

# Electrochemical supercapacitors: Energy storage beyond batteries

A. K. Shukla\*, S. Sampath and K. Vijayamohan

*Recently, a new class of reversible electrochemical energy storage systems have been developed that use: (a) the capacitance associated with charging and discharging of the electrical double-layer at the electrode–electrolyte interface and are hence called electrical double-layer capacitors (EDLCs), and (b) the pseudocapacitance with electrosorption or surface redox reactions which are referred as pseudocapacitors. While EDLCs with capacities of many tens of farads per gram of the electrode material have been achieved employing high surface-area carbon powders, fibres, or felts, much higher capacitance values are accomplished with pseudocapacitors employing certain high surface-area oxides or conducting polymers. These electrochemical capacitors are being envisaged for several applications to complement the storage batteries. This article provides a brief introduction to scientific fundamentals and technological applications of electrochemical supercapacitors. It is also stressed that there is a substantial scope for technology development in this newly emerging area, where materials science and polymer technology will have a pivotal role in conjunction with electrochemistry.*

AS the concern grows over fossil fuel usage, in terms of global warming and resource depletion, there will be a progressive swing to renewable energy. This will necessitate the development of improved methods for storing electricity when it is available and retrieving when it is needed. Electrical energy can be stored in two fundamentally different ways: (i) indirectly, in batteries as potentially available chemical energy requiring faradaic oxidation and reduction of the electroactive reagents to release charges that can perform electrical work when they flow between two electrodes having different electrode potentials, and (ii) directly, in an electrostatic way as negative and positive electric charges on the plates of a capacitor by a process termed as non-faradaic electrical energy storage. A storage battery has two different types of active materials entrapped in a suitably conductive matrix as anodes and cathodes to sustain the net cell reactions, while a capacitor comprises a dielectric sandwiched between two identical electrodes.

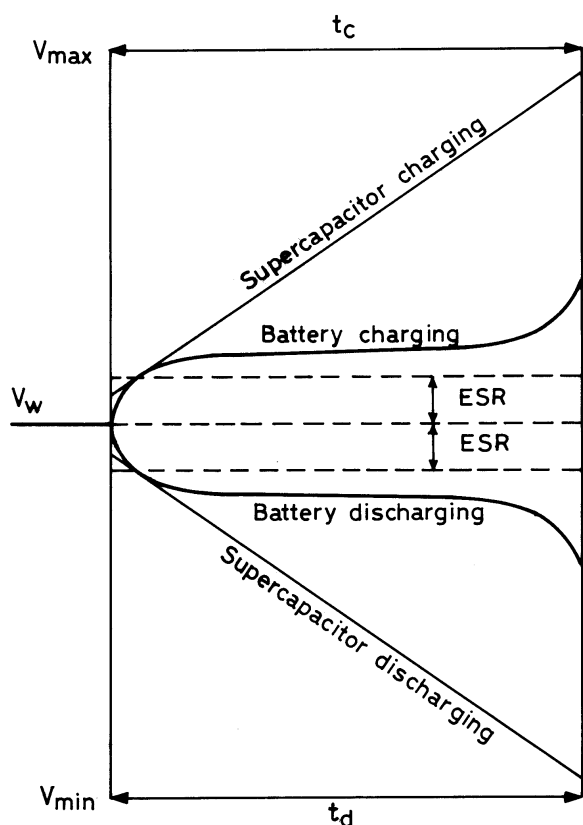
During the storage of electrochemical energy in a battery, chemical inter-conversions of the electrode materials occur usually with concomitant phase changes. Although the overall energy changes can be conducted in a relatively reversible thermodynamic route, the

