S}/\text{cm}$ ; rectangular closed packed arrangement of pores  $10^{13}/\text{cm}^2$ ; constant phase element exponent  $0.98$ .

$$\text{Low frequency} \quad Z(0) = \frac{1}{j\omega C}$$

$$\text{High frequency} \quad Z(\omega \rightarrow \infty) = \sqrt{\frac{R_w}{j\omega C}}$$

where  $R_w$  represents the low frequency resistance spanning the  $45^\circ$  Warburg region and  $C$  represents the low frequency capacitance, which is determined by the double layer capacitance times the total pore surface area. The total impedance of a capacitor would also include the ionic resistance of the bulk electrolyte and separator as well as any contact resistance in the system. The total impedance would then be  $R_{\text{contacts}} + R_{\text{sol}} + Z(\omega)$ .

For a porous, highly conducting layer with a liquid electrolyte filling the pores, the low frequency resistance  $R_w$  depends only on the porosity and on the apparent conductivity  $\kappa$  of the electrolyte.  $\kappa$  may appear to be somewhat smaller than the bulk electrolyte conductivity if the pores are tortuous instead of straight [29].

$$R_w = \frac{L}{3\pi r^2 n \kappa} \quad (5)$$

Where  $L$  is the active layer thickness (the length of the pores for straight, cylindrical pores),  $r$  is the pore radius, and  $n$  the number of pores. The porosity, the volume fraction of pores, would be  $\pi r^2 n / A$ , where  $A$  is the geometric electrode area and  $n$  the number of pores per volume.

For a theoretical estimation of the contribution of the active porous layer to the series resistance we apply the DeLevie transmission line model of a porous electrode with straight pores considered as cylindrical capillaries [28]. The electrolyte conductivity is  $0.8 \text{ S}/\text{cm}$  ( $3\text{M H}_2\text{SO}_4$ ) and the double layer capacitance at the walls of the pores is assumed to be  $10 \mu\text{F}/\text{cm}^2$ . The pores have a diameter of  $3 \text{ nm}$  and are arranged in a rectangular closed packed manner. The resulting porosity of the layer is  $78\%$  with a pore density of  $10^{13}/\text{cm}^2$ . Such a layer has a volumetric capacitance of  $105 \text{ F}/\text{cm}^3$  and a specific resistance of  $0.53 \Omega\text{cm}$  ( $1.9 \text{ S}/\text{cm}$ ).

The impedance plots and the capacitance versus frequency plots are shown for such a layer in Figs. 6 and 7 for three different thicknesses. The capacitance is calculated from the imaginary part of the complex impedance according to

$$C = -1/[\omega \text{Im}(Z)] \quad (6)$$

The impedance plot is equivalent to that sketched in Fig. 4 and the typical  $45^\circ$  Warburg region is visible for the three thicknesses. In this high frequency domain the porous character of the active layer dominates. In the capacitance versus frequency plot, the capacitance starts to decrease noticeably at high frequency. The cut-off frequency is roughly related to the  $RC$  time constant of the single electrode capacitor. At lower frequencies the impedance plot (Fig. 6) approaches a

vertical line. A CPE of 0.98 was assumed for the calculation. In the corresponding capacitance versus frequency plot the capacitance levels off at lower frequencies.

Assuming an organic electrolyte with a specific conductance of 0.04 S/cm the very same electrode has a specific resistance of 10.6  $\Omega\text{cm}$  (0.09 S/cm).

The effect of active layer thickness is demonstrated in Figs. 6 and 7 where the capacitance versus frequency plots are shown for electrodes with active layer thicknesses of 25, 50, and 100  $\mu\text{m}$ . The increased film thickness leads to a higher capacitance at low frequencies and of course to an increased distributed resistance of the film. These two factors cause a higher time constant  $RC$  that is reflected by the lower cut-off frequency for thicker electrodes. The effect of the pore number and the pore diameter is simply understood in the simple porous layer model. The equivalent resistance of the porous layer is directly proportional to the porosity of the layer, i.e. to the volume of the electrolyte within the porous structure. Thus, an increase of the pore number with constant radius or an increase of the pore diameter at constant pore number results in increased capacitance and reduced resistance. An example is given for an increase of the pore diameter from 2 to 20 nm at constant pore number of  $2.5 \cdot 10^{11}/\text{cm}^2$ . The respective porosity increases from 0.8 to 78%. The capacitance versus frequency plot in Fig. 8 shows the increased capacitance and the increasing cut-off frequency.

#### 4.2. Maximum achievable energy density and power density

The maximum achievable power and energy densities of an EC can be calculated from Eqs. (2) and (3) assuming reasonable values for electrode and electrolyte layer thickness and conductance. Such a plot is shown in Fig. 9, where the active layer thickness is the parameter along the curve with a thickness of 1  $\mu\text{m}$  at the left end and 1000  $\mu\text{m}$  at the right end of the curves. We assumed for the parameters a volumetric capacitance of 100  $\text{F}/\text{cm}^3$  for the single electrode, a current collector thickness of 25  $\mu\text{m}$  and an electrolyte/separators thickness of 25  $\mu\text{m}$ . The separator has a porosity of 50%. As already mentioned, the active layer thickness is varied from 1 to 1000  $\mu\text{m}$ . The two curves in Fig. 9 represent a capacitor with aqueous electrolyte and a 1 V potential window and a capacitor with organic electrolyte and a potential window of 2.3 V. The conductance of the aqueous electrolyte is 0.8 S/cm while for the organic electrolyte a conductance of 0.02 S/cm was assumed.

