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The comparison of two supercapacitors lifetime estimated on the basis of accelerated degradation tests by means of stochastic models

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The paper presents the results of the comparison of the lifetime estimation of two supercapacitors on the basis of the accelerated degradation tests by means of stochastic differential models. The acceleration of degradation processes was fulfilled by the increase of the operating voltage of the capacitors, while their reliability was assessed on the basis of the changes in equivalent series resistance. The reliability distribution function was determined using stochastic differential models. The model parameters were assessed based on the changes of supercapacitor parameter at the beginning of the testing process. In order to eliminate the effect of other factors accelerating the ageing process, supercapacitors were placed in a temperature chamber that provided a constant temperature during the tests. The paper describes the construction of the test setup, the tests procedure, and the method of reliability estimation. The use of two capacitors with different nominal voltages allowed for assessment of properties of particular parts of the test setup, as well as the proposed procedure for the tests and analysis of the results.

KEYWORDS: supercapacitor, accelerated degradation tests, degradation processes, stochastic differential models, reliability

1. Introduction

The increase in the user demands in terms of the operation of elements and electronics and the increase in competitiveness, compel producers to implement products that meet higher and higher reliability requirements on the market. However, constant technology development, new solutions or new materials lead to the fact that designers and producers have less and less time to test newly developed and introduced products [8].

The lifetime estimation for elements that have very high reliability is extremely difficult. Very long nominal time to failure renders it almost impossible to conduct the lifetime distribution tests of appliances or elements under their nominal conditions. Therefore, the use of accelerated ageing tests is a practical solution.

Normally, the reliability assessment is carried out on the basis of accelerated ageing tests that lead to failure. However, these types of test are not very effective in case of elements that have extremely high reliability. In spite of the acceleration of ageing processes, failure may be caused very rarely and only after a very long testing time. The solution to this problem may be the inference about the reliability of the devices based only on the observation of the changes of certain parameters, thus their degradation during such tests. The so–called *accelerated degradation tests* allow for the estimation of the distribution of the reliability function on the basis of observation, and then the estimation of times to failure before they are reached.

During accelerated degradation tests, both the proper determination of the effect of conditions accelerating degradation processes and the choice of mathematical models that describe the change behaviour of the parameters observed are of very high importance [7].

The paper presents the results of the estimation of the distribution of supercapacitor times to failure. For these types of elements, the time may be estimated on the basis of observing changes in two parameters: capacitance and equivalent series resistance. The results in the paper represent only the interference on the basis of the changes in equivalent series resistance. The increase in the capacitor operating voltage was assumed as a factor affecting the acceleration of the ageing process. On the other hand, stochastic differential equations were used to develop the mathematical model that describes degradation processes. A stochastic factor occurring in these types of model allows for the consideration of a random character of many phenomena occurring in elements and processes. The studies were conducted for two types of supercapacitor with different nominal operating voltages.

2. Basic principles

2.1. Stochastic models of degradation process

The general form of the stochastic process can be presented as

$$\mathrm{d}y_t = F(t, y_t)\mathrm{d}t + G(t, y_t)\mathrm{d}W_t , \tag{1}$$

where the functions $F(t,y_t)$ and $G(t,y_t)$ are called drift and process variation, respectively. Their form may be a function of the process state y_t and time t. On the other hand, $\mathrm{d}W_t$ is a Wiener process determined for $t \geq 0$. Taking the appropriate form of the function $F(t,y_t)$ and $G(t,y_t)$, relationship (1) may simulate the incremental degradation processes progressing according to various trends. Fig. 1 shows the examples of linear, concave, and convex processes [6, 9].

Taking the form of the drift and variation function as

$$F(t, y_t) = \alpha y_t \text{ and } G(t, y_t) = \beta y_t \tag{2}$$

and after the substitution into equation (1), we obtained the process, defined by the relationship