charge and discharge processes in a storage battery often involve irreversibility in inter-conversions of the chemical electrode-reagents. Accordingly, the cycle-life of storage batteries is usually limited, and varies with the battery type. By contrast, with energy storage by a capacitor, only an excess and a deficiency of electron charges on the capacitor plates have to be established on charge and the reverse on discharge, and no chemical changes are involved. Accordingly, a capacitor has an almost unlimited recyclability, typically between  $10^5$  and  $10^6$  times. But, unlike storage batteries, capacitors can store only a very small amount of charge unless they are large. As a result, capacitors have a substantially low energy-density. However, charged electrode/solution interfaces contain double layers that have capacitances of  $16\text{--}50\ \mu\text{Fcm}^{-2}$ , and with sufficiently large accessible surface-electrode-areas realizable with high surface-area ( $1000\text{--}2000\ \text{m}^2/\text{g}$ ) carbon powders, felts, and aerogels, capacitances as large as  $\sim 100\ \text{F/g}$  can be achieved. In recent years, the practical realization of this possibility has led to the development of a new type of capacitors termed as electrochemical supercapacitors or ultracapacitors. At present, these capacitors are progressing as energy devices to complement the storage batteries<sup>1–12</sup>. A schematic comparison between the charge–discharge profiles of a battery and a supercapacitor is presented in Figure 1.

In this article, we briefly describe the types of supercapacitors and origin of their capacitances, their characteristics *vis-à-vis* a rechargeable battery along with their envisaged applications.

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**Figure 1.** Schematic comparison of the galvanostatic charge-discharge profiles of a supercapacitor and storage battery for similar charge ( $t_c$ ) – discharge ( $t_d$ ) durations.  $V_w$  represents the operating voltage of the supercapacitor akin to the open-circuit voltage of a storage battery,  $V_{max}$  and  $V_{min}$  represent the end-of-charge and end-of-discharge, respectively, and ESR is the equivalent series resistance of the capacitors.

### Supercapacitor types and origin of their capacitance

When a metal (or an electronic conductor) is brought in contact with a solid or liquid ionic-conductor, a charge accumulation is achieved electrostatically on either side of the interface, leading to the development of an electrical double-layer which is essentially a molecular dielectric. No charge transfer takes place across the interface and the current observed during this process is essentially a displacement current due to the rearrangement of charges (conventionally described as an ideally polarized electrode). Therefore, this process is non-faradaic in nature. Besides, the charge storage is also achieved by an electron transfer that produces oxidation state changes in the electrostatic materials according to Faraday's laws in relation to electrode potentials (the so-called ideally reversible electrode). Thus, this process is faradaic in nature. Accordingly, two types of supercapacitors have been developed and tested. One operates, by charging and discharging of the interfacial electrical double-layer. In the second type, often called pseudocapacitors or redox capacitors, the charge-

discharge mechanism involves the transfer of electric charge between the phases but without any bulk phase transformation. The electrons involved in the non-faradaic electrical double-layer charging are the itinerant conduction-band electrons of the metal or carbon electrode, while the electrons involved in the faradaic processes are transferred to or from valence-electron states (orbitals) of the redox cathode or anode reagent. The electrons may, however, arrive in or depart from the conduction-band states of the electronically-conducting support material depending on whether the Fermi level in the electronically-conducting support lies below the highest occupied state (HOMO) of the reductant or above the lowest unoccupied state (LUMO) of the oxidant. In pseudocapacitors, the non-faradaic double-layer charging process is usually accompanied by a faradaic charge-transfer.

Accordingly, the capacitance ( $C$ ) of supercapacitor is given by

$$C = C_{dl} + C_F \quad (1)$$

where  $C_{dl}$  is the electrical double-layer capacitance and  $C_F$  is its pseudocapacitance.

The double-layer capacitance ( $C_{dl}$ ) is expressed as

$$C_{dl} = \epsilon A / 4\pi t, \quad (2)$$

where  $\epsilon$  is the dielectric constant of the electrical double-layer region,  $A$  is the surface area of the electrode, and  $t$  is the electrical double-layer thickness. It is obvious from eq. (2) that for a larger  $C_{dl}$ , it would be mandatory to produce a thin, high surface-area electrical double-layer and it is this combination of high surface area (e.g. 2000 m<sup>2</sup>/g) with extremely small charge separation ( $t \sim 10 \text{ \AA}$ ) which is responsible for the origin of high value of double layer capacitance. In contrast, the best type of ceramic multilayer capacitors use a combination of high  $\epsilon$  (6500 to 10000) and low  $t$  (few microns), but have lower capacitance values.

