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Journal of Power Sources 154 (2006) 556-560

www.elsevier.com/locate/jpowsour

JOURNAL OF

Short communication

# Temperature and dynamics problems of ultracapacitors in stationary and mobile applications

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#### Abstract

Ultracapacitors as a powerful energy storage systems are used in various areas of power electronics. Depending on the application, temperature and dynamics properties of these components have to be considered. These properties strongly depend on the characteristics of basic materials of the capacitors.

The frequency and temperature dependence of the capacitance as well as of the internal resistance, ESR, is manly affected by the electrodes of activated carbon and the electrolyte. Under operating conditions differences of 15% and more of the capacitance due to a different structure of the electrodes are observed. Due to the reduced solubility of the conducting salt and the increased viscosity of the solvents for temperatures below freezing point the conductivity of the electrolyte drops drastically with decreasing temperatures. Thus, increases of the ESR between 200 and 700% between room temperature and -30 °C depending on the electrolyte are registered. Due to the slightly different selfdischarge of the single capacitors equivalent to a voltage drop of 4-12% within 3 days, the individual cell inside a module has to be protected by a cell voltage balancing unit. By an active cell voltage balancing unit connected in parallel to the capacitors a voltage drop will be leveled out after 1 h.

In addition to the electrical characteristics of the ultracaps also the thermal properties of the single cell as well as of the modules have to be considered for the design in of these storage devices. By cooling elements integrated in the surface of the module casing and forced cooling the effective current load can be nearly doubled. Based on this know how ultracap modules were designed, which fulfill all the requirements of the applications in automotive and industrial electronics.

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Keywords: Ultracapacitors; Ultracap modules; Temperature characteristics; Frequency characteristics; Selfdischarge; Cell voltage balancing

# 1. Introduction

A maintenance free reliable energy back up under various environmental conditions especially at temperatures down to -30 °C, as, for example, the start of the diesel of an emergency power supply is one of the key requirements for ultracaps. Power in and output with high charge and discharge currents is an important requirement for the use of ultracps in mild hybrid vehicles for boosting and recuperation of the breaking energy. Even though the efficiency of ultracaps for a charge and discharge cycle is well above 90%, the selfheating of the components cannot be neglected and in applications with a high frequency of the charge and discharge cycles a proper cooling for the ultracaps has to be provided. Thus, the knowledge of the dynamic and temperature properties of the single capacitors as well as of the

0378-7753/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jpowsour.2005.10.084 ultracap modules is of high importance for the design of suitable components.

#### 2. Performance of single cells

The impact of the different basic materials on the electrical performance of the ultracaps was analyzed with a set of 200 F capacitors impregnated with three electrolytes of increasing conductivity by impedance spectroscopy. Fig. 1 shows the real part of the impedance Z' of the ultracaps. Evidently Z' of the capacitors impregnated with the high conductive electrolyte is much lower at all frequencies than for the capacitors with less conductive electrolytes. The conductivity of the electrolyte determines in interaction with the porosity the ionic resistance of the separator, which is soaked with the electrolyte. An electrolyte with a low conductivity will increase the ionic resistance of the separator. Since the ionic resistance of the separator contributes to Z' also at high frequencies (>10 Hz) the test cells with the varied electrolytes have different Z' values already in the high frequency

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Fig. 1. Real part of the impedance of 200 F ultracaps with various electrolytes.

region (>10 Hz). With decreasing frequencies the resistance of the electrolyte in the pores of the electrode becomes the determining factor because at lower frequencies more and finer pores of the electrode contribute to Z'.

The capacitance was calculated from the impedance according to  $C = 1/(2\pi f |Z''|)$ , with Z'' a synonym for the imaginary part of the impedance. The plot of the capacitance in dependence of the frequency shown in Fig. 2 reveals that ultracaps with high conductive electrolytes retain their capacitive behavior up to higher frequencies than those with electrolyte of lower conductivity. At 100 mHz the cells with the high conductive electrolyte have already reached 94% of their maximum capacitance whereas the devices with the other electrolytes show only 58 or 46% of their maximum capacitance. In addition the pore structure of the electrodes also has an impact on the frequency–response curve of the capacitance. For example, for electrodes of activated carbon cloth a 15% lower capacitance at 100 mHz in comparison to electrodes of activated carbon powder was achieved by using the same electrolyte.

