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Measurement Considerations on Some Parameters of Supercapacitors

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Abstract: The paper is focused on identification and measurement of the main parameters of the stacked supercapacitors (SC). The volt-ampere method was used to measure the charge/discharge characteristic, impedance spectroscopy method for measurement of the equivalent serial resistance and analysis of the dynamic parameters. The measured and calculated parameters are: equivalent serial resistance (ESR), capacitance, self discharge resistance, maximum power and energy, energy efficiency.

Keywords: Supercapacitor, self discharge, parameters, impedance spectroscopy.

1. Introduction

Energy storage represents one of the key problems in present day research to increase the energy efficiency of processes. The development of nanotechnology creates premises for the use of new types of devices (Li-ion batteries, supercapacitors, different kinds of fuel cells), which are more adequate for modern energy efficient solutions.

The supercapacitors have a bidirectional power flow exchange efficiency up to 98%, available only for superconductivity applications. There is a lack of knowledge in the characterization of these new devices, like how the device is integrated into a system. Some parameters can be defined to characterize the ability of integration of devices in a system: life span, aging and the finite character of the provided power / energy. The development of nanotechnology led to high performances of symmetrical supercapacitors, such as: equivalent serial resistance (ESR), self discharge resistance, resistance of losses, power and energy density.

In the transportation area supercapacitors proved their important role in combined solutions (supercapacitors, batteries and intelligent controllers) to increase the energy efficiency. Solutions consisting in a simple parallel connection of batteries and supercapacitors proved to be inefficient and new intelligent control systems must be developed to improve the energy efficiency. In the development of a test system for the analysis of the parameters of supercapacitors the benefits of new acquisition systems have to be taken into account which can assure portability, reliability, availability and autonomy. Supercapacitors are able to fill the gap between batteries and classical capacitors (see also Ragone diagram) [2]. A system containing battery and supercapacitor provides not only high energy density but also high power density. They also allow to fulfil a carbon-free desiderate by “eco-footprint” solutions [3].

2. Supercapacitors (SC)

Supercapacitors are rapid release storage devices with capacitance up to thousands of Farad. The main applications of the supercapacitors are related to high power density, large peak power requirements, load smoothing, backup power for mobile applications and different kinds of recovering systems. Supercapacitors can be easily and rapidly charged from various electrical supply sources and also, their voltage - current characteristics and charging / discharging behaviours are not influenced by the over-current, deep discharge and temperature variations (-40^{o}C to +70^{o}C [4]). Supercapacitors are able to support up to millions of lifecycles [5].

In mobile applications the batteries are often under high peak power stresses, which can dramatically reduce their life span. The combination of batteries with supercapacitors can improve dramatically the life span of batteries.

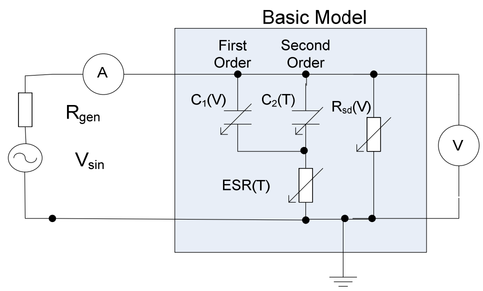

Figure 1: Basic equivalent model of a supercapacitor.

The amount of the stored energy is different, depending on the type of the supercapacitor, the size of the ions, the electrode surface and the level of the electrolyte decomposition voltage [6]. In supercapacitors the charge transfer is performed by electrons and ions: at the collector (metal electrodes) the charge transfer is assured by electrons and in the electrolyte (inside of the supercapacitor) the charge transfer is ionic.

Taking into account the above mentioned considerations we suggested a basic model presented in *Figure 1*, model which was used for definition of parameters in our experiments.

The experiments started with the following assumptions: the equivalent serial resistance (ESR) depends on temperature, voltage and frequency; the resistance of losses (self discharge resistance - R_{sd}) is voltage dependent; the parallel connected equivalent capacitances are voltage and temperature dependent; C_1, C_2 are the equivalent serial capacitances of the double layer supercapacitor. Generally ESR has values of tens to hundreds of mΩ and the resistance of losses has values of tens to hundreds of kΩ.

3. Parameter evaluation for supercapacitors

3.1 Data acquisition system, impedance spectroscopy

A symmetric (stacked) supercapacitor contains multiple cells connected in series and in parallel. As an improper overvoltage is applied, a particular cell could be damaged, therefore, electronic control methods have to be developed. The test setup developed in our laboratory permanently controls the voltage of the supercapacitor and assures the voltage limitation below the preset value.