The pseudocapacitance ( $C_F$ ) is brought about by a surface redox-reaction of the type



where  $O_{ad}$  and  $R_{ad}$  are the adsorbed oxidants and reductants, and  $n$  refers to the number of electrons ( $e$ ). The special aspects of pseudocapacitance arising due to the process of adsorption-desorption phenomenon of  $O_{ad}/R_{ad}$  on the electrode process could be understood by considering a simple model of potential variation due to coverage. According to Frumkin, for an electrical double-layer, the charge on the metal surface ( $q_m$ ) can be expressed as

$$q_m = q_0(1 - q) + q_1 q, \quad (4)$$

where  $q_1$  is the charge associated with the coverage ( $q$ ) of the adsorbed species, and  $q_0$  is the charge associated with the bare surface ( $1-q$ ).

Accordingly, the capacitance ( $C$ ) of the supercapacitor can be expressed as

$$C = dq_m/dV = (1-q)dq_0/dV - q_0dq/dV + qdq_1/dV + q_1dq/dV, \quad (5)$$

where  $V$  refers to the voltage developed across the supercapacitor.

Or,

$$C = C_1(1-q) + C_2q + (q_1 - q_0)dq/dV, \quad (6)$$

where  $C_1 = dq_0/dV$  and  $C_2 = dq_1/dV$ .

According to Frumkin's isotherm:

$$\{q/(1-q)\}e^{-2gq} = KC_i, \quad (7)$$

where  $g$  is the interaction parameter,  $K$  is a constant that depends on the field  $V$  and  $C_i$  is the concentration.

On taking logarithm, eq. (7) can be written as

$$\ln q - \ln(1-q) - 2gq = \ln K + \ln C_i. \quad (8)$$

Differentiating eq. (8) we get,

$$\{(1/q) + (1/1-q) - 2g\}(dq/dV) = d\ln K/dV = (q_1 - q_0)/RT\Gamma_m, \quad (9)$$

where  $\Gamma_m$  is the maximum amount of adsorbed species.

Substituting for  $dq/dV$  in eq. (6) we get,

$$C = C_1(1-q) + C_2q + \{(q_1 - q_0)^2/RT\Gamma_m\} \times \{q(1-q)/1-2gq(1-q)\}, \quad (10)$$

which is also referred as Temkin's isotherm.

The first two terms in eq. (10) correspond to  $C_{dl}$ , while the last term corresponds to  $C_F$ .

When adsorbate-adsorbate repulsive interaction is negligibly small,  $g = 0$  and  $C_F$  takes the following form.

$$C_F = \{(q_1 - q_0)^2/RT\Gamma_m\} \cdot \{q(1-q)\}, \quad (11)$$

which is referred as Langmuir's isotherm.

A plot of coverage ( $q$ ) vs potential (Figure 2) shows that the potential region where the capacity is found to be high, is narrow when there is no repulsive interaction, i.e.  $g = 0$ . However, if repulsive interaction between the adsorbed species prevails, i.e.  $g > 0$ , the adsorption pseudocapacitance will be constant over a large potential-region. Strong repulsive interactions could extend the voltage region by as much as one volt exhibiting constant  $C_F$ .