As the conductivity of the electrolytes decreases at falling temperatures due to an increase of the viscosity of the solvent and a decrease of the solubility of the conducting salt dramatic changes of the capacitance and ESR occur in particular at temperatures below freezing point (Figs. 3 and 4). All values were



Fig. 2. Capacitance as a function of the frequency of 200 F ultracaps with various electrolytes.



Fig. 3. Capacitance as a function of T.

measured with impedance spectroscopy at 10 mHz. The plot Z' in Fig. 4 reveals that the ESR at 10 mHz increases significantly at low temperatures for ultracaps with electrolytes of low conductivity. For the acetonitrile based electrolyte of high conductivity the ESR at 10 mHz stays more or less constant independent from the test temperature. When the resistance of the capacitor increases, the fraction of the electrical energy which is converted into heat during charge and discharge increases. Furthermore, the increase of the resistance at low temperatures causes the reduction of the capacitance as can be seen in Fig. 3. At temperatures above room temperature a second effect becomes important. The averaged distance of the Helmholtz layer to the electrode surface is increased caused by the increased Brownian motion of the ions at higher temperatures. Since the capacitance is inversely proportional to the distance between the Helmholtz layer and the electrode surface the capacitance of all tested is reduced slightly at 70 °C.

Based on these measurements for simulation purposes equivalent circuit diagrams, which include the dependence of the capacitance and ESR from the frequency as well as from the temperature were developed, which can be provided for each individual capacitor.

A reduction of the distance between the charge carrier in the double layer by electrostatic forces is an explanation for the



Fig. 4. ESR as a function of T.



Fig. 5. Voltage dependence of capacity at 50 mHz.



Fig. 6. Selfdischarge of an 1800 F capacitor at 25 and 70 °C.

observed increase of the capacitance with increasing voltages at a fixed frequency (50 mHz) and fixed temperature ( $25 \,^{\circ}$ C) as shown in Fig. 5. Due to temperature enhanced reactions at the boundary between the solid electrode and the electrolyte the ultracaps possess a temperature sensitive selfdischarge. The characteristic devolution of the selfdischarge measured for an 1800 F capacitor at 25 and 70 °C (Fig. 6) is representative for all ultracaps. After 10 days at 25 °C the voltage drops by 6% thus still nearly 90% of the initially stored energy is available. Due to the considerably stronger voltage drop of about 30% at 70 °C the capacitor looses 50% of the stored energy within the same period. As in modules, where several ultracaps are connected in series, due to the losses during rapid charge and discharge cycles the selfheating of each individual capacitor will be different and thus their terminal voltage will vary accordingly.

### 3. Characteristics of ultracap modules

Due to deviations of the capacitance of each cell from the mean value and by different selfdischarge performances during the charging process the whole module as well as each individual cell might be overcharged, cells and modules therefore should be protected against excessive voltages. This can be done by an



Fig. 7. Active cell balancing 150 F module.

active cell voltage balancing unit, an electronic circuit which is connected in parallel to each cell. These electronics will act like a switch. At voltages above 2.35 V a low ohmic bypass will be opened. Thus, via this bypass each cell is discharged to its nominal voltage. To verify the functionality of this protection system a module (67 F/42 V) was charged up to 45 V and preconditioned at this voltage for 15 min. Then the current of the power supply was reduced to 0.5 A, a value lower than the current which will flow through the electronic bypass. The voltage drop of the module and each cell were registered (Fig. 7). Even though the cells were charged up to voltages between 2.41 and 2.54 V after nearly 1 h all cell were balanced to an equilibrium voltage of 2.35 V which corresponds to the total voltage of the module of 42.3 V.