The data acquisition system, which also fulfils the impedance spectroscopy requirements, is presented in *Figure 2*.

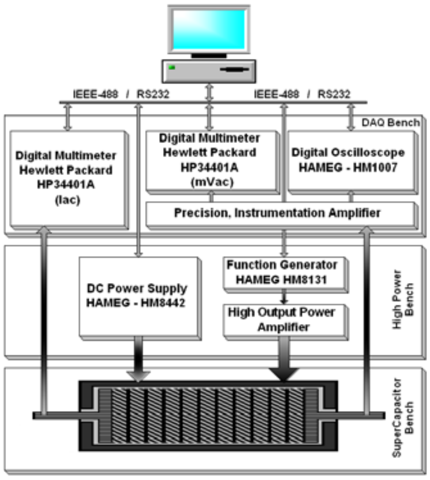

Figure 2: The configuration of the data acquisition system.

The data acquisition system has the following components: DC Power supply driven by an ATMega128 microcontroller-based system, HP 34401A multimeter, digital oscilloscope, function generator, amplifiers. All the acquired data were transmitted to a computer and the stored data were processed with Matlab software.

3.2 Capacitance measurement and its temperature dependence

A volt-ampere method was used to determine the capacitance of two types of aqueous electrolyte stacked supercapacitors of 40F/14V and of 350F/14V, manufactured in Russia by ECOND Ltd.

If the requirements related to the voltage are respected, the performances of the supercapacitors are practically unchanged in a wide range of temperature, as experimental diagrams show in *Figure 3* (supercapacitor of 40F/14V).

The capacitance can be determined using the basic equation:

$$i = \frac{dq}{dt} = C \cdot \frac{du}{dt} \approx C \cdot \frac{\Delta u}{\Delta t}, \tag{1}$$

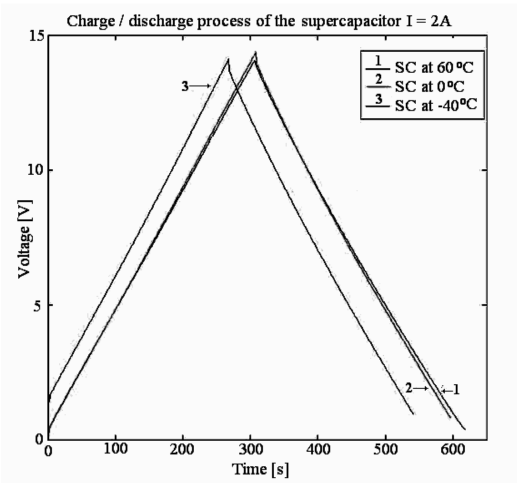

Figure 3: Charge / discharge process at constant current and different temperatures.

which gives the relation:

$$C = I \cdot \frac{t_2 - t_1}{U_2 - U_1}, \tag{2}$$

valid for I = constant. The indices 1 and 2 indicate two arbitrary moments of time (and the corresponding voltage values) either on the charging or on the discharging segment of the supercapacitor.

The capacitance of the 40F /14V supercapacitor (a charge / discharge process at constant slope) is practically not influenced by the temperature (in the range of -40°C to +60°C). The measurements for the charge / discharge process at a constant current of 2A were performed. In the model, ESR and C_2 are the parameters of the supercapacitors which are temperature dependent. Their influence on the equivalent total capacitance is practically negligible [7].

3.3 Determining the ESR parameter

ESR is an important parameter of the supercapacitors and depends on many factors such as the resistance of the electrode materials, the resistance of the electrolyte, the resistance of wires, the voltage and the frequency.

The influence of ESR occurs in the first milliseconds of the self discharge process, following the disconnection of the supercapacitor from the charging system. A plot of the self discharge process of supercapacitors is presented in *Figure 4*.