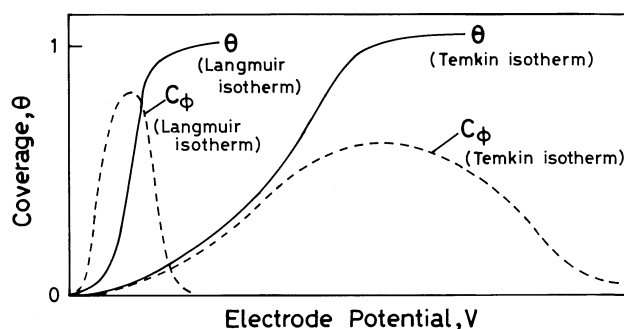


Figure 2. Variation of coverage ( $q$ ) and pseudocapacitance ( $C_F$ ) with electrode potential in accordance to Langmuir and Temkin isotherms.

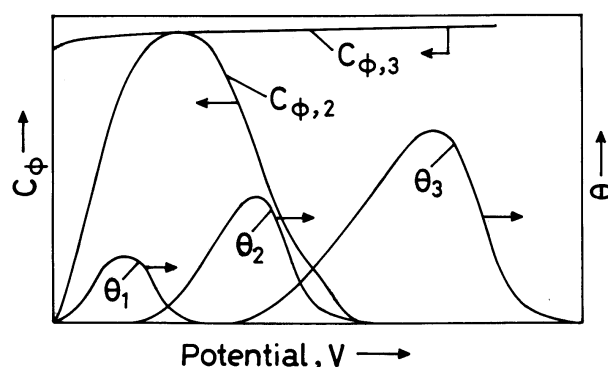


Figure 3. Variation of pseudocapacitance and coverage with potential when more than one adsorbate is involved in the electrode reaction.  $C_{F,2}$  indicates the pseudocapacitance variation with only two intermediates ( $q_1$  and  $q_2$ ), while  $C_{F,3}$  indicates the variation of pseudocapacitance with potential for three intermediates ( $q_1$ ,  $q_2$  and  $q_3$ ).

Based on the above considerations, it is apparent that the capacity of a supercapacitor will be large if two or more adsorbed intermediates of varying coverages ( $q$ ) participate in reaction (3). Two or more intermediates will ensure not only a larger capacitance, but also a large potential range with constant capacitance. This is schematically shown in Figure 3, where  $C_F$  is plotted against applied potential. This clearly reveals that the potential region with a high capacitance is large for a reaction in which three intermediates participate, compared to a reaction with two intermediates in the reaction scheme. This is true especially when the reversible potentials for each of these couples are widely separated and the saturation charge of the second is greater than the first. If the charge associated with the saturation coverage of the two species is the same, then only a single capacitance peak would be observed, no matter how widely the reversible potentials of these species are separated. In general,  $C_F$  (typically,  $q_F = 220 \mu\text{Ccm}^{-2}$ )

$C_{dl}$  (typically,  $q_{dl} = 20 \mu\text{Ccm}^{-2}$ );  $q_F$  and  $q_{dl}$  are respective charges associated with the pseudocapacitance

and the electrical double-layer. It is estimated that the energy ( $E = \frac{1}{2}CV^2$ ) stored in a one-Volt electrical double-layer capacitor with porous carbon electrodes having a surface area of  $1000 \text{ m}^2/\text{g}$  is  $\sim 28 \text{ Wh/kg}$ . For comparison, a one-Volt supercapacitor with a pseudocapacitance ( $q = 0.2$ ,  $n = 1$  and  $g = 0$ ) held between carbon electrodes of a similar surface area could store as large as  $\sim 1876 \text{ Wh/kg}$  of energy. In practice, however, it has not been possible to achieve these energy densities with any of the supercapacitors developed so far. But, this suggests a definite scope for technology development in supercapacitors.

