TESTING AND CHARACTERIZATION OF AQUEOUS STACKED SUPERCAPACITORS

M.C. CARP[1] A.M. PUŞCAŞ[1] P.N. BORZA[1]

Abstract: *Supercapacitors are promising storage energy devices which have a wide range of potential applications. The present paper describes the measurement and determination process of the electric series resistance for a supercapacitor ECOND 14 V/40 F. The impedance spectroscopy method was used in order to determine how the electric series resistance of the supercapacitor is influenced by the frequency, current and voltage variation. Also, a model of a supercapacitor is analysed and its simulated values are compared with the measured values.*

Key words: *supercapacitor, electric series resistance, impedance spectroscopy.*

1. Introduction

Supercapacitors have rapidly found their way in a wide range of applications, from static to dynamic.

In all the domains where energy is converted from electrical to mechanical or chemical, the rapid release storage devices have a crucial role by assuring the necessary amount of power [1].

In many applications, either capacitance or electric series resistance (ESR) is more critical. For example, applications like power and memory backup require increased capacitance in order to provide properly run-time. Also, assuring low ESR is mandatory to decrease drop voltage for pulse power applications. Thus, the main factors that reduce the life time of the supercapacitors are the variation of the capacitance and ESR with voltage. To improve the quality of the supercapacitors first it has to be decided which of the processes affects more the comportment of the supercapacitor: decreasing capacitance or increasing ESR.

As storage devices, the goal of the supercapacitors is to fill the gap between batteries and capacitors [5]. Thus, a system composed by a battery and a supercapacitor not only provides high energy density but it also assures high power density.

A supercapacitor can not be easily characterised because of its complexity. Thus, the goal of the paper is to develop a standard and reproducible method able to measure the variation of the electric series resistance with frequency and voltage.

2. Supercapacitors

Supercapacitors are rapid release energy storage devices which provide high power density and can be rapidly charged or discharged. Compared with the batteries or other chemical or electrical power supplies, supercapacitors have unique features consisting in a very high efficiency of bidirectional power transfer and a very high cyclability - two-three order higher than batteries. Also, supercapacitors are less affected than batteries by the deep discharge

[1] Dept. of Electronics & Computers, *Transilvania* University of Braşov.

processes, by temperature (the operating rage is −40 °C to +70 °C) and they work well in harsh conditions. These devices are based on the latest developments in the electrical storage devices and nanotechnology fields, especially related to the huge surfaces obtained on materials like activated carbon, MnO_2 and others [2].

If usual capacitors are composed from a conductive material and a separator, the supercapacitor crosses into the technology of the battery, being made from electrodes (activated carbons, metal oxide, polymers) and electrolyte (aqueous or organic). The electric double layer supercapacitor (EDLC) can be easily developed, has reduced manufacturing costs and is frequently used in many applications nowadays. The internal structure of an EDLC is shown in Figure 1.

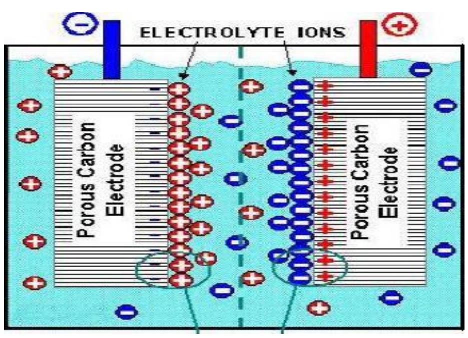

Fig. 1. *EDLC internal charge separation process* [9]

Function of the type of the electrolyte, the decomposition voltage can have values between 1.2 V (aqueous electrolyte) and 2.7 V (organic electrolyte), or even more. This value of the voltage limits the energy density that can be stored on supercapacitors. Other important features are: (*i*) the specific surface of the activated carbon have values between 2000-3800 m^2/g of material; (*ii*) the specific capacitance have values between 100 and more than 200 F/g; (*iii*) price/farad is around 0.025 till 0.1 $/F; (*iv*) the specific power density has values between 2-4 kW/kg; (*v*) and the specific density have values between 2-3 Wh/kg.