As is evident from Fig. 9 on the basis of these theoretical considerations a power density of up to  $2 \cdot 10^6$  W/l can be achieved for the aqueous electrolyte and a maximum energy density of about 20 Wh/l can

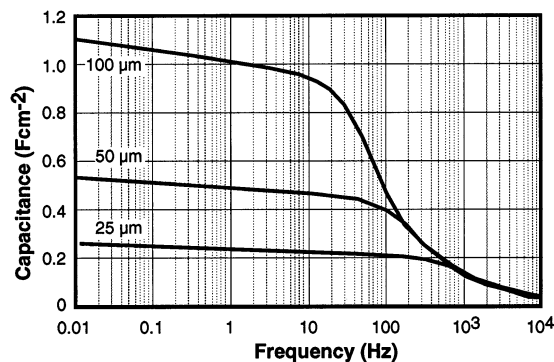


Fig. 7. Capacitance versus frequency plot for the electrodes of Fig. 6.

be reached for the organic electrolyte. From this plot it is evident that very thin films ( $< 10 \mu\text{m}$ ) result in a decreased energy density at almost constant power density because the internal resistance is totally determined by the electrolyte. The same is true on the other end of the plot where thick films ( $> 100 \mu\text{m}$ ) result in reduced power at constant energy density, because now the internal resistance is determined by the porous layer.

In order to increase EC performance, the material properties have to be investigated and improved. The resistance of the electrolyte and, particularly, the contact resistance have to be controlled. An optimized electrolyte and electrode material may allow for potential windows wider than 3 V. The effect of the nominal voltage of the capacitor cell in case of an organic electrolyte is plotted in Fig. 10 for potentials of 2, 3, 4 V. With an organic electrolyte and a 4 V cell voltage the capacitor comes close to the power performance of the capacitor using aqueous electrolyte.

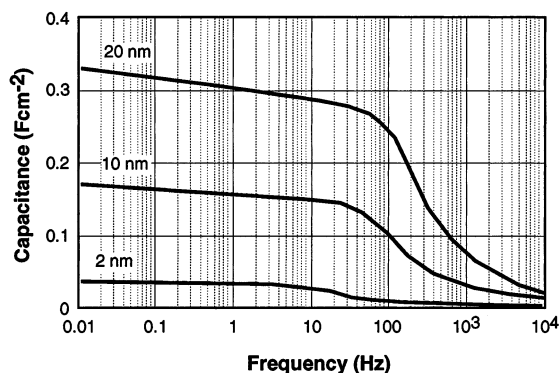


Fig. 8. Effect of pore diameter on the capacitance versus frequency performance of a single porous electrode. Thickness of porous layer: 100  $\mu\text{m}$ , CPE: 0.98, double layer capacitance 20  $\mu\text{F}$ , number of pores  $2.5 \cdot 10^{11}/\text{cm}^2$

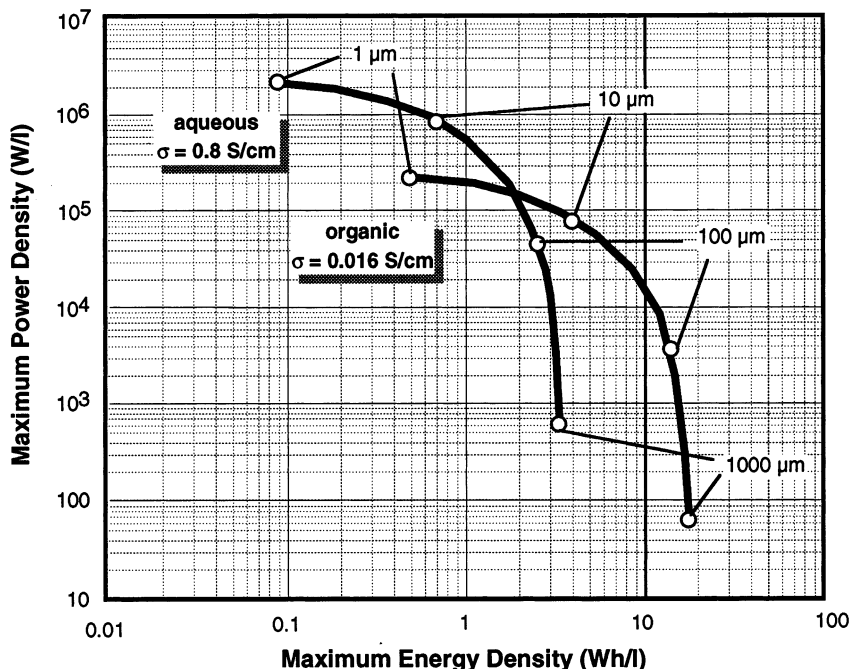


Fig. 9. Calculated maximum achievable power density and maximum achievable energy density for two capacitors with aqueous (1 V) and organic electrolyte (2.3 V). The parameter on the curves is the active porous layer thickness. Assumptions: separator thickness: 25 μm, separator porosity: 50%, volumetric capacitance of porous layer: 100 F/cm<sup>3</sup>.

#### 4.3. Ragone plots

Although similar, the above plots do not correspond to Ragone plots. The Ragone plot relates power and energy density for one single device: they provide the energy available for a constant power load. The maximum values discussed in Figs. 9 and 10 are only end points of Ragone plots where the maximum energy density is related with a vanishing power density and vice versa. Electrochemical impedance data, the phase angle  $\varphi$ , and the corresponding Ragone plots for a Panasonic GoldCap (10 F and 2.5 V) and an aqueous capacitor developed in our lab [23,30] with 5 V and 0.8 F are shown in Figs. 11a, b and 12. Calculation of Ragone plots for a constant power discharge of a capacitor is analytically not possible for a general frequency dependent impedance [31,32]. There is, however, a simple linear approach [32] to present energy and power in a Ragone plot, which was used for the plots in Fig. 12.