$$\mathrm{d}y_t = \alpha y_t \mathrm{d}t + \beta y_t \mathrm{d}W_t . \tag{3}$$

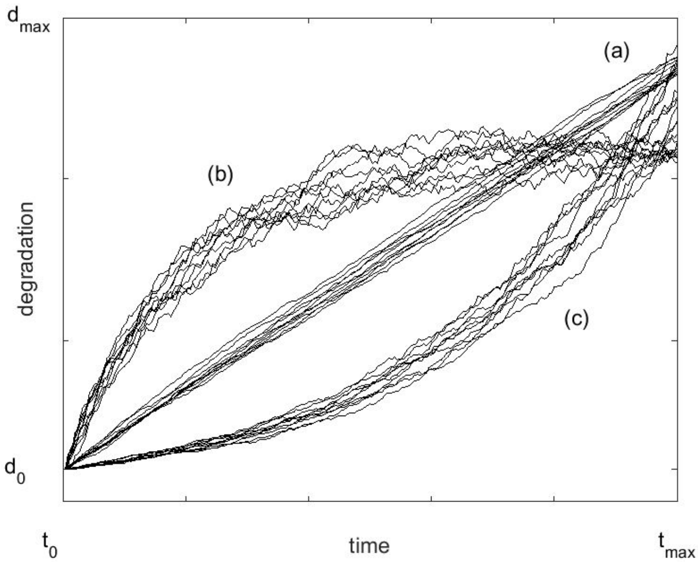

Fig. 1. Examples of the progressing degradation processes, defined by: linear (a), concave (b), and convex (c) models

Taking the initial condition $y(t_0) = y_0$ and applying for the process defined by the equation (3), the Itô integral, we obtained the solution in the form, as:

$$y_t = y_0 \exp\left[\left(\alpha - \frac{\beta^2}{2}\right)t + \beta W_t\right]. \tag{4}$$

This process is in the form of an exponential function and is called a geometric Brownian motion [4, 10, 11]. On the other hand, the parameter values of the model are determined on the basis of a series of differences calculated as

$$y_i = \ln \frac{p_{i+1}}{p_i}, \tag{5}$$

where p_i are the measured values of the quantity describing the degradation process.

2.2. Reliability estimation by means of stochastic models

The values of times to failure t_F can be determined by observing the progressing degradation processes in tested elements and assuming a given threshold level h, the exceeding of which is treated as element failure [1]. However, in case of elements that have high reliability, these times are very long. A significant time reduction in the estimation of reliability is achieved by using accelerated degradation tests. During such tests, the parameters changes of a tested element are observed in a short time at the beginning of their use (Fig. 2, range ①). Next the parameters of the mathematical model are estimated on the basis of these measurements. Further simulations (Fig. 2, range ②) allow for the determination of the time when the degradation process reaches the critical (threshold) level (Fig. 2, range ③) that defines the moment of failure.

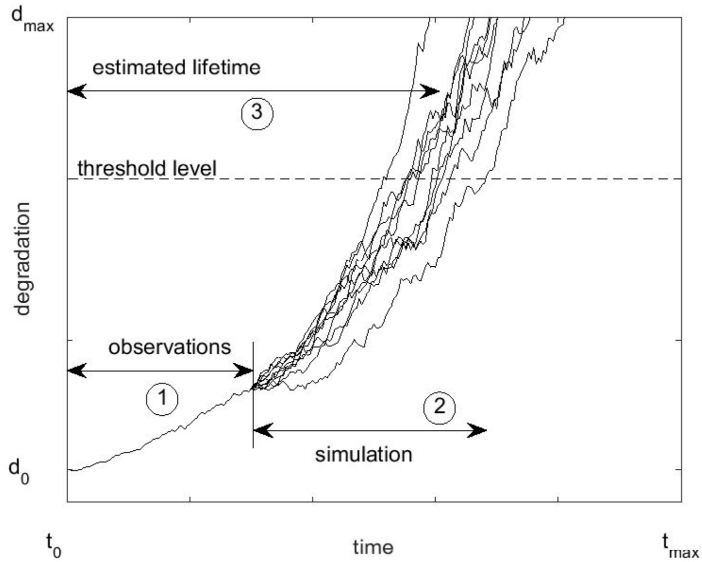

Fig. 2. The lifetime estimation based on the observation of the progressing accelerated degradation processes at the initial phase of operation

On the basis of the values of the times obtained until exceeding threshold values, the parameters of the probability density and reliability functions may be estimated. The model depends on the nature of the degradation process defined by relationship (1). In case of linear processes, the probability density and reliability functions are defined by the inverse Gaussian distribution. On the other hand, taking the process defined by equation (3), the distribution of times to failure will take the form of the normal distribution with the probability density function defined as

$$f(x;\mu,\sigma)=\frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{(x-\mu)^2}{2\sigma^2}} \tag{6}$$

and the cumulative distribution function as

$$F(x;\mu,\sigma)=\frac{1}{2}\left[1+\operatorname{erf}\left(\frac{(x-\mu)}{\sigma\sqrt{2}}\right)\right], \tag{7}$$

where the function $\operatorname{erf}(x)$ is called the error function and is defined as

$$\operatorname{erf}(x) = \frac{1}{\sqrt{\pi}} \int_{-x}^{x} e^{-t^2} \mathrm{d}t \,. \tag{8}$$

