Thermal study of supercapacitor serial resistance

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Abstract

The electric serial resistance ESR of supercapacitor cell is strongly dependent on the electric resistivity of the electrolyte used and of the size of the ions from the electrolyte that diffuse into and out the pores of the microporouse electrode particles. Supercapacitor efficiency is a function of electric serial resistance (ESR). To use supercapacitor in transportation and because of supercapacitor power dissipation, it is necessary to characterize the thermal variation of ESR. This paper discusses the thermal behavior of the supercapacitor ESR. Experimental study is reported. ESR is determined for different supercapacitor temperatures. Based on experimental results, an analytic model is proposed to be implemented with Saber software for simulation.

1 Introduction

Supercapacitors represent one of the most interesting new developments in the field of energy storage. Potential applications concern short time uninterrupted power supplies and peak load in combination with batteries or fuel cell. Supercapacitors can be used in numerous applications, in electric or hybrid vehicles in order to provide peak power for improved acceleration, or in parallel with the vehicle battery during start up of an internal combustion engine (ICE) with the purpose of decreasing the dimensions and the power of the battery or in fuel cell vehicles ... [1, 2].
It is well known that the power output capability of electrical capacitors depends strongly on the series resistance, which needs to be minimized [3]. For supercapacitors, the serial resistance (ESR) is the sum of two major terms, namely an electronic contribution and an ionic one. Another parameter, which is important for the limitation of the supercapacitor power output, is the temperature. The high electrolyte resistance also affects the equivalent distributed resistance of the porous layer and consequently reduces the maximum usable power.
Efficiency is a very important issue for supercapacitor in electric or hybrid vehicles applications. Part of the available energy is dissipated at the internal resistance ESR. At high power and high current, this losses can become dominant. In a recent comparison of supercapacitor and batteries in electrical vehicle applications, Burke and Miller [4] 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 is 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:

- electrolyte including separator
- current collector
- porous layer including contact to current collector
- other contact resistances

All electrochemical energy storage devices experience changes of temperature upon charging and discharging. In the case of batteries and fuel cells, the thermal effects are of from the joule heating and from the heat change generated from the Faradic cell reaction. In the supercapacitor only joule heating is again important because is no Faradic processes.

Supercapacitor performances and cycle life depend on temperature. However, electrolyte conductivity is one of the most important properties that is temperature dependent. So, supercapacitor ESR and capacitance depend on temperature.
In this paper we study the thermal behavior of 2700 F and 3700 F supercapacitor and especially their serial resistance, and deduce the influence on their performances. Especially the power loss and the efficiency of supercapacitor in transportation applications. Using experimental results, an analytical model is presented and will be implemented in Saber and Spice for simulation.

2 Supercapacitor description

Double-layer capacitor (supercapacitor) consists of two activated carbon electrodes and a separator that prevent physical contact of the electrodes but allows ion transfer between them. A carbon-blinder mixture is deposited on aluminum foil to form the electrodes.
Supercapacitor is based on the double-layer capacitance at the solid/electrolyte interface of high surface area material, which is activated carbon. Similar to a traditional electrolytic capacitor, the electrical energy storage is based on the separation of charged spacies in an electrolytic double-layer across the interface of electrode/electrolyte. When DC voltage is applied to the interface of an electrode, electric double-layer is then established to store electric energy.