Batteries can provide high power only if the cycling duty is reduced. Instead, supercapacitors are commercially available to extend the life time of the battery in the electronic equipments [8].

The electrolyte of the *aqueous supercapacitors* can be KOH or H_2SO_4 solutions. The ions of these solutions have high mobility and can penetrate relatively easily and fast the huge surface of armatures thus assuring a low electric series resistance and a high power density. Also, these kinds of supercapacitors have low decomposition voltage that involves low energy density. For *organic electrolytes*, the mobility of the charge is lower and depends on the temperature. The temperatures below zero Celsius degree have a bigger impact on the parameters of the supercapacitors increasing the value of the ESR and reducing the values of the power density. But, supercapacitors have relatively high decomposition voltage that involves high energy density.

Even if the elementary cells are composed by two devices connected in series (double layer capacitors), the connectivity between these elementary cells became, for practical reasons, the most important. Thus, in order to assure higher operating voltages, the supercapacitors are connected in series and to decrease the value of the electric series resistance they are connected in parallel. For the elementary cells, the chemical and technological aspects are dominant and they are designed to obtain good performances and adequate voltage for different applications. For these reasons, using a proper electrical model of the supercapacitors is essential to obtain similitude between simulation and experiments. The comportment of the supercapacitor will be analysed by identifying its parameters using the spectroscopy impedance method and volt-ampere methods.

3. Test Bench (TB)

It was developed a test bench that includes calibrated and verified instrumentation (wave form generators and measuring instruments). Also, we developed several subsystems such as: power amplifiers and instrumentation amplifiers necessary to adapt the signals at the requirements of the device under test (DUT) (stacked aqueous supercapacitor 40 F/14 V produced by ECOND). The implemented test bench is shown in Figure 2.

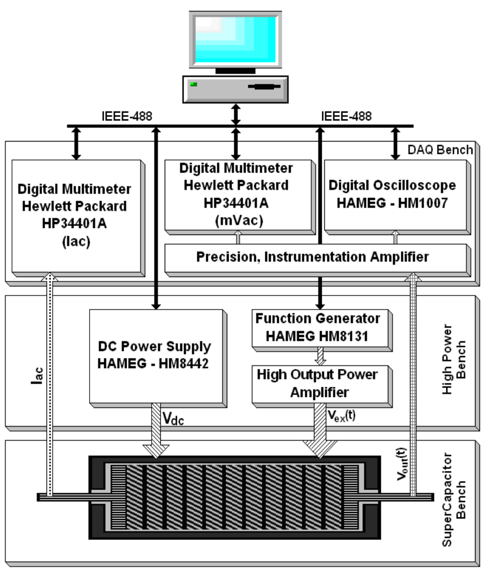

Fig. 2. *Test bench*

The implemented test bench is composed by: (*i*) DUT - supercapacitor; (*ii*) high power supply consisting in a HM8442 DC power supply, a HM8131 used for generating the AC signal which is amplified and applied to the supercapacitor; (*iii*) data acquisition system composed by a HP34401A multimeter used to measure the alternative current, a HP 34401A used to measure the voltage of the amplified signal, a HM1007 digital oscilloscope used to preview in real time the parameters and to locally store them. All the acquired data were sent to a Laptop - Intel Centrino Duo, 2 GHz - using IEEE-488 (GPIB) interface (PCMCIA - GPIB adaptor from National Instruments) in order to process them and to raise the corresponding plots.

Before testing the supercapacitor the whole test bench was calibrated thus validating the measurement system.

Using our high output power amplifier we have provided maximum 10 A at maximum 16 V. The distortion level was maintained on the full range below 0.1%. For all the range of the voltage, the frequency domain was varied between 10 Hz to 10 kHz, as it is illustrated in Figure 3. It was observed that even if we have disconnected the power supply from the terminal of the SC, the voltage was varied with several mV. In order to be able to compare the measurements, our methodology included two types of waiting periods (relaxation time): 600 s for voltage variation and 10 s for frequency variation. For DUT, the relaxation time for each of the charging level of the SC was determined when the variation of the voltage was less than 0.001% during 30 seconds.

