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Supercapacitors aging diagnosis using least square algorithm

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\textbf{Abstract}

Supercapacitor aging is mainly related to thermal and voltage constraints. This aging causes degradation in the supercapacitor performances which can lead to the failure of this component. To avoid this failure, it is necessary to determine the supercapacitor state of health. The aim of this study is the supercapacitor diagnosis. In this paper, aging tests of supercapacitor subjected to calendar aging constraints are presented. The supercapacitor is aged at constant temperature and constant bias voltage. During the aging process, the variations of the supercapacitor equivalent series resistance (ESR) and equivalent capacitance (C) are measured and analyzed. For diagnosis, a least square algorithm is used. This algorithm is used for ESR and C identification during the supercapacitor operation. For vehicle applications, the supercapacitor is considered as aged when the capacitance loss is in order of 20\% of its initial value, or if the value of the equivalent series resistance increases by a factor of 2.

\textbf{1. Introduction}

Supercapacitors are used to assist the power of a battery or a fuel cell in numerous applications. They can be used to store energy and to provide peak power demands, in power electronic systems, in parallel with batteries or fuel cells. For example in a hybrid vehicle the supercapacitor can provide peak power requirement in transient state and to store the regenerative energy \cite{1–6}. In several applications, supercapacitors are charged and discharged at high current. This effect causes heating in the supercapacitor and accelerates their aging. It is known that the supercapacitor aging is mainly related to thermal and voltage constraints applied to the device \cite{7–11}.

In several applications, the improvement of supercapacitors reliability is fundamental. The follow-up of the supercapacitor state of health and the detection of an aging state enable to avoid some breakdowns. The knowledge of the system’s state permits to avoid operational failures and thus to intervene at the convenient moment before a breakdown occurs. Several diagnosis methods exist \cite{14,15} which permit from adequate measures, to analyze the aging state of this component.

Finally, our work deals with the diagnostic of the supercapacitor aging state based on the estimation of both the series resistance and the capacity. This algorithm uses the measurement data which are the voltage and the charge/discharge current of the component. This is the first study presented in the literature that deals with the diagnosis of the failures due to the aging phenomenon by an optimization using a least square algorithm.

This method is based on the estimation of the electrical equivalent circuit parameters of the component. Identification test at the beginning and at different phases of the supercapacitor calendar aging is realized. This method is used to identify the values of the equivalent series resistance and the capacitance at different stages of the operation process. The comparison is performed between initial and the following states, respectively. Supercapacitors offer a high number of charge and discharge cycles. The device’s lifetime is very long. In order to carry out this study during a reasonable time, an accelerated supercapacitor calendar aging process is realized.

\textbf{2. Calendar aging protocol}

In order to perform the aging test, a dedicated test bench was developed (Fig. 1).

A supercapacitor is placed inside a climatic chamber at 60 °C and polarized at 3 V voltage during the aging process. Taking into account the boiling point temperature of the electrolyte which is in order of 81.6 °C (at atmospheric pressure), the temperature value is selected in order to make it possible to observe the aging rather quickly. Supercapacitor aging is carried out following several phases. The durations of the different phases are given in Table 1.

Initially and after each phase of the aging, the supercapacitor is characterized at room temperature. This characterization consists of charging and discharging the supercapacitor by using the test bench presented in Fig. 1, at constant current (10 A) as shown in Fig. 2.
The parameters of the device such as the equivalent series resistance (ESR) and the equivalent capacitance \( C \) are measured before and after each aging phase. The test bench is monitored using an acquisition board with an implemented MATLAB program. These experimental results are used to identify the evolution of the ESR and the capacitance.

The calculation of the equivalent series resistance ESR and the equivalent capacitance \( C \) is based on the following expressions:

\[
\text{ESR} = \frac{\Delta V}{I} \quad \text{and} \quad C = \frac{I}{\Delta V_0} / \Delta t_0
\]

The different parameters used in the above expressions are presented in Fig. 2.

The voltage drop \( \Delta V \) is measured between the current interruption and the intersection with the linear regression of the self-discharge curve, as described in the standard IEC62391.

As described previously, the aging behavior is determined by the increase of the ESR and by the loss of the equivalent capacitance. For this reason, these parameters were measured before and after each aging phase. Figs. 3 and 4 present the supercapacitor voltage variation with time during charge and discharge at constant current (10 A) and for various aging time. It can be seen that the time of charge and discharge decreases with the duration of aging. This phenomenon is related to the reduction in the supercapacitor capacitance with aging process.