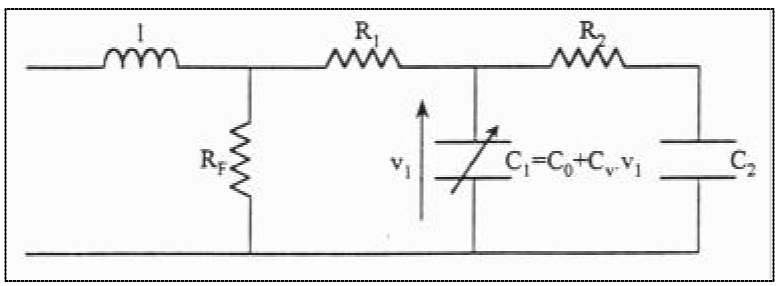

Figure 1 : Supercapacitor equivalent circuit

Supercapacitors cannot be modeled as a simple capacitor. To determine the structure of the equivalent circuit, different aspects of the physics of the supercapacitors should be taken into account. The equivalent electric circuit achieved describes the electrical and thermal behavior of the supercapacitors.
To take into consideration the interfaces between layers that constitutes the supercapacitors, the model consists of several RC cells [5, 6]. Figure 1 represents an equivalent electric supercapacitor circuit. The R_1C_1 cell is the main branch, which determines energy evolution during charge and discharge cycles; it is called a fast branch. C_1 is the capacitance between electrode/electrolyte interface; R_1 is the equivalent serial resistance (ESR). The R_2C_2 cell is the slow branch; it completes the first cell and describes the internal energy distribution at the end of the charge (or discharge). R_f represents the leakage supercapacitor resistor. A series inductance may be added for pulse applications, but measurements show that it is so small (some nH) that it can be neglected in most applications.
To take into consideration the interfaces between layers that constitute the supercapacitor, we adopt a capacitance modeled as a constant capacitor and a capacitor whose value varies linearly with its voltage V_1 [5] : $C = C_0 + C_v * V_1$.
In this study, during the dynamic regime, we can neglect the small temperature variations of the slow branch R_2C_2, The inductance and the leakage supercapacitors resistor effect is neglected.
The equivalent electric circuit parameters are determined from experimental tests consisting of supercapacitor charge and discharge at constant current for different temperatures.
To use supercapacitor in electric or hybrid vehicle, it is necessary to study its electric and thermal behavior in its operational environment. Moreover, we need to establish an electric model of supercapacitor for simulation which takes into account the temperature variation, in order to optimize the

operation of the system with supercapacitor. For these reasons, an experimental test bench has been realized.

3 Experimental re sults

3.1 Experimental setup

The experimental setup consists of a non-isolated buck converter. It is composed of a MOSFET power switch and a fast recovery rectifier diode used as a free wheel diode, necessary to evacuate accumulated energy in the high pow er inductance. The supercapacitors are put inside a temperature controlled climatic room. The temperature can vary between 233 K and 323 K.

A data acquisition system is used to process the output thermocouple signals and the different current and voltage sensors. The acquisition system is controlled by LABVIEW Software.

The parameters of the proposed model with RC branch can be identified by carrying out a single fast current controlled charge. The parameters will be identified by charging at constant current the supercapacitor, at different temperature values, from zero to rated voltage and by observing the terminal voltage during the internal charge redistribution.

2 Variation of supercapacitor serial resistance with temperature

When the current source is switched on, the current rises to the set value I_{ch} in less than 20ms. Because of the serial resistance, the output voltage rises instantaneously from 0 to the voltage drop with serial resistance V= R_1 I_{ch} figure 2. Afterwards, the s upercapacitor is charged at constant current. R_1 is deduced by measuring the voltage drop.

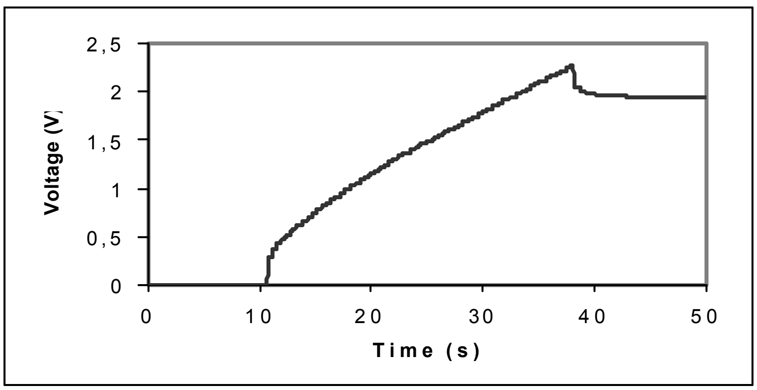

Figure 2 : Charge of 2700 F supercapacitor I_{ch} = 135 A.

For different temperatures of the climatic room, we have done repetitive charge cycles with 2700F and 3700F supercapacitor. Table 1 gives supercapacitor serial resistance R_1 values of 2700 F.

Temperature K	238	253	283 318
ESR(R1 (mΩ))	2.12	1.64	1.73 1.5

Figure 1 :Supercapacitor serial resistance of 3700 F for different temperatures

For example, when the supercapacitor temperature varies from 248 K to 298 K, R_1 decreases from 2.13mΩ to 1.1mΩ. Thus, the supercapacitors power dissipation by Joule effect increases and the supercapacitor efficiency decreases.

Figure 3 shows R_1 variations as a function of temperature. These results show that the resistance R_1 varies greatly for negative temperature values, but low variations are measured for positive temperatures. It is thus clear that serial resistance decreases as the temperature increases. When the temperature rises from 248 K to 298 K, the resistance varies by about