### Materials for supercapacitors

The critical components of supercapacitors include the electrodes, electrolyte and the separator. The characteristics of electrode materials for supercapacitors include high cyclability, long-term stability, high surface areas, and resistance to electrochemical oxidation/reduction. The focus seems to be, however, on achieving high surface areas with low 'matrix' resistivity. Carbonaceous materials have been particularly popular owing to their large surface areas. High temperature heat-treatment of active carbon precursors such as coconut shells, wood powders, coal tar, resins and resorcinol-formaldehyde and related polymers yield active electrode materials with surfaces ranging between  $1000$  and  $1500 \text{ m}^2/\text{g}$ , that result in capacities as high as  $500 \text{ F/g}$  in alkaline electrolytes. Another class of materials includes modified carbon and carbon-composites such as activated carbon-polyacene, platinized activated carbon, polyoxometalate modified carbon and carbon-inert particulate-material which have led to capacitance values between  $150$  and  $200 \text{ F/cm}^2$ . Besides, conducting metal oxides such as  $\text{RuO}_2$  and  $\text{IrO}_2$  yield capacities of the order of  $150\text{--}250 \text{ }\mu\text{F/cm}^2$ , which happen to be several times larger than the carbon-based capacitors. These values arise from pseudocapacitance believed to occur between the surface ruthenium ions and protons. Indeed, substantially high specific capacitance values near  $768 \text{ F/g}$  have been achieved when a sol-gel derived amorphous  $\text{RuO}_x \cdot x\text{H}_2\text{O}$  is used as the electrode material. Activated glassy carbon and high surface area gold are planar or extended area electrode materials that provide both high and short pulse charges. The absence of porous character associated with the electrode structure and/or the absence of any faradaic process is required for short-pulse capacitors with their overall capacitance arising from electrical double-layer. Conducting polymers are complementary materials to carbon and metal oxides. A wider voltage window is achieved with derivatized polythiophenes in non-aqueous solutions. However, long-term stability is still a problem. Recently, nitrides of molybdenum, titanium and iron, carbon nanotubes

and mesoporous carbonaceous materials have been proposed as potential electrode materials for supercapacitors.

The voltage window of a supercapacitor is dictated by the operating pH and the thermodynamic stability of various species in the electrolyte. Aqueous solutions have an inherent disadvantage of a 'restricted' voltage-window resulting from redox reactions involving water on the surface of electrodes. Carbon-based electrode materials, however, give high capacitances in acidic and alkaline solutions. A cursory review of the literature reveals that a wide variety of non-aqueous solvents have been examined. Various combinations of propylene carbonate, dimethoxy ethanol, diethyl carbonate, 1,3-dioxolane, tetrahydrofuran, acetonitrile, succinonitrile and glutaronitrile have been reported to yield energy densities of the order of  $10 \text{ Wh/kg}$  when used with carbon electrodes. The electrolytes used are  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$  and quarternary phosphonium salts. The choice of electrolytes demands the requirement for hermetic seals. This has led to the use of solid polymer electrolytes which are usually ionomers. Donor polyether solvents such as polyethylene oxide (PEO), where anions are usually not coordinated to the solvent molecules unless through hydrogen bonding to hydroxyl end groups, are quite frequently used along with a plasticizer. The commonly used anions in preparing polymer-salt complexes follow the trend,  $\text{SCN}^- > \Gamma^- > \text{ClO}_4^- > \text{CF}_3\text{SO}_3^-$  for the binding capacity in aprotic solvents. Polyacrylonitrile (PAN)-based gel electrolytes have been proposed as an alternative to PEO-based systems, that lead to high conductivity and good mechanical properties such as ease of fabrication, high flexibility and low density. Composites of PEO with PAN and polymethylmethacrylate (PMMA) have also been attempted and specific capacitances of the order of  $0.6 \text{ F/cm}^2$  have been obtained. These capacitors have energy density of  $0.85 \text{ Wh/kg}$  and a power density of  $300 \text{ W/kg}$ .