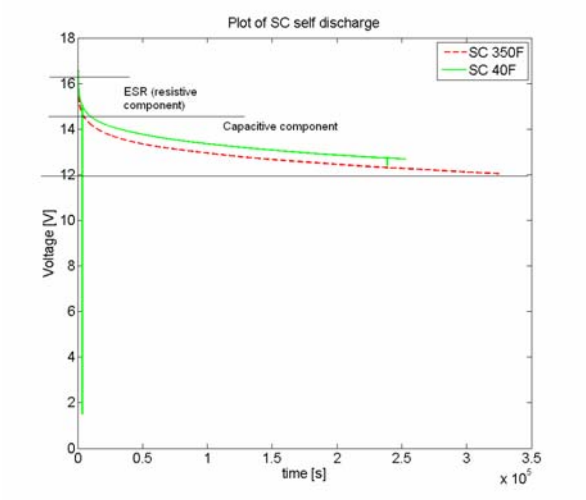

Figure 4: The self discharge process of the 350F and 40F supercapacitors.

Thus, after the ESR influence, the supercapacitor discharges on the internal resistance of losses. In order to observe that, both supercapacitors were charged to 16V with a 2A active load and the self discharge rate was monitored with the data acquisition system described above (the process was monitored during more than four days).

Impedance spectroscopy is one of the most important methods used to determine the equivalent impedance value of a storage device at various frequencies.

In our tests, in order to determine the ESR variation in function of frequency, we used the impedance spectroscopy method. We approximated the equivalent impedance measured by the impedance spectroscopy method with the value of the ESR, as at these very high values of the capacitance (40F and 350F) the capacitive reactance is negligible (at AC sinewave signal of 10Hz to 10 kHz). The test setup for impedance spectroscopy was already presented in *Figure 2*. Manufacturers usually specify the ESR value at a fixed frequency of 1 kHz [9].

Figure 5 presents voltage dependence of ESR of the 40F/14V supercapacitor at different frequency values.

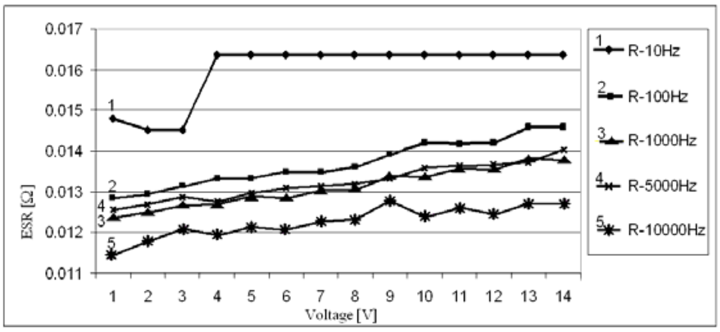

Figure 5: Voltage and frequency dependence of ESR (SC of 40F).

As *Figure 5* shows, the ESR value decreases with the frequency. The values of the recorded data are presented in *Table 1*.

Table 1: ESR at different frequencies for the 40F/14V supercapacitor.

Frequency [Hz]	Average ESR [mΩ]
10Hz	15.99
100Hz	13.69
1kHz	13.24
5kHz	13.23
10kHz	12.26

Table 2: ESR at different frequencies for the 350F/14V supercapacitor.

Frequency [Hz]	Average ESR [mΩ]
10Hz	1.8
100Hz	2.6
1kHz	4.1
5kHz	7.3
10kHz	8.7

In *Figure 6:* The ESR – voltage dependence of the 350F/14V supercapacitor is presented at different frequency values.

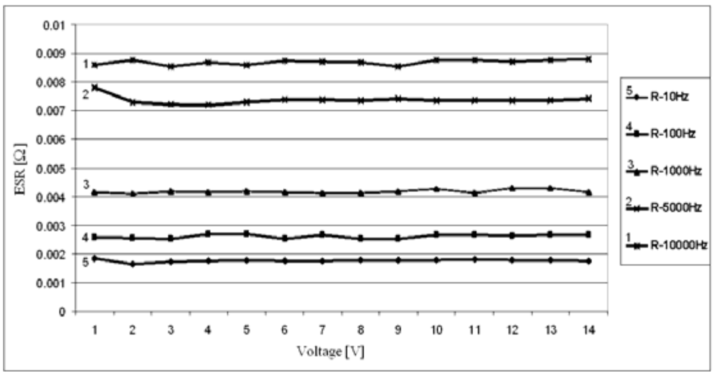

Figure 6: Voltage and frequency dependence of ESR (SC of 350F).

As *Figure 6* shows, the values of the ESR increase with the frequency and the values of the recorded data are presented in *Table 2*.

Depending on the final application, supercapacitors can be designed for high nominal voltage or high capacitance by connecting multiple packages in series and/or in parallel. Therefore internal structure of the supercapacitors is different depending on their voltage and capacitance, so the equivalent impedance can have different behaviours with the frequency (as it can be seen in *Table 1* and *Table 2*), originated in the internal parasitic impedances of SC.