These results show also that the drop of the voltage at the end of the supercapacitor charge (current interruption) increases with the duration of calendar aging. This means that the equivalent series resistance ESR increases. This phenomenon is accelerated by increasing the temperature and by imposing a high bias voltage. We synthesized these results in Table 1.

It can be seen that the ESR increases and \( C \) decreases with aging time. For example, when the supercapacitor is polarized at 3 V and the temperature is fixed at 60 °C and after 536 h of calendar aging, the ESR increase is in order of 116% and the capacitance decrease is in order of 25%.

For vehicle applications, the supercapacitor is considered as aged when the capacitance loss is in order of 20% of its initial value, or if the value of the equivalent series resistance increases by a factor of 2. Thus, it is very important to consider these two parameters as some good indicators of aging in order to perform a diagnosis method for the supervision of the device state during its operation. The degradation of ESR and \( C \) will have a considerable impact on the ability of the energy storage of the supercapacitor.

The energy depends particularly on the value of the capacitance \( C \) and the performance of the supercapacitor depends on the quantity of energy losses and thus on the evolution of the ESR.

### 3. Identification methodology

#### 3.1. Model description

Among the equivalent electrical models proposed in the literature, a commonly used model is a model including a resistance and a series of \( n \) RC parallel branches [12]. Here, we have focused on the simple RC series circuit represented in Fig. 5. This model is not suitable for an accurate modeling of the supercapacitor dynamic behavior in a wide frequency range, however this model will be considered reliable enough given the current profile used and the frequency range of this current (the sampling period will be chosen sufficiently small). Also note that here we are interested in a degradation of parameters over time and not in an accurate assessment of their values.

The input/output behavior of the model is given by:

\[
\Delta V = G_1 I + G_2 U
\]

![Fig. 1. Overview of the test bench.](image1)

![Fig. 2. Identification method of \( C_0 \) and ESR.](image2)

![Fig. 3. Supercapacitor charge at 10 A constant current for different aging times.](image3)

<table>
<thead>
<tr>
<th>Aging time (h)</th>
<th>0</th>
<th>327</th>
<th>536</th>
<th>774</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESR (mΩ)</td>
<td>2.4</td>
<td>4</td>
<td>5.2</td>
<td>6.2</td>
</tr>
<tr>
<td>( C ) (F)</td>
<td>380</td>
<td>313</td>
<td>283</td>
<td>238</td>
</tr>
<tr>
<td>ESR variation (%)</td>
<td>0</td>
<td>66</td>
<td>116</td>
<td>158</td>
</tr>
<tr>
<td>( C ) variation (%)</td>
<td>0</td>
<td>–7</td>
<td>–25</td>
<td>–37</td>
</tr>
</tbody>
</table>

Table 1
Supercapacitor ESR and \( C \) variations according to the calendar aging time.

The parameters of the device such as the equivalent series resistance (ESR) and the equivalent capacitance \( C \) are measured before and after each aging phase.

The test bench is monitored using an acquisition board with an implemented MATLAB program. These experimental results are used to identify the evolution of the ESR and the capacitance. The calculation of the equivalent series resistance ESR and the equivalent capacitance \( C \) is based on the following expressions:

\[
\text{ESR} = \frac{\Delta V}{I} \quad \text{and} \quad C = \frac{I}{\Delta V_0} / \Delta t_0
\]

The different parameters used in the above expressions are presented in Fig. 2.

The voltage drop \( \Delta V \) is measured between the current interruption and the intersection with the linear regression of the self-discharge curve, as described in the standard IEC62391.

As described previously, the aging behavior is determined by the increase of the ESR and by the loss of the equivalent capacitance. For this reason, these parameters were measured before and after each aging phase. Figs. 3 and 4 present the supercapacitor
On that frequency range, the simple RC series circuit can approximate the behavior of the supercapacitor. A more accurate modeling would be obtained with a higher measurement time and therefore a significant change in voltage. The estimation algorithm presented in the next subsection is based on this discrete time model.

3.2. Estimation algorithm

Estimation of the parameters treated in this paragraph is presented under the following formulation. The goal is to calculate the values of ESR and C by having measurements values of input \( I(t) \) and output \( U(t) \) on the time interval \( \left[ T_s \cdots N \cdot T_s \right] \). To achieve this goal, Eq. (2) can be rewritten in a regression form \( U(t) = \Phi(t) \theta \), with:

\[
\theta = \begin{bmatrix} R \\ 1/C \\ C^{\text{eq}} \end{bmatrix} \quad \text{and} \quad \Phi(t) = \begin{bmatrix} I(t) \\ I_i(t) \\ 1 \end{bmatrix}
\]