Besides low ESR values of the individual capacitors low ohmic contacts between the single cells of the module are necessary to limit the selfheating. For example, at 2700 F capacitors the contact resistance between the bus bars and the capacitor terminals could be reduced from 3.0 to  $3.7 \text{ m}\Omega$  for screwed terminals to  $1.0-1.8 \text{ m}\Omega$  for fully welded joints.

However, in case of rapid charging and discharging due to the electrical losses heat is generated inside the capacitors which must be dissipated to the ambient. In general the heat can be emitted from the core of the capacitor by heat conductance to the surface of the casing and then by radiation and convection to the ambient.

In ultracaps were designed, whose active part of the capacitor, where the heat is generated, is a jelly roll, which is shut between the lid and the bottom of the casing and is more or less thermally insulated from the wall by an air gap. Thus, most of the heat will dissipate from the core in the axial direction of the jelly roll via conductance before it is emitted over the surface of the casing to the ambient. By attaching cooling elements to the bottom of the casing the thermal resistance between the capacitor and the ambient can be reduced significantly. But by attaching cooling elements to the ultracapacitors it has to be considered that a high voltage could be applied to the lid as well as to the bottom of the case. Thus, a proper way of attaching the cooling elements with high electrical insulating and high thermal conductivity is requested. Tests with a plastic molding of high thermal conductivity and high electrical insulation at 2700 F capacitors were performed. For a thickness of the mold-

| Tal | ble | 1 |
|-----|-----|---|
|     |     |   |

Table 2

Load increase by forced cooling

Thermal constants of a 150 F/42 V module,  $C_{\text{Th}}$ : thermal capacity of the module,  $R_{\text{ThCM}}$ : thermal resistance between cell casing and module casing,  $R_{\text{ThMA}}$ : thermal resistance between module casing and ambient

| Cooling element | $C_{\rm Th}  ({\rm kJ}  {\rm K}^{-1}  {\rm kg}^{-1})$ | $R_{\rm ThCM}$ (K W <sup>-1</sup> ) | $R_{\text{ThMA}}$ (K W <sup>-1</sup> ) |
|-----------------|---|-------------------------------------|--|
| Without         | 0.94  | 0.11                                | 0.40                                   |
| With            | 0.88  | 0.046                               | 0.39                                   |

ing of 1.5 mm an insulation of more than 1500 V and a thermal resistance of just  $0.11 \text{ K W}^{-1}$  were achieved.

Based on these experiences modules with cooling elements in the bottom of the module casing were designed. In these modules the lid and the case of the individual capacitor are thermally connected by the plastic molding to the cooling element of the module casing.

For a 150 F/42 V module the thermal constants with and without cooling elements were determined (Table 1). Because of the bigger mass of the cooling element the thermal capacity of this module is higher. This generates a larger time constant for the selfheating of this module. The excellent thermal contact between the individual capacitor and the cooling element reduces the inner thermal resistance to less than 50%. As without forced air cooling the cooling element does not contribute to the heat transfer to the ambient no reduction of the thermal resistance is achieved under these premises.

Based on these data the temperature increase dT for an effective current load *I* or the allowable effective current load *I* for a constant temperature increase dT can be calculated by Eq. (1).

$$dT = I^{2} \times \text{ESR} \times (R_{\text{ThCM}} + R_{\text{ThMA}})$$
$$\times \left(1 - \exp\left(\frac{-t\,(\min)}{\tau}\right)\right)$$
(1)

The results are summarized in Table 2. For a temperature increase of 30 K only a 10% higher effective current can be applied to the module with the cooling element. As for this module the external thermal resistance can be drastically lowered to a value of  $0.05 \text{ K W}^{-1}$  by forced air cooling the effective current load can be nearly doubled under these preconditions.