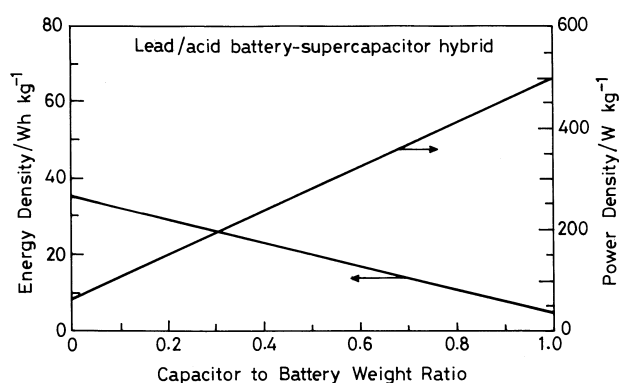
### Technology development

In recent years, phenomenal progress has been made in the development of supercapacitors. For example, different types of ceramic and polymeric materials for electrodes and electrolytes have been developed to make both types of supercapacitors. Conducting polymer-based supercapacitors using proton and lithium ion-conducting solid electrolytes have received considerable attention recently and several supercapacitor modules have been fabricated using polythiophene, polypyrrole, polyaniline and their related composites to achieve energy storage of about  $200 \text{ F/g}$ . Generally the voltage of a supercapacitor is dictated by the available potential window prior to the commencement of any irreversible

anodic and cathodic faradaic processes. The range with aqueous systems is about 1.23 V, but can be extended by a judicious choice of the supporting electrolyte and/or a solvent with high anodic and cathodic overpotential for the appropriate irreversible anodic and cathodic faradaic reactions. At present, the development of non-aqueous systems appears to be gaining momentum due to the increased energy density of such systems. Gel electrolytes hold the promise of combining the advantage of solid-polymer electrolytes with the increased voltage of non-aqueous systems. Nevertheless, only the carbon and the  $\text{RuO}_x$  systems have so far been commercialized, while other systems are under various stages of development. Several characteristic features of carbon like high corrosion resistance, acceptable electronic conductivity, high surface area after activation, wide availability in different structural forms and reasonable cost are specially significant for its use in supercapacitors and this coupled with hydrated ruthenium oxide in the form of a composite gives one of the best values for capacitance (700 F/g). Nevertheless, the total charge stored in a porous carbon-based electrode cannot be abstracted at short times and different types of mesoporous carbonaceous materials and carbon nanotubes are under development to alleviate this limitation.

### Technological applications

The applications of supercapacitors are primarily envisaged in the load-levelling function and hybridized with rechargeable batteries such as lead-acid batteries in electric vehicle-drive systems. The latter application arises from the perceived highpower capability of supercapacitors which can, with suitable interfacing, take the main load from the battery component during vehicle acceleration on a gradient. Regenerative-braking systems with supercapacitors are also envisaged for partial recharging and overall energy economy. For example, 20% range enhancement can be accomplished merely by the incorporation of regenerative braking using appropriate supercapacitor packs. Supercapacitors can store  $\sim 10 \text{ Wh/kg}$  of the energy which is about a third of the energy density of the lead-acid batteries. But the supercapacitors have nearly five times the power density of the lead-acid batteries. Under high-power conditions, i.e. at high discharge rates, the supercapacitors actually exhibit higher energy density than the lead-acid batteries. The variation of energy density and power density with weight ratio for a supercapacitor/lead-acid battery hybrid is shown in Figure 4. The data suggest that the supercapacitor power density increases relative to the energy density of the hybrid combination because a greater component of capacitor is present. Besides, supercapacitors have also been



**Figure 4.** Relationship between energy density and power density with supercapacitor weight ratio for a lead-acid battery-supercapacitor hybrid system.



**Figure 5.** A supercapacitor being used to light a 36 watt incandescent tube light. (Courtesy, CSIRO, Australia.)

proposed for bridge power and pulse power applications like memory protection, automotive subsystems, military systems, etc. For example, Figure 5 shows a supercapacitor being used to power a 36 watt fluorescent-light tube. Similarly, they can be extremely valuable for energy-rich (high flux), power-poor (low-voltage) applications like charging using photovoltaic panels.