The two devices cannot be compared directly because the Panasonic device is commercially available, while the PSI capacitor is a laboratory type device only, without a professional housing. From both plots it is evident that the maximum power is available only with very low energy, i.e. for very short time. The phase angle  $\varphi$  of the impedance plot (see also Fig. 4) for both capacitors is shown in Fig. 11b. The efficiency of a capacitor is related to the loss factor  $d_c$ ,

$$d_c = \tan(\delta) = \tan(90^\circ - \varphi) \quad (7)$$

which is a measure for the quality of the capacitor. The power dissipated as heat in the internal resistance is determined by the cosine of  $\varphi$ . A loss factor of 0.5 ( $\varphi = 60^\circ$ ) is achieved at a frequency of 12 Hz for the PSI and of 0.25 Hz for the Panasonic capacitor. At a

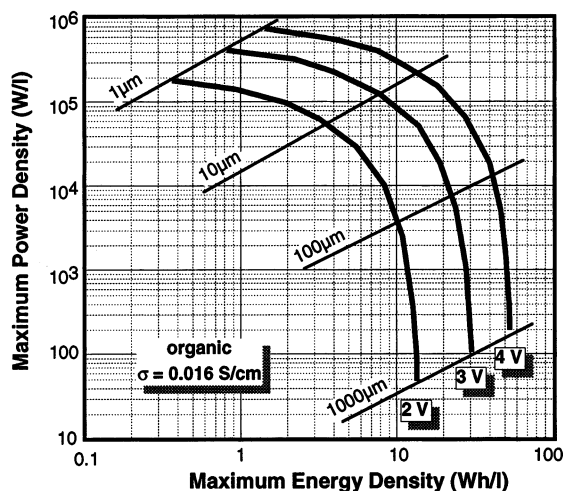


Fig. 10. Effect of nominal cell voltage on the maximum achievable power and energy density of Fig. 9 for the capacitor with organic electrolyte.

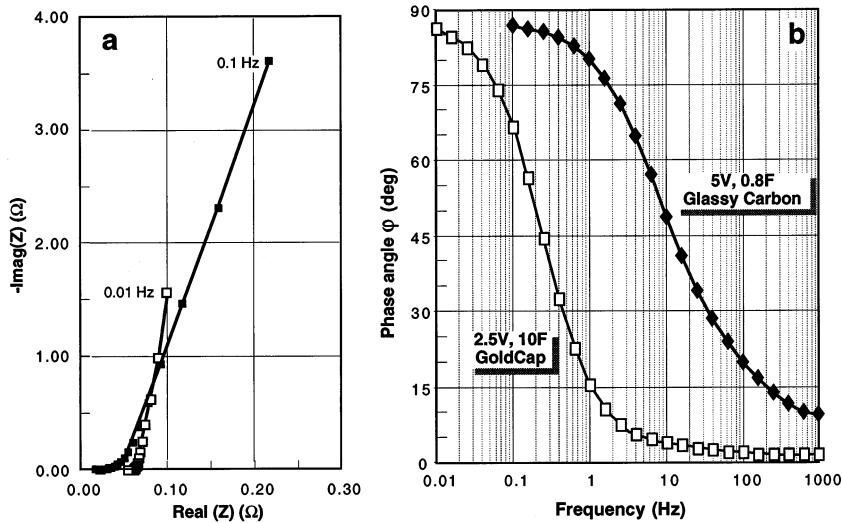


Fig. 11. (a) Measured electrochemical impedance plots for a commercial Panasonic capacitor (10 F, 2.5 V, open squares) and a laboratory type capacitor (0.8 F, 5 V, filled squares) based on glassy carbon electrodes built at the PSI. (b) Phase angle for the same two capacitors. (Open symbols Panasonic 'GoldCap', closed symbols PSI-cap)

phase angle of  $45^\circ$  about 70% of the power corresponds to heat production at the internal resistance.

## 5. Cell design

Efficiency is a very important issue for EC in electric vehicle (EV) applications. Part of the available energy is dissipated at the internal resistance ESR. At high power, i.e. high current, this loss can become dominant.

In a recent comparison of ECs and batteries in EV applications, Burke and Miller [33] found that there is a slight advantage of a good capacitor over a good battery in terms of round trip efficiency, the efficiency of the capacitor being 92% and that of a NiMH battery about 85%. Therefore, ESR reduction of electrochemical capacitors is very important in order to compete with other storage devices. There are at least four different contributions to the ESR originating from the (i) electrolyte including separator, (ii) current collector,