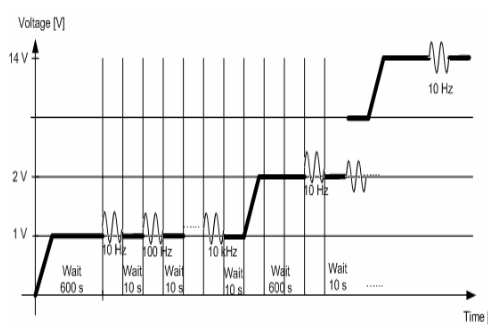

Fig. 3. *Flow chart for ESR determination*

4. Electric Series Resistance

The basic model of the electric double layer supercapacitor used to perform the measurements is shown in Figure 4.

EDLC is consisting of two capacitances and an ESR connected in series and dependent on voltage and temperature. In parallel with these are connected other two elements: the parasitic capacitance (C_p) and the self discharge resistance (R_{sd}).

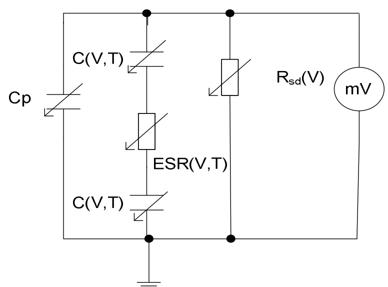

Fig. 4. *Basic model of a supercapacitor*

This model was completed with values for each component using two different correlated methods: (*i*) static: volt-ampere method that determines the C(V,T) capacitance and R_{sd} (V) (*ii*) impedance spectroscopy method that determines C_p and ESR. Another test was performed in order to measure the self discharge resistance of the same device. The variation is illustrated in Figure 5.

The main parameters that influence the life time of a supercapacitor are the capacitance function of voltage and temperature C(V,T) and the ESR(V,T) which also varies with voltage and temperature.

ESR is an important parameter that depends on multiple factors like: the electrolyte resistance, the electrode materials resistance (including the interface between the activated carbon layer and the collector electrodes). While the characteristics of the supercapacitors are deteriorating, the value of the ESR increases and thus the value of the capacitance decreases.

ESR is also composed from two basic conduction processes: electronic and ionic. The electronic influence is due to the ohmic resistance in the conductor and in the carbon particles and the ionic influence is due to the ions mobility from the electrolyte and the dimension of the carbon activated porous [6].

Because the impedance measured at the terminals of the supercapacitor is also dependent on voltage and frequency variation, *impedance spectroscopy* method was used to determine the impedance and ESR parameter of a 14 V/40 F ECOND supercapacitor.

Generally, ESR has values in tens-hundreds of mΩ and its values increase with voltage and decrease with frequency. In a lot of applications it is possible to appear over voltages on the supercapacitors. In such cases, we do not find in literature data about their comportment. Thus, we decided to test which is the variation of the *self discharge process* of the device when it is charged with 15% more than its nominal voltage. The influence of the ESR value it can be observed at the very beginning of the self discharge process, in the first seconds, when the drop voltage has increased values.

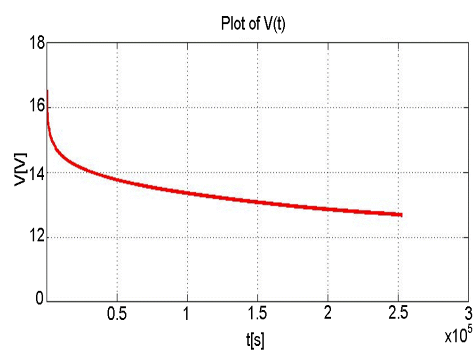

Fig. 5. *Self discharge process*

As it can be seen in Figure 5, at the excess voltage period, the self discharge resistance is lower than in the case of the supercapacitor charged in the nominal range.

Supercapacitors have two mainly limitation: ESR and high capacitance loss.

Parameters like voltage, current, temperature, capacitance C(V,T), parasite capacitance (C_p) and ESR influence the life time of the supercapacitors. While the supercapacitors are deteriorating, the ESR is increasing thus decreasing the capacitance [4].

5. Impedance Spectroscopy

Impedance spectroscopy method is one of the most important analytical and electrochemical techniques used to identify the values of the parameters of the supercapacitors and to analyze them [3].