These outstanding characteristics of these ultracap modules are the base for the applications of these components in various equipments of power electronics.

| 4. Examp | les | of | use |
|----------|-----|----|-----|
|----------|-----|----|-----|

In the pitch control of a wind generator they serve as a reliable, maintenance free energy back up for the emergency system under extreme environmental conditions. As they are mounted inside the nacelle close to the blades they are exposed to a heavy mechanical stress. In this application thousands modules, where more than 30 capacitors are connected in series, have proven already their reliability in a 24 h all year operation for more than 3 years.

After successfully passing a 1-year test ultracap modules of 220 F/28 V were approved by the German TÜV as energy storage system for starting large volume diesel engines of emergency generators. Here as well as in trucks, tanks and locomotives by the use of ultracaps the size of the storage system for the electrical energy can be reduced by 50% and its reliability improved. In these applications the excellent low temperature performance of the ultracap modules based on a selection of the proper material is of high value.

Outstanding charge and discharge characteristics are required in many automotive applications. For example, Honda has presented its FCX, a fuel cell vehicle, where an ultracap module is used for the power storage system [1]. Due to the combination of fuel cells with ultracaps this car features a power of 78 kW.

A considerably more powerful ultracap module was installed in a SUV X 5 by BMW. The 4.41V8 combustion engine of this test vehicle with a torque of 350Nm at 1000 rpm is supported by an electric drive train with a powerful ultracap module as the energy storage system which is able to deliver an extra torque of 650Nm [2]. In comparison to the standard production vehicle this test car features a by 30-40% improved acceleration. Despite this remarkable driving performance a 15% reduction of the fuel consumption was achieved in test runs for this vehicle due to the fact that kinetic energy could be stored in the ultracaps during breaking and push phases.

In diesel electric busses during the decelerating electrical energy can be recaptured and stored in an ultracap storage system and be used during the acceleration [3]. Here an energy up to 300 kWh has to be stored during each cycle. Therefore, a much larger storage system was used. Eight modules with 36 single cells are able to store 300 kWh and can deliver an average power of 90 kW for 13 s. This system was tested successfully in a MAN bus in the city of Nuremberg. During the 3-month test a reduction of the fuel consumption of approximately 20% was

|   | Without cooling element | With cooling element | Plus forced cooling (estimated) |  |  |
|---|-------------------------|----------------------|---------------------------------|--|--|
| $R_{\rm Th}$ (K W <sup>-1</sup> )                     | 0.51                    | 0.436                | 0.1                             |  |  |
| $C_{\rm Th}~({\rm kJ~K^{-1}})$                        | 14.1                    | 18.7                 |                                 |  |  |
| $c_{\rm Th}  ({\rm kJ}  {\rm K}^{-1}  {\rm kg}^{-1})$ | 0.94                    | 0.88                 |                                 |  |  |
| ESR $(m\Omega)$                                       | 5.4                     | 5.4                  | 5.4                             |  |  |
| dT(K)   | 30                      | 30                   | 30                              |  |  |
| $P_V(W)$  | 59                      | 69                   | 200                             |  |  |
| I <sub>RMS</sub> (A)                                  | 104                     | 113                  | 192                             |  |  |
|   |                         |                      |                                 |  |  |

achieved. As the bus could be accelerated at a bus stop with the electrical drive train only, the low noise emission in this case was an additional benefit.

#### 5. Summary and outlook

A broad understanding of the impact of the basic materials on the performance of the ultracaps and the development of components with an excellent heat dissipation are the preconditions for designing ultracaps and modules of ultracaps which are well suited for the use in power electronics. Thus, today components are offered which fulfill all fundamental requirements in the applications.

The energy back up for the pitch control in wind generators and the source of electrical energy for the start of heavy diesel engines of emergency generators are two examples, where these components already have proven their fitness for use on a large scale in serial products.

Step by step they will also be used in cars. For example, Toyota is already using an ultracap module for the energy back up of the breaking system of its hybrid vehicle Prius. Intense research in area of the activated carbon for the electrodes and conducting salts of the electrolytes will on one hand create the base for further improvements of the performance of the components and on the other hand will provide the opportunity for further cost reduction.

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