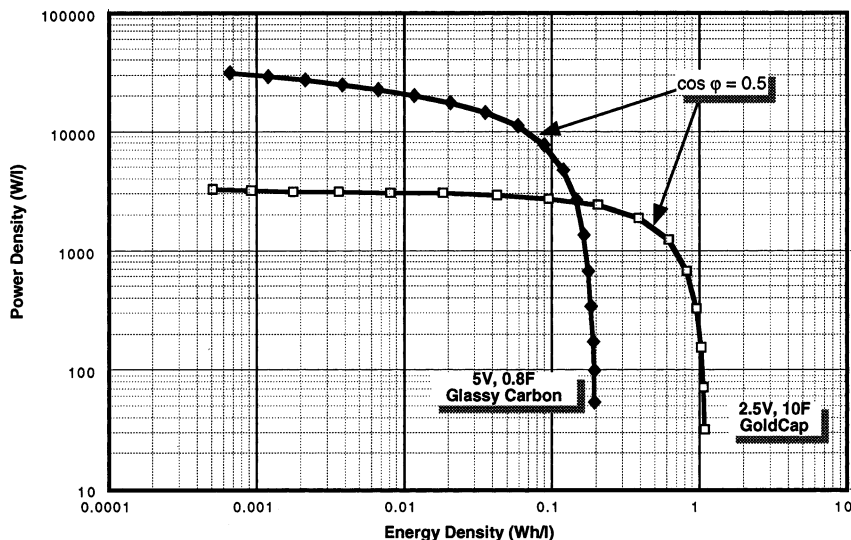


Fig. 12. Ragone plots calculated from the measured impedance for the two capacitors of Fig. 11. (Open symbols Panasonic 'GoldCap', closed symbols PSI-cap)

(iii) porous layer including contact to current collector, and (iv) other contact resistances.

In order to prevent short circuits between neighboring capacitor electrodes, a porous separator has to be used as a spacer. Independent of the choice of electrolyte the spacer has to be thin and highly porous in order to keep the resulting resistance low. The conductance  $\sigma$  of an electrolyte in a porous non-conducting separator is a function of the porosity  $p$  and the specific conductance of the electrolyte  $\sigma_0$ , according to [34]

$$\sigma = \sigma_0 p^\alpha \quad \text{with } 1.5 < \alpha < 2 \quad (8)$$

Consequently, the choice of electrolyte, separator thickness, and porosity is a complex issue, keeping mechanical stability, volume, and resistance in mind.

For a monopolar cell arrangement, current flow along a thin current collector at high currents, which can be expected for fast discharge applications, may well contribute to ohmic losses. Homogeneous current distribution in monopolar electrochemical cells, especially at high currents, is an important issue.

In case of a bipolar EC, where the current flows normal to the current collector (bipolar plate) from one to the next cell, the contribution from the current collectors to resistance is negligible.

Compared to conventional capacitors, ECs have the disadvantage of a rather low cell voltage. In order to achieve several hundred volt capacitor voltage, which is typical for EV and other applications, many single cells have to be connected in series. The bipolar cell design is an elegant way to connect many cells in series without introducing extra wiring and contact resistance. However, a bipolar cell stack requires a sophisticated sealing concept for each cell.

In order to have a good voltage balance over all units, these have to have equal performance. Otherwise different cells will experience different voltage, which may be higher than the nominal voltage. Such problems have to be overcome by very narrow manufacturing tolerance or by extra electronic controls providing over-voltage protection. These electronic control circuits can be easily added to the single monopolar cells of a capacitor stack, but it will be difficult to add these extra protections to the single cells of a bipolar capacitor stack.

## 6. Applications

Many applications are demanding local storage or local generation of electric energy. This may be required since they are in portable or remote equipment, since the supply of power may be interrupted or since the main power supply is not able to deliver the peak power. Local generation of energy (Diesel generator, fuel cell, gas turbine, photovoltaics, etc.) normally

means a more complex system than a storage system, but it is most adequate if a large amount of energy is needed for a long time. Storage of electric energy can be done in electric fields (capacitors), by means of chemical reactions (batteries), in magnetic fields (SMES: superconducting magnetic energy storage) or by transferring the electric energy to mechanical (flywheel) or potential (pumped hydro) energy or to pressure. The choice of the energy storage device should be adequate for the application. Similarities and differences between batteries and electrochemical capacitors were discussed by Conway et al. [35,36].

The ideal applications for ECs are all those demanding energy for a duration in the time range  $10^{-2} \text{ s} \leq t \leq 10^2 \text{ s}$ . For those applications, as well for batteries as for conventional capacitors, the ratio of stored energy to available power is unfavorable and the devices have to be over-dimensioned due to either the power or energy demands. The needs for long lifetime, for many charge-discharge cycles (e.g., in combination with photovoltaics) or for fast recharging rates may increase the time range to days and weeks. The poor energy density of low voltage capacitors makes ECs also attractive for pulse power applications in the ms range.

The basic technology of ECs with carbon electrodes is independent of polarity. Nevertheless, present ECs are not suitable for AC applications and for applications involving a high ripple current. Their internal resistance is higher than the one of conventional capacitors and thermal degradation may occur. In addition, some manufacturers use asymmetric electrode systems or have special treatments of one of the two electrodes causing a polarity of the devices.

Most ECs are short circuit proven. On one hand, the larger internal resistance in comparison to conventional capacitors limits the peak power. On the other hand, the smaller amount of energy stored in comparison to batteries allows only a limited heating of the ECs, so that self-ignition does not occur. Another important advantage of ECs is that in general, they do not contain hazardous or toxic materials and that they are easy to dispose. They do not need any servicing during their life and can withstand a huge number of charge-discharge cycles [37,38]. In a properly designed system, cycling efficiency is 95% and higher. They are applicable in a large temperature range. Particularly at low temperature, they substantially outperform conventional batteries. Short-term (ms–s) over-voltage is in general not critical to the devices. If the applied voltage exceeds the nominal voltage for longer duration, the lifetime of the EC will be shortened. Gas may be produced which can cause leakage or rupture of the device. The characteristic time for self-discharge is in the order of days to months. The low voltage of the unit cells allows an easy adoption to the desired voltage level by connecting cells into series and a modular construction of large banks.