The distribution parameters $f(x;\mu,\sigma)$, called expected value and standard deviation, are estimated based on the observed times x_i, i.e. the times that the degradation cross the threshold level h. In this case, the parameter values of the model are estimated as the typical parameters of the normal distribution

$$\hat{\mu} = \frac{1}{n} \sum_{i=1}^{n} x_i \tag{9}$$

and

$$\hat{\sigma} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \hat{\mu})} \,, \tag{10}$$

while the reliability function is defined as

$$R(x;\mu,\sigma) = 1 - F(x;\mu,\sigma) \,. \tag{11}$$

The possibility to apply a linear transformation for the normal distribution has particular importance in accelerated ageing tests. In this case, the scale procedure may be applied

$$X \sim N(\mu,\sigma^2) \Rightarrow kX \sim N(k\mu,|k|\sigma^2), \tag{12}$$

where the scale factor k will correspond to the acceleration ageing process factor, as it is shown in Fig. 3.

While assessing the lifetime distribution of the elements on the basis of observing accelerated degradation processes, it should be assumed that the analyzed processes that take place in the element are irreversible and that the model assumed corresponds to a single degradation mechanism. It is also assumed that the degradation level of the element before the tests and the measurement uncertainty of the degradation changes are negligible. The important condition for undergoing accelerated ageing tests is also the assumption that the failure process under ageing acceleration conditions is the same as under nominal conditions.

2.3. Supercapacitors reliability parameters

The basic parameters that define the reliability properties of supercapacitors are their capacitance C and equivalent series resistance ESR. The change in the value of these parameters over time is a result of progressing degradation processes inside the capacitor. These processes include the oxidation of carbon electrodes, the reduction of the effective surface area of electrodes, and the reduction of the number of ions as a result of the electrolyte depletion. This results in the reduction of capacitance and the increase in equivalent series resistance.

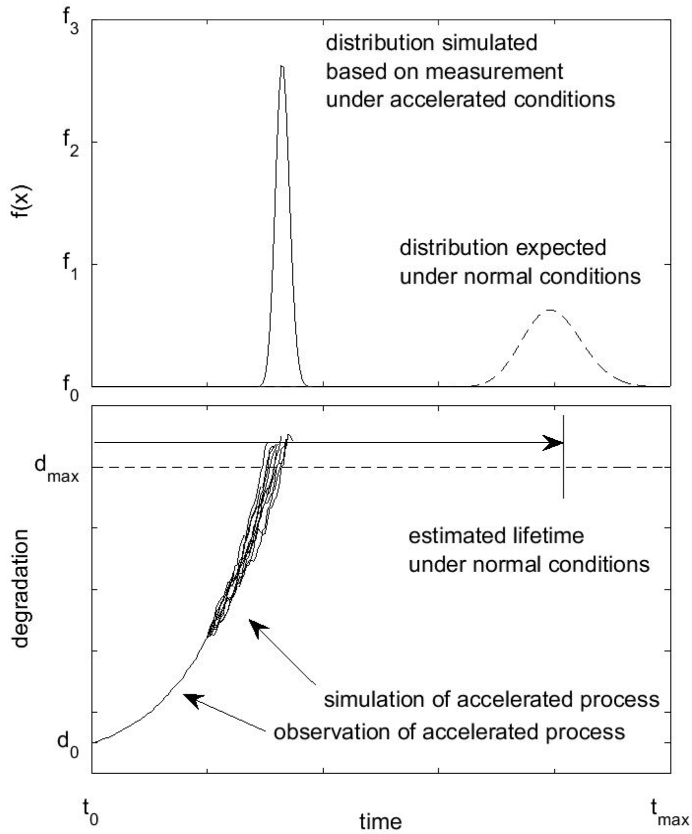

Fig. 3. Determination of the probability density function based on the observing times to parametric failure during accelerated ageing tests

In automotive industry, it is assumed that the reduction of capacitance by 20% in comparison to the nominal capacitance or the increase in equivalent series resistance by 100% should be regarded as the parametric failure of the supercapacitor. In such case, the capacitor should be withdrawn from operation (see Fig. 4).