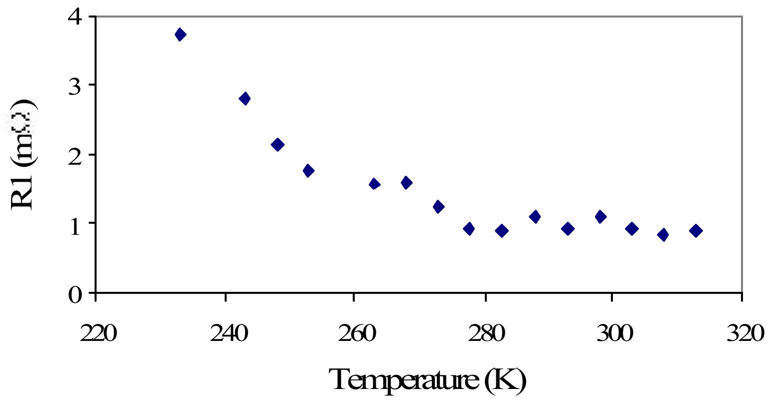

Figure 3 : Evolution of 2700 F serial resistance with temperature

52%. This effect thus influences power dissipation by Joule effect. Consequently, for negative temperatures, the power dissipation is higher than for positive temperatures, and thus, the supercapacitor power efficiency decreases with temperature.

In order to establish an analytical relation between R_l and the temperature, we consider that the relation between the resistance and electric conductivity is $R_l(T) = \frac{m}{s\,(T)}$ [7] , where m is a coefficient of proportionality and σ (T) the electric equivalent conductivity, expressed in (Ω^{-1} cm^{-1}). In this equation only R_l and σ vary with temperature.
Using this relation and the experimental values of R_l, we have deduced the equivalent electric conductivity σ (T) for several temperatures. Figure 4 represents the variation of the supercapacitor equivalent electric conductivity with temperature. This result shows that the relationship between the logarithm of the electric equivalent conductivity and the temperature is linear. This result confirms the work published by S. L. di Vittorio [8] where he concluded that the resistance of activated carbon fibers increases rapidly at low temperatures. He has demonstrated that the activated carbon electric conductivity has a linear evolution in semi-log coordinates. We confirm this law as it can be seen in figure 4.

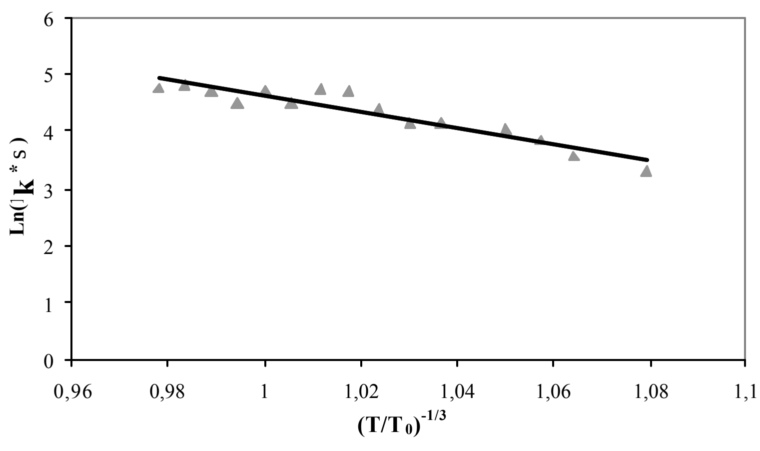

Figure 4 : Evolution of the electric conductivity with temperature, k is a constant

Using this linear curve fit, we can thus establish an analytical relation of R_1 according to the temperature:

$$R_1(T)=bR_1(T_0)\exp\left(a\frac{T}{T_0}\right)$$; with a=13.94 and b=10^{-6} for 2700 F supercapacitors. T_0 is the ambient temperature.

This model is relatively simple, but makes it possible to describe correctly the variation of supercapacitor serial resistance according to the temperature. However to establish a complete model, it is necessary to make a chemical and physical study of different supercapacitor constituting properties according to the temperature. Several authors [8, 9, 10, 11] showed that the supercapacitor serial resistance depends on the electric and ionic conductivities of the electrolyte and the activated carbon used for the electrodes. But it is very difficult to quantify the variation of serial resistance directly.

We can thus conclude that the analytical model established from the experimental tests makes it possible to describe the thermal behavior of R_1, and it is relatively simple to be implemented with Saber or Spice software for simulation.

Concerning the supercapacitor global capacitance, the charging time duration is larger at T=298 K; the time duration is in order of 36s; that at T= 248 K; where the time duration of charge is in order of 22s. These results are measured in the same condition of charge. This variation is due to two different effects. The first one is due to temperature variation of the supercapacitor serial resistance, and consequently, temperature variation of the time constant. Indeed, the voltage across the supercapacitor can be described by the following equation : $V(t)=R_1I+V_c(t)$, where $V_c(t)$ is the voltage which depends only on the supercapacirtor capacitance aspect. Voltage Vc(t) is directly proportional to the supercapacitor charge time Δt. For a given charge voltage, the serial resistance increases when temperature decreases, thus causing a decrease of the voltage $V_c(t)=V(t)-R_1I$ and hence the supercapacitor charge time decreases with temperature. The second effect is due to decrease of the total supercapacitor capacitance with temperature. Indeed, the capacitance variations due to variations of the activated carbon characteristics used in supercapacitor, of the electrical conductivity of the electrolyte, and of the double layer effective thickness as a function of temperature [3].