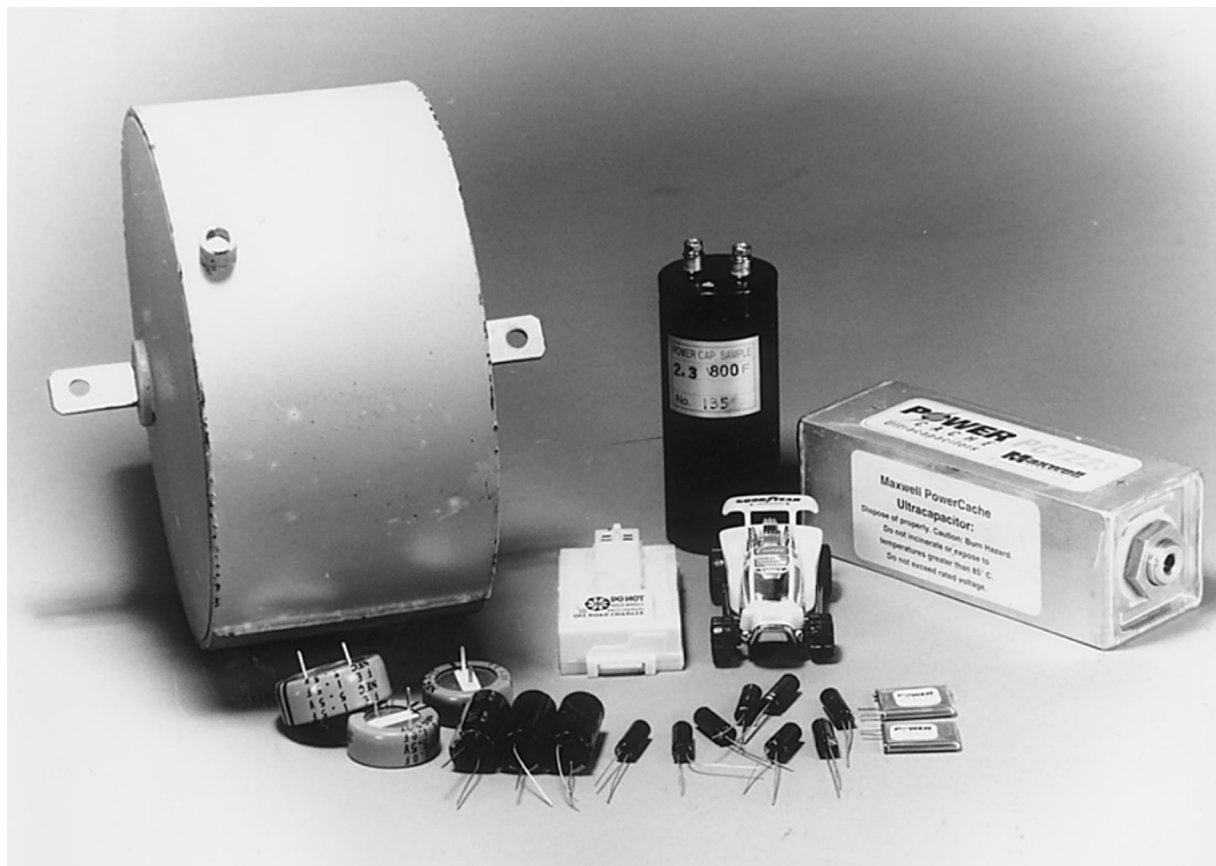


Fig. 13. Commercial electrochemical capacitors and toy equipped with an Electrochemical Capacitor.

### 6.1. Overview of commercially available ECs

The first ECs appeared on the market in 1978 (Gold Capacitors from Panasonic/Matsushita) and in 1980 (Supercap from NEC/Tokin). Two other Japanese companies entered into the markets with products of comparable ratings end of the eighties (Dynacap from ELNA, Polyacene Capacitor/Battery from Seiko Instruments). All those manufacturers have products with nominal voltage in the range 2.3–6 V and capacitance values of  $10^{-2}$  F to several Farads. Tokin also offers capacitors at 11 V. The costs of those ECs are in the order of a few to a few ten cents per Joule. The  $RC$ -time constant (defined as the low frequency capacitance times the 1 kHz resistance) is several s. They are most suitable for consumer electronic applications. Several hundred million ECs are manufactured and shipped per year.

Since the beginning of the nineties, two Russian companies are selling ECs (PSCap from Econd, SC from ELIT). They offer capacitors with nominal voltage in the range 12–350 V and capacitance values

of 1 F to several hundred Farads. The  $RC$  time constant is about 0.3 s. The capacitors are most suitable for starter and actuator applications.

Panasonic sells for several years cylindrical single cell capacitors with capacitance up to 1500 F (Power Capacitor, 2.3 V). Maxwell has prismatic shaped ECs (PowerCache Ultracapacitors, 2.3 V) with capacitance values between 8 and 2700 F. Recently Siemens Matsushita (now EPCOS) started to offer identical products. Those capacitors have  $RC$ -times in the range 0.6–3 s. The manufacturing capabilities of those types of ECs are presently strongly increased.

A selection of ECs is shown in Fig. 13. They are all based on carbon electrodes. Various other companies are developing ECs and may soon appear on the market. At present, the ECs take up <1% of the world market for electric energy storage (batteries, capacitors) [39]. They show nicely growing market numbers. The improving performance, the drop of prices, and new applications lead to the prediction of an exciting future for ECs.