The parameters of the supercapacitors may be determined during special diagnostic procedures or during their normal use. As in the case of classic capacitors, the values of the parameters are determined during their discharging cycle as it is shown in Fig. 5. The value of equivalent series resistance ESR is estimated on the basis of the voltage drop ΔU_{ESR} caused by the discharging current I_2, therefore

$$ESR = \frac{\Delta U_{ESR}}{I_2}, \tag{13}$$

while the capacitance C is determined on the basis of the change in voltage ΔU_C caused by the change in charge ΔQ_C over time Δt_C, therefore

$$C = \frac{\Delta Q_C}{\Delta U_C} = I_2 \frac{\Delta t_C}{\Delta U_C}. \tag{14}$$

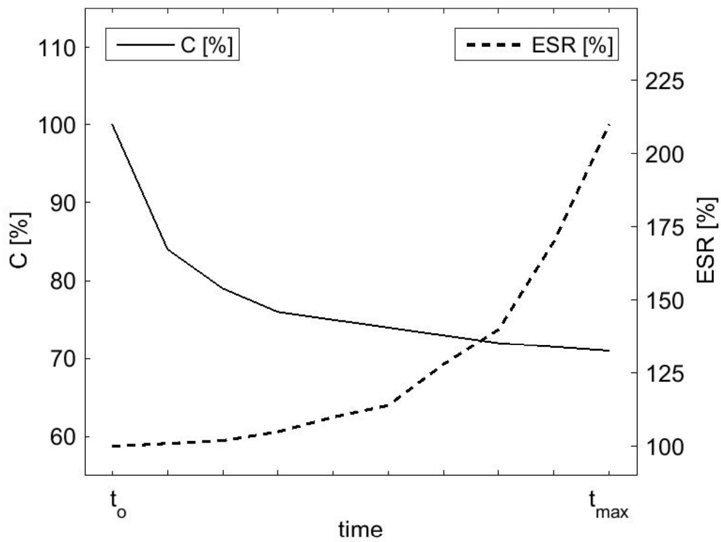

Fig. 4. Examples of relative changes in capacitance C and equivalent series resistance ESR of the supercapacitor over time

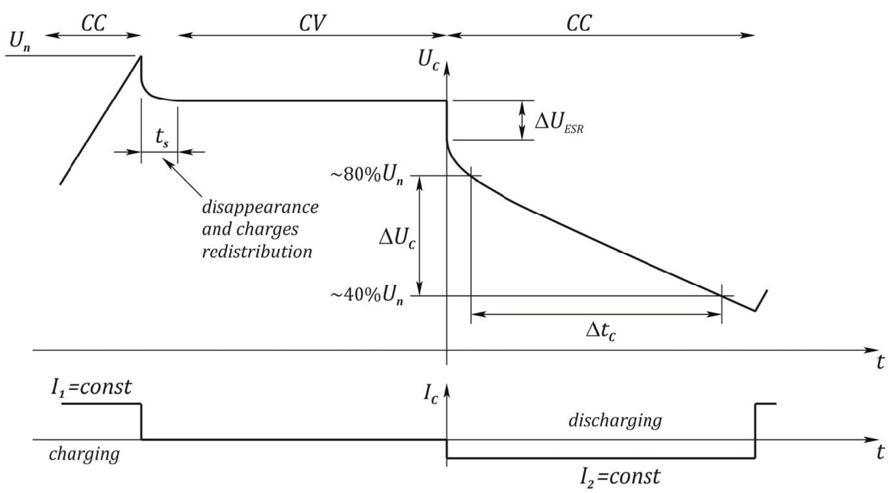

Fig. 5. The measurement procedure of the equivalent parameters of the supercapacitor determined during their discharging cycle

2.4. Acceleration of ageing processes

There are a few methods for accelerating the ageing processes of supercapacitors. The increase in temperature and also operating voltage may affecting the faster progress of degradation processes. The impact of these factors on the operation of electronic components is described by various mathematical models. For temperature, the coefficient accelerating the ageing processes is defined by the Arrhenius or Eyring equation. In case of the increase in voltage, the lifetime is estimated based on the so–called inverse power law [2, 6]. According to this, the value of the coefficient accelerating the ageing process is defined as

$$AF_U = \frac{T_N}{T} = \left(\frac{U}{U_N} \right)^{\delta}, \tag{15}$$

where U_N is the nominal operation value of the component, and U the increased voltage that accelerates the degradation processes. The value of the coefficient δ defines impact of the increase in voltage, and was estimated experimentally. The value of the coefficient accelerating the degradation processes AF_U, as defined above, will correspond to the coefficient k from equation (12) that renders it possible to undergo the scale process defining reliability under nominal operation conditions.