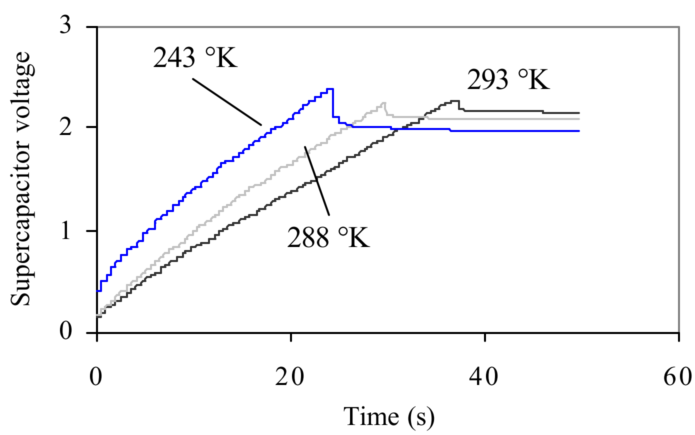

Figure 5 : Charge of 2700 F supercapacitor at constant current

In order to determine the thermal evolution C_0 and C_v, we first report their thermal variation in figure6. Afterwards, we interpolate these curves by polynomial functions, which give a good approximation of the experimental results. The later show that we may define two intervals. The first one (zone 1) is situated between 233 K and 273 K, the second (zone 2) corresponds to positive temperature values (T>273 K). In zone 1, C_0 increases according to the temperature and C_v decreases. In zone 2, we notice a low variation C_v and C_0 according to the temperature.

The value of C_0 at 243 K is approximately 23% of its value at 20°C, and C_v is in order of 28% of its

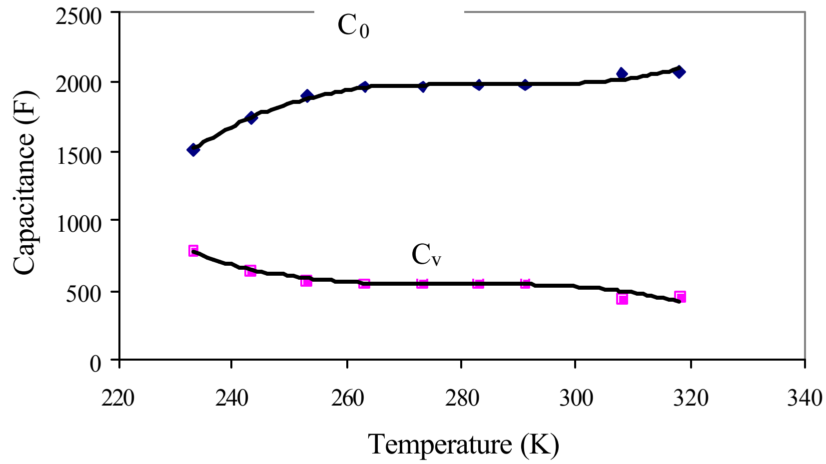

Figure 6 : Variation of C_0 and C_v with temperature

value at 293 K. However, the supercapacitor global capacitance decreases when the temperature increases as figure 5 shows it.

The equivalent electric model of the suparcapacitor, for which R_1, C_0 and C_v take into account the temperature influence, has been implemented in the Saber and Spice software. The first results are in good agreement with experimental ones. This confirm the good behavior of the proposed model.

4 Conclusion

We thus showed that supercapacitor ESR increases when temperature and capacitance decrease. This increases the power dissipated and decreases the energy stored in the supercapacitor. Consequently the efficiency of the supercondensator decreases.

It can be seen that the proposed model of the supercapacitor ESR is in good agreement with some physical studies concerning the thermal behavior of the inner materials of the capacitors like active carbon and organic electrolyte. The proposed model will be easy to use in several analog simulators. It is well adapted to some studies concerning behavior of supercapacitors when used in automotive applications thanks to sensitivity analysis induced by thermal parameters.

In automotive applications, supercapacitors are used as a source of energy in dynamic regime. For example, when the supercapacitor current is in order of 100A, the power dissipated is approximately 10W and 18 W for 20°C and -20°C. Thermal management of supercapacitor must be studied. It is what we study now at L2ES laboratory.

The model described in this paper, can thus describe the behavior of a supercapacitor as a function of temperature. Experimental results are in good agreement with

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