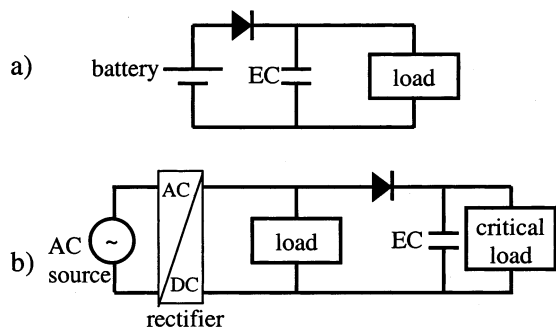


Fig. 14. Use of ECs in electronic circuits. (a) shows a battery powered device where the EC provides power backup of the load in case of disconnection of the battery. (b) shows an AC-voltage powered device involving heavy switching currents. The EC protects the critical load (e.g. memory) from large voltage drops.

## 6.2. Present applications

The largest part of the ECs sold nowadays is used in consumer electronic products, where they mainly serve as backup sources for memories, microcomputers, system boards, and clocks. In these applications there is a primary power source which normally supplies the load. The basic setup is shown in Fig. 14. In case of power outages due to disconnection or turn-off of the primary source, contact problems due to vibration or shocks, or a drop of the system voltage due to switching-in of other heavy loads, the EC can supply the critical consumers. The EC should be mounted as close to the critical load as possible. Some typical applications are [40,41]:

- Video recorders, TV satellite receivers: backup of TV-channel setting, recording times, and clock time. The backup is provided for a duration of h to weeks.
- Car audio system, taxi meter: backup of radio station memory, taxi fare programs and accumulated fare data while the car-radio or the taxi meter is taken out of the car or the car battery is disconnected. Backup for a few h to a few days.
- Alarm clock radios, process controllers, home bakery, coffee machines: protects clocks and programmed functions from getting lost in case of temporary power outage. Backup for min to h.
- Photo and video cameras, programmable pocket calculators, electronic agendas and organizers, mobile phones, and pagers. The backup is provided during the replacement of the batteries for s to min.

In many of those applications, the cost of an EC is lower or comparable to the costs of a rechargeable battery. The most important benefits of ECs are the longer lifetime, the larger cycling capability, the possibility of fast recharging, and the environmental compatibility.

In another series of applications the EC is used as the main power source. The EC delivers one or several large current pulses of several ms to several s duration. Afterwards the EC is recharged by a power supply of low power rating. Typical applications are:

- Toys: for example cars with ‘rechargeable motors’ [42] contain an EC which can be recharged from a battery- or mains-powered charger. The charging takes about 10 s and power is supplied to the car for several 10 s. Due to compactness and low weight the cars can accelerate very fast.
- Fail-safe positioning: the EC provides the power for open or close positioning in case of power failures. In the past, mostly spring systems have been used. The use of electric actuators with ECs allows to make smaller, cheaper and faster systems.
- Starter applications: the EC provides the main part of the pulse power for starting of, e.g. Diesel locomotives [43]. It is charged within <1 min from lead-acid batteries. It allows to start the Diesel engine at very low temperature (Siberia). The size of the battery system may be reduced by up to 50%. Since the pulse currents drawn from the batteries are much smaller, the life of the batteries doubles.

In a third type of applications the ECs are used as alternating power sources, e.g. on a day-night basis. During the day the electric load is supplied by, e.g. solar cells, which also recharge the EC. During the night the power is delivered by the EC. Typical applications are:

- Solar watch: After being completely charged the EC may feed the watch for several days. The watch does not need any battery replacement during its lifetime.
- Solar lanterns, road marking lanterns, lighting of time-tables at bus stop, illumination of parking meters, traffic warning signals: the combination of solar panels, LEDs instead of incandescent bulbs and ECs makes a reliable system with a long lifetime and no needs for maintenance.

The possibility for a huge number of charge-discharge cycles, the long lifetime, the large temperature range, the high cycling efficiency and the low self-discharge makes ECs very suitable for this type of applications.

## 6.3. Upcoming applications

The recent market introduction of low cost ECs with large capacitance and the capability of using them at high voltage allows a large number of new applications. Under the most considered ones are electric vehicles (EV), hybrid electric vehicles (HEV) [44], and fuel cell vehicles. In all three cases the EC will serve as a short-time energy storage device with high power capability and allow to store the energy obtained from regenerative braking. This energy will be reused in the

next acceleration phase and boost the acceleration. It allows to reduce the size of the primary power source (batteries (EV), internal combustion engine (HEV), fuel cell) and keep them running at an optimized operation point. Buses, delivery vans and cars in city areas where many go-stop intervals exist are most beneficial. For example, for an 18t-bus the minimum energy content of the EC should be about 2 MJ. Energy savings of 20–30% can easily be obtained on an intra-urban line, what corresponds to many thousand litres of fuel per year. With nowadays ECs such a capacitor bank can be realized with a mass of about 300 kg. Most vehicles with electric drives use an operating voltage in the range 300–500 V. A possible setup of a drive system is shown in Fig. 15. Since the voltage of the EC decreases during discharge, it has to be adapted to the DC-link voltage by means of a DC-DC converter. Discharge to half of the nominal voltage allows the use of 75% of the EC's total energy content. If the capacitor is further discharged at high power most of the energy gets lost in the internal resistance. The characteristic time for the acceleration/braking phases is 10–30 s. With a RC-time constant of the EC of about 1 s or less and including the efficiency of the DC-DC converter, a round-trip efficiency of 90% can be obtained.

The automotive market and transportation business offers additional opportunities for ECs. A combination of a battery and an EC can provide a more powerful and reliable system for engine starting, may deliver high current for fast preheating of catalysts, may assist the electric power steering, and provide local power for actuators and distributed power systems. Aircraft and ships have similar needs as land-based vehicles. For market penetration a system consisting of a battery of reduced size and an EC has to be commercially competitive with the battery-only system.