3. Measuring system and testing procedure

The tests on accelerated degradation procedures were conducted in the system shown in Fig. 6 [3]. The supercapacitors tested were placed in a temperature chamber that provided a constant reference temperature.

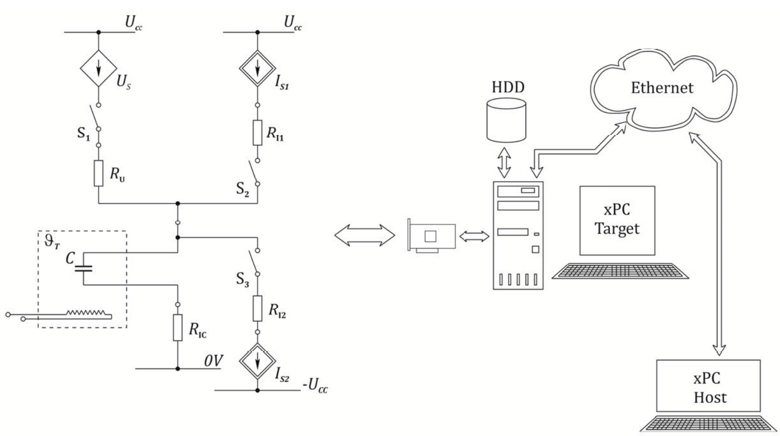

Fig. 6. Schematic diagram of the measurement system for supercapacitors testing [3]

The charging and discharging process was carried out by current sources I_{s1} and I_{s2}, whereas during the redistribution of charge cycle, the capacitors were connected to a voltage source U_S. The entire system was controlled and managed with the use of a computer equipped with the measuring card. The algorithm for the system operation was prepared in the Matlab program, while the results were saved on the hard drive of the target computer (xPC Target).

Two supercapacitors of nominal capacitance C_N = 10 F were tested. However, the capacitors differed in nominal voltage (U_{N1} = 2.7 V and U_{N2} = 2.5 V) and equivalent series resistance (ESR_{DC1} < 0.14 Ω and ESR_{DC2} < 0.16 Ω). For both capacitors the capacitance tolerance was defined as ±20%. The capacitors were charged and discharged with constant current $I_1 = I_2 = 1\text{A}$, for different values of upper charge voltage: 2.8 V, 3.2 V and 3.7 V for capacitor 1, and 2.7 V, 3.0 V and 3.3 V for capacitor 2 For each voltage the new supercapacitor was used. From several hundred to several thousand charging and discharging cycles were completed for each voltage. The parameters value of the supercapacitor were determined during its discharging cycle in accordance with Fig. 5, according to the equations (13) and (14).

4. Analysis of results

Figures 7a and 8a show the example fragment of discharging cycles of capacitor 1 and 2 for U_A = 3.7 V and U_A = 3.3 V voltages respectively. The values of capacitance and equivalent series resistance were determined on the basis of such cycles [5]. The obtained results of the changes in resistance are shown in Figures 7b and 8b. Based on the results, the parameters of the models of the geometric Brownian motion were estimated. The results of the measured value parameters of the models and the values of capacitance and resistance for particular voltages are shown in Table 3.1 for supercapacitor 1 and in Table 3.2 for supercapacitor 2. Additionally, the average time to parametric failure was estimated, i.e. until the simulated degradation process reached a value of 200% of the initial resistance.

Table 3.1. Estimated parameters of the degradation models and the measured values of the equivalent parameters of the supercapacitor obtained during the accelerated ageing tests for first supercapacitor

U_N = 2.7 V, C_N = 10 F, $ESR_{DC} \le 0.14\,\Omega$							
No.	U_A [V]	C_A [F]	ESR_A [Ω]	$\hat{\alpha}$	$\hat{\beta}$	$\overline{t_F} \pm k_\alpha u_{ct}$ [h]	$\bar{\delta}$
1	2	3	4	5	6	7	8
1	2.8	8.83	0.0425	6.61e–10	5.36e–3	268800±27204	17.17
2	3.2	8.91	0.0464	4.86e–9	4.91e–3	31344±748	
3	3.7	8.92	0.0530	5.02e–8	4.20e–3	2275±51	

The expanded uncertainty obtained by multiplying the combined standard uncertainty u_{ct} by a coverage factor k_{α}. Considering probability distributions of t and u_{ct} are approximately normal and the effective degrees of freedom of u_{ct} is of significant size, one can assume that taking k=2, produces an interval having a level of confidence of approximately 95%. The average values of the coefficient δ for the two capacitors were determined based on the estimated time to failure and taking into account the voltage accelerating the ageing processes.