This formulation allows us to use identification methods such as those described in [13]. In this study, the well-known least squares method has been chosen, this method makes the solution simpler and more intuitive in the authors view. This method consists of adjusting the parameters so as to minimize the sum \( \sum_{k=1}^{N} \left[ U(k \cdot T_s) - \Phi(k \cdot T_s) \cdot \theta \right]^2 \). The optimum can be analytically computed, which gives, provided the indicated inverse exists,

\[
\hat{\theta} = \left( \Phi \cdot \Phi^{\text{eq}} \right)^{-1} \cdot \Phi \cdot U
\]

With

\[
\Phi = \begin{bmatrix} \Phi(T_s) \\ \Phi(2 \cdot T_s) \\ \vdots \\ \Phi(N \cdot T_s) \end{bmatrix}
\]

and

\[
U = \begin{bmatrix} U(T_s) \\ U(2 \cdot T_s) \\ \vdots \\ U(N \cdot T_s) \end{bmatrix}
\]

3.3. Experimental study

The parameters of the supercapacitor have been estimated over 500 ms. This experimental condition induces low level voltage variation so that the voltage can be considered constant. Consequently, the capacitance \( C \) can be assumed to be a constant, a necessary condition for the application of the estimation procedure. Because of measurement noise, a shorter measurement time may degrade the quality of the estimation. The sampling period has been fixed at \( T_s = 10 \text{ ms} \). On that frequency range, the simple RC series circuit can approximate the behavior of the supercapacitor. A more accurate modeling would be obtained with a higher sampling period, however the estimation would require a longer measurement time and therefore a significant change in voltage.

The amplitude of the excitation is \( \delta = 0.4 \text{ A} \). Several steps of current \( i \) have been successively applied.

Fig. 4. Supercapacitor discharge at 10 A constant current for different aging times.

Fig. 5. Simple RC series circuit.

\[
U(t) = R \cdot I(t) + \frac{1}{C} \int_0^t I(\tau) \cdot d\tau
\]

Fig. 6. Parameters estimation.

\[
U(t) = R \cdot I(t) + \frac{1}{C} \int_0^t I(\tau) \cdot d\tau + C^{\text{eq}}
\]
We validated our result, in this section, by estimating the indicators of aging at the beginning (0 h aging), the middle (after 327 h aging) and the end of the process (after 774 h aging).

At each phase of calendar aging and by using the least squares algorithm, the identification of the equivalent series resistance is carried out.

Fig. 8 shows the evolution of these estimates according to the supercapacitor voltage. On these curves, each point corresponds to an estimate on 500 ms.

We note that the increase of ESR according to the aging time is confirmed.

The comparison between the ESR values obtained from the experimental charging curves with that implemented from the identification least squares algorithm is made.

For this purpose, we have calculated at each stage of calendar aging the average value of the estimated ESR.

The ESR evolution obtained from experimental results (standard IEC62391) and the estimated one are plotted in Fig. 9.

The difference between the two methods for determining the ESR is due to the fact that the method using the least squares algorithm is based on a simple model.

This model describes only a part of the behavior of the component (the gap will not be filled with a longer measurements interval or a higher SNR). However, the trend on these two curves is in good agreement and consequently the observation of the estimated ESR is enough to assess the performance decay with aging.

A second indicator of supercapacitor aging is represented by the equivalent capacitance $C$ on which we paid a special attention to examine it. Thus, the value of the supercapacitor capacitance at the initial state and at each stage of its aging is identified. The estimated value by the least squares algorithm depends on the supercapacitor voltage value. The obtained results are presented in Fig. 10, which gives the variation of the estimated capacitance according to the voltage. It can be noticed that the average value of $C$ varies linearly with the supercapacitor voltage.

**4. Conclusion**

This paper presents calendar aging of activated carbon and organic electrolyte supercapacitor. The aging of supercapacitors is related to the voltage and to the temperature. To investigate this effect, a test bench of accelerated supercapacitor calendar aging was conducted. Experimental tests are performed at constant temperature (60 °C) while the supercapacitors are polarized at 3.0 V. In order to quantify the supercapacitors aging, the equivalent series resistance and the capacitance are measured using the DC characterization method. The experimental results have shown that the supercapacitor equivalent series resistance increases with calendar aging and the capacitance decreases. These two indicators are used for the supercapacitors aging diagnosis.

A method based on a least square algorithm is used to estimate the supercapacitor parameters over the aging time. The obtained results show that the method used for ESR and $C$ estimation is satisfactory and can be used easily for supercapacitor diagnosis. The identification process can be implemented in a microcontroller or a DSP.

**References**