Transportation vehicles like people movers on fairs, carriers in hospitals, warehouses or factories, airport buses, wheelchairs, and child and amusement minicars can be operated in a similar way to the toy described above. The ECs will rapidly be recharged at the stops where people or goods get on and off board. The braking energy can be reused. The vehicles are not bound to any fixed tracks and free of emissions. Due to their small mass they can accelerate very fast. Permanent operation without change of batteries is possible. A disadvantage is the limited range.

A major part of the operation costs of electric railway systems is due to the electricity costs. Very often, the braking energy is only partly recuperated due to various reasons [45]. An energy storage device at the supply substations, along the railway track, or onboard the train may considerably improve the situation. The benefits are load leveling and support of the mains voltage, lower energy costs, reduction of investment costs since less substations are needed, and emergency supply in case of power failures. For a tramway with 780 V supply, the stationary energy storage should contain about 10 kWh and have a power of 1 MW. Flywheel and SMES installations are also considered for this application. The requirements for the energy storage device are: large cycling capability, high efficiency, absolute safety, low investment and operating costs, easy control.

Electric actuators cause the tilting of the coaches of a tilting train. Large peak power is needed in irregular intervals, depending on the actual railway track and curves. Simulations have shown that the average power needed on a winding track is only about 15% of the peak power as shown in Fig. 16 [46]. If ECs are used as energy storage devices they can deliver part of the peak power and the rating of the supply converter can be reduced. In addition, after a turn, when the railway

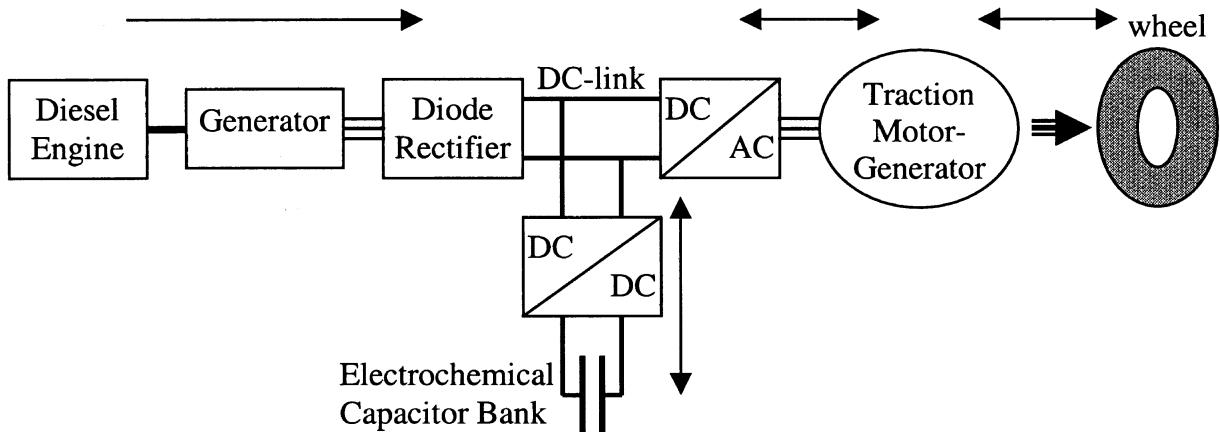


Fig. 15. Schematic of the driveline of a hybrid electric bus using Electrochemical Capacitors as storage device for regenerative braking. The arrows indicate the flow of energy.

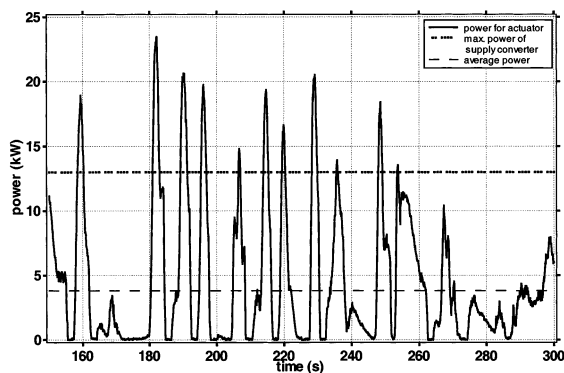


Fig. 16. Power needs of a tilting actuator of a high-speed tilting train. The dotted line indicates the maximum power demand from the supply converter if ECs are used. The recuperated energy is not included in the simulation.

coach is moving back to its center position, the tilting mechanism releases energy, which can be fed back and taken up by the EC. Substantial energy savings are possible. In case of a power failure the energy stored in the ECs allows to move the coach back to its central position. The EC for this application should have a capacitance of about 60 F at 48 V and, due to the high current, a low internal resistance.

Important applications also appear in telecommunications, particularly associated with cellular phones. The miniaturization of the phones is also demanding for a reduction of the size of the batteries. In the global system for mobile communication (GSM) format, current pulses of about 0.5 ms duration are needed every 5 ms. The pulse power is about ten times larger than the average power. A combination of a battery with an EC may substantially improve the power output and increase the life of the battery [47,48]. The EC delivers the largest part of the pulse power. Between the pulses the battery recharges the EC. The nominal voltage of the EC has to correspond to the voltage of Li-ion batteries. The EC must have high cycle-life, small size, low cost, and should have a typical RC-time well below 1 s.