Table 3.2. Estimated parameters of the degradation models and the measured values of the equivalent parameters of the supercapacitor obtained during the accelerated ageing tests for second capacitor

U_N = 2.5 V, C_N = 10 F, $ESR_{DC} \leq 0.16\ \Omega$							
No.	U_A [V]	C_A [F]	ESR_A [Ω]	$\hat{\alpha}$	$\hat{\beta}$	$\overline{t_F} \pm k_{\alpha} u_{ct}$ [h]	$\bar{\delta}$
1	2	3	4	5	6	7	8
1	2.7	9.49	0.1294	7.19e–8	5.98e–3	2640±8.5	16.37
2	3.0	9.58	0.1349	1.99e–7	5.85e–3	919±1.8	
3	3.3	9.79	0.1634	5.27e–7	5.97e–3	262±0.4	

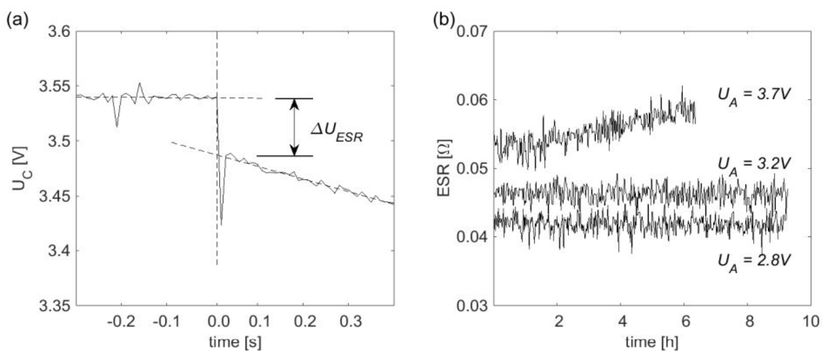

Fig. 7. The voltage drop ΔU_{ESR} at the series resistance ESR caused by the incorporation of discharging current I_2 =1 A for ageing voltage U_A = 3.7 V (a), and measured values of ESR for different voltages accelerated ageing processes (b), for capacitor 1

Assuming the estimated values of the model parameters for voltage U_A = 3.7 V, U_A = 3.2 V and U_A = 2.8 V for first supercapacitor, and for voltage U_A = 3.3 V, U_A = 3.0 V and U_A = 2.7 V for the second, the examples of degradation processes performances were generated and the time for the processes to reach the assumed threshold value was determined. Regarding these times as the time to failure, the distributions of probability density and reliability functions were determined for accelerated conditions. Then, considering the coefficient of accelerating the ageing process, the distributions of mentioned functions were determined for nominal conditions, i.e. for U_{N1} = 2.7 V and U_{N2} = 2.5 V.

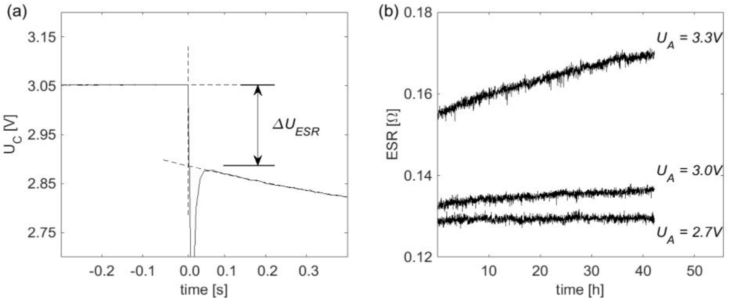

Fig. 8. The voltage drop ΔU_{ESR} at the series resistance *ESR* caused by the incorporation of discharging current I_2 =1 A for ageing voltage U_A = 3.3 V (a), and measured values of *ESR* for different voltages accelerated ageing processes (b), for capacitor 2

Based on model parameters calculated using measured data in *ESR* changing during degradation procedures for different accelerating voltage, the relative changes in series resistance were determined (Fig. 9).