Real applications have elements that can not permit to analyse a circuit from the resistance point of view. Thus, the impedance concept represents a method to generally approximate the parameters of a circuit. Impedance represents the ability of a circuit to support the electrical current flow and it is measured when applying a small AC signal (1 V, 10 A) to the input of the circuit and varying the frequency. The current and voltage are measured at the circuit's output [7].

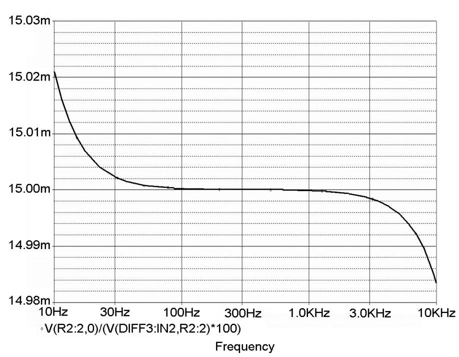

Fig. 6. *ESR variation function of frequency - simulation*

The range of the considered frequency was chosen thus to minimize the influence of the imaginary part of the impedance (represented by the capacitive and inductive reactance). Thus, the basic model illustrated in Figure 4 was simulated and the results are shown in Figure 6.

As it can be observed in Figure 6, the first part of the simulation (10 Hz - 30 Hz) represents influence of the capacitive reactance, the second part (30 Hz - 1 kHz) represents the ESR variation and the third part of the simulation (1 kHz - 10 kHz) represents the influence of the ESR parasite capacitance.

Because of the ESR parasite capacitance, the values of the electric series resistance decreases with frequency. The experimental results are presented in Figure 7.

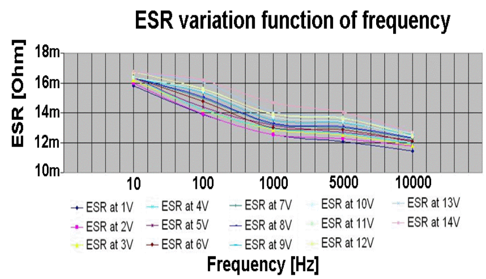

Fig. 7. *ESR variation function of frequency - experimental results*

As it can be seen in Figure 7, the variation of the parameters of the supercapacitors with frequency is approximately similar with the simulated model. Thus, the basic model illustrated in Figure 4 was validated by the experimental results shown in Figure 8.

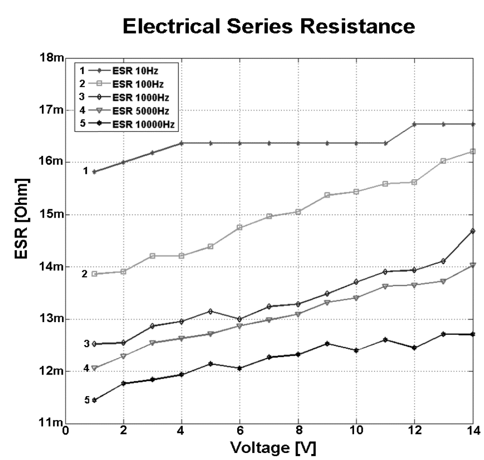

Fig. 8. *ESR variation function of frequency and voltage - experimental results*

As it can be seen in Figure 8, the ESR is dependent on voltage and frequency. Its values are decreasing while increasing the frequency and are increasing while increasing the voltage.

6. Conclusions

As promising storage energy devices, the landscape of the supercapacitors is complex, actually incomplete known and under research because of their power delivery capabilities [4]. Also, their parameters are very important while developing specific power applications.

As it is presented in the present paper, the electrical impedance and implicitly the electric series resistance of the ECOND 14 V/40 F supercapacitor is dependent on frequency and voltage variation, electrical impedance increasing with voltage and decreasing with frequency.

Because of the considered frequency and voltage range, the distributed values of the supercapacitor were easily determined, the ESR having its measured value in range of mΩ.

Thus, as it can be observed from the experiments, because of the reduced ESR value (under 20 mΩ) and their high performances the supercapacitors are properly to be used especially in transitory applications.

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