Some industrial processes (e.g. semiconductor, chemical, pharmaceutical, paper, textile industry) are very sensitive to short interruptions and disturbances of the mains voltage and may result in expensive loss of production. Power Quality (for ms to s) [49] and UPS devices ('Uninterruptable Power Supply', for s to min) may protect the sensitive loads. A statistical analysis of power failures shows that most of them have a duration of < 1 s. Nowadays either capacitors or batteries are used for providing the energy. ECs offer a much better ratio of energy to power for those applications and will allow to reduce size and costs of the systems and to make them more reliable. The power needs for the industrial processes mentioned above are in the order of

100 kW to several MW. A 100 kW, 650 V ride-through system, providing power for 5 s has recently been presented [50]. In cases where a Diesel generator is available for backup power, the UPS device has to feed the load for a maximum of 10–20 s until the Diesel engine is running.

Many actuator applications need high power for a duration suitable for ECs. Magnetic medium or high voltage switchgear-systems need current pulses of 50–70 ms for switching [46]. Pace makers, defibrillators and X-ray generators are applications in the medical area. Various military and space applications exist, e.g. actuators for flood-control of submarine systems, launching of aircraft on NAVY aircraft carriers, starting of tanks and trucks in very cold or hot climate, thrust vector control actuators on launch vehicles, bridge power for submarine computer systems, detonators, pulse lasers. Load leveling in combination with wind turbines, photovoltaic generators or wave energy devices may also become important for ECs. Powering of remote weather stations, monitoring systems, buoys, vending machines, emergency lights, etc. in combination with e.g. photovoltaic modules are other future applications. The dynamic response of fuel cells can be improved by using ECs for short-term energy storage. If only little power is needed from a fuel cell (e.g. during the night), the ECs can supply the base load and the auxiliary system (pump, compressor, reformer) of the fuel cell can be shut down. This results in an improved efficiency. For elevators, cranes, etc., ECs can provide emergency power in case of power failures. In addition they can be used for load leveling and recuperate energy when the cage is moving down, enabling energy savings.

As shown above, ECs are in many cases used in combination with batteries in so-called hybrid systems. The battery provides the base load power or recharges the EC at low power rating. In the same way a combination of conventional capacitors and ECs is also possible if energy is needed on a shorter time scale. In this case the capacitor delivers the peak power. We have realized in our lab a hybrid capacitor bank consisting of polymeric film capacitors (3 mF) and ECs (0.8 F). The bank is used for testing of high-temperature superconducting material. The bank voltage is 1200 V. The film capacitor delivers a peak current of 6 kA for several 100 ms, which is quenching the superconductor. A steady current of about 2 kA is delivered by the ECs for about 100 ms, allowing to study the thermal behavior of the superconductor. A discharge of the bank on a 160 mΩ load is shown in Fig. 17. If the steady current is interrupted, the film capacitor is recharged from the ECs and is then able to supply another current pulse.

Many more applications can be imagined, but we emphasize that an EC is not 'the' universal energy storage device. Its strength is in the area shown on the

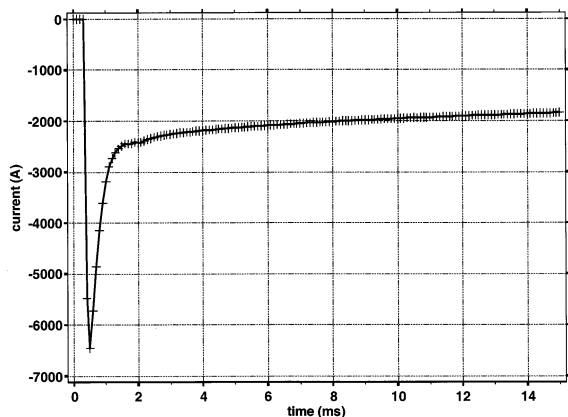


Fig. 17. Discharge current of 1200 V hybrid-capacitor bank consisting of a combination of 0.7 F Electrochemical capacitors and 3 mF polymeric film capacitors.

Ragone plot of Fig. 1, corresponding to a ratio of energy (in J) to power of about 1. For much larger and much smaller ratios, conventional capacitors and batteries, respectively, are more adequate, unless other criteria like cycling performance or environmental requirements become important.

## 7. The challenge for electrochemical capacitors

For most of the applications described above, solutions with conventional devices, i.e. either batteries or capacitors exist. Those devices are available on the market for >100 years, have technically been optimized, and use elaborated manufacturing methods. Although the energy to power ratio of ECs is often more adequate, batteries or capacitors are chosen for commercial reasons. Therefore ECs have to be cost competitive. For electronic applications, it has been shown that it is possible to produce ECs at high volume, low cost, and having high reliability. We are convinced that this will be soon also the case for ECs with large capacitance.

Another challenge is the high voltage demanded for many applications. Due to the restriction of single cells to a low voltage, several dozens or even many hundreds of cells have to be connected in series. Capacitance as well as leakage resistance of the individual cells have to be very uniform during the whole life of the EC. Otherwise, in a series connected string some cells may see an overvoltage and get damaged. One single damaged cell may deteriorate the performance of the whole capacitor system. Precautions are therefore necessary to guarantee the balancing of cell-voltages. The balancing system should be very reliable, have low cost, and if ever possible, be integrated into the EC.

In comparison to flywheel, SMES, and battery systems, which also have high specific energy and power, ECs offer distinct advantages. ECs have no rotating parts, are very safe devices, do not require cooling and other auxiliary installations, have a large modularity with respect to voltage and capacitance, low self-discharge, high cycle-life, can be produced at low costs, do not need any servicing, and do not contain any environmentally dangerous materials or heavy metals.

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