3.4 Resistance of losses (self discharge resistance R_{sd})

The resistance of losses depends on the dielectric resistance and can be determined using the equation:

$$U_{SC}(t) = U_{SC_{\max}} \cdot e^{-\frac{\Delta t}{R_{sd} \cdot C}} \tag{3}$$

For the 350F/14V supercapacitor the average resistance of losses was determined as $7.9 \cdot 10^3\ \Omega$, with the average standard deviation of 0.32%. For the 40F/14V supercapacitor the value obtained was $7.5\ 10^4\ \Omega$, with the average standard deviation of 0.3%.

Figure 7 illustrates the variation of the losses resistance in different time intervals. In order to obtain this variation, five windows of 18,000 samples (3,000 considered, 15,000 ignored) from the self discharge process illustrated in *Figure 4* were considered. The average values of all samples from the five considered windows were calculated and are illustrated in *Figure 7*.

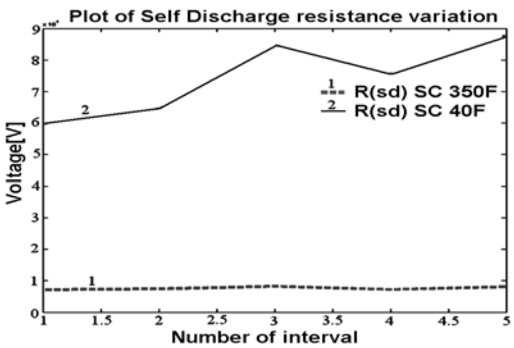

Figure 7: Variation of the self discharge resistance.

As *Figure 7* shows, the resistance of losses varies in time. Thus, in the case of the 350F/14V supercapacitor, for the first considered interval the resistance of losses was $7.1\cdot10^3\ \Omega$ with a standard deviation of 0.39% and for the last considered interval the resistance of losses value was $8.3\cdot10^3\ \Omega$ with a standard deviation of 0.26%. In the case of the 40F/14V supercapacitor the resistance of losses for the first considered interval was $5.9\cdot10^4\ \Omega$ with a standard deviation of 0.42% and for the last considered interval the resistance of losses was $8.8\cdot10^4$ Ω with a standard deviation of 0.24%.

4. Energy efficiency

The power density expresses the maximum amount of energy transferred in a time unit, divided by the weight/volume, as the energy density represents the total energy that can be extracted from a supercapacitor, divided by the weight/volume. In order to improve the energy efficiency, the minimum voltage on SC during the discharging process has to be limited by the extraction factor (*d*), as it follows:

$$d = \frac{U_{\min}}{U_{\max}} \cdot 100\ \% \tag{4}$$

Usually, the value of the extraction factor is *d* = 50%. Thus, the useful energy can be computed using the equation:

$$W_u = W_{SC} - W_{\min} = W_{SC}(1 - (\frac{d}{100})^2) \tag{5}$$

The energy efficiency is determined by:

$$\eta = \frac{W_u}{W_{SC}} \tag{6}$$

Table 3: Energy of the two types of supercapacitors.

	40F/14V	350F/14V
W_{SC} [Ws]	3920	34300
W_u [Ws]	980	8575

The electrical energy stored in the SC is determined as $W_{SC} = \frac{C \cdot U^2}{2}$. The considered extraction factor was 50% and thus it was calculated the useful energy that can be provided by the supercapacitors [10].

As it can be seen in Table 3, both supercapacitors can provide increased energy. More than that, if a supercapacitor is used with a battery, the system can assure the necessary amount of power and energy for many applications with high peak power requirements.

5. Conclusions

In order to determine the behaviour of the parameters of supercapacitors two different measurement methods have been implemented: volt-ampere method with constant-current charge and discharge process and impedance spectroscopy method. The measurements demonstrate a different behaviour of the SC under investigation (40F and 350F, 14V SCs), in relation with the voltage value and the test frequency applied. A different behaviour of the supercapacitors is observed depending on the internal serial and parallel connections of the capacitor cells (packages).

The measurements also demonstrate an insignificant influence of the temperature on the capacitance of SCs, in the temperature range of -40^{o}C to +60^{o}C. Also energy efficiency was determined.

Supercapacitors are suitable for multiple applications for a large range of temperatures, assuring high power requirements, having a long life span, low maintenance costs, and light weight compared with their capacitance.

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