Supercapacitors may have to function over a wide range of temperatures and in certain environments, such as in enclosed compartments of electric vehicles or in military applications, as also for cold cranking in northern climate or under hot-ambient conditions in tropical locations. Under high-power operating conditions, internal heat production will lead to excessive heating of the device. Thus, the factors that determine the temperature dependence of the supercapacitor performance could be of vital significance in the operation of supercapacitors for various applications, for example, with regard to power availability and cycle-life. The effect of

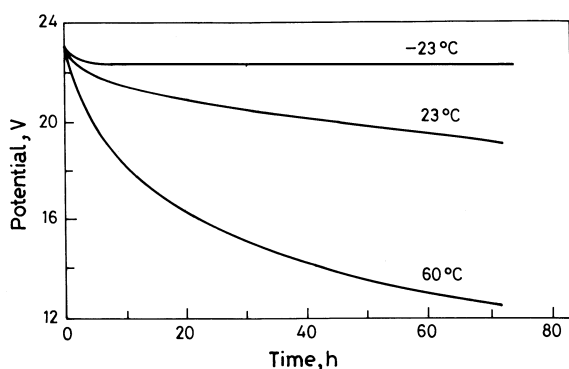


Figure 6. Self-discharge of a supercapacitor at various temperatures.

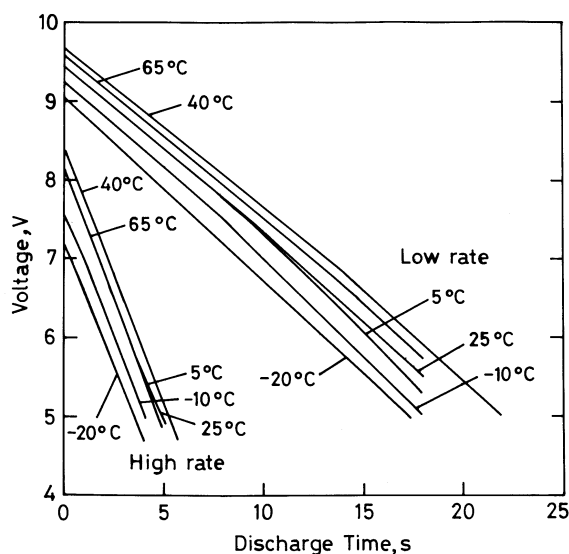


Figure 7. Discharge pattern for a commercial 10 V, 1500 F Panasonic supercapacitor at high (300 A) and low (100 A) discharge at varying temperatures.

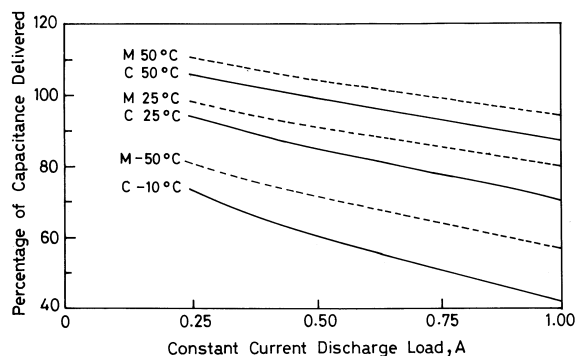


Figure 8. Comparison of constant-current discharge of two commercial 5 V supercapacitors as a function of temperature. M, Max-cap, and C, Capattery.

temperature on the performance of supercapacitors is shown in Figures 6–8. The self-discharge data as presented in Figure 6 plays an important role for a given application, as the leakage current has to be initially estimated as a function of the temperature.

## Conclusions

Electrochemical capacitors are devices capable of higher charge storage several hundred times more than conventional capacitors. They are different from batteries and for certain types of application have several advantages. The state-of-charge is a simple function of voltage and this coupled with high power density and good cycle-life enable them to be useful in applications ranging from light-weight electronic fuses, memory back-up power sources, surge protection devices to pulse power sources for smart weapons. Such devices are also likely to help the global transition to more energy-efficient technologies.

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Received 10 August 2000; revised accepted 9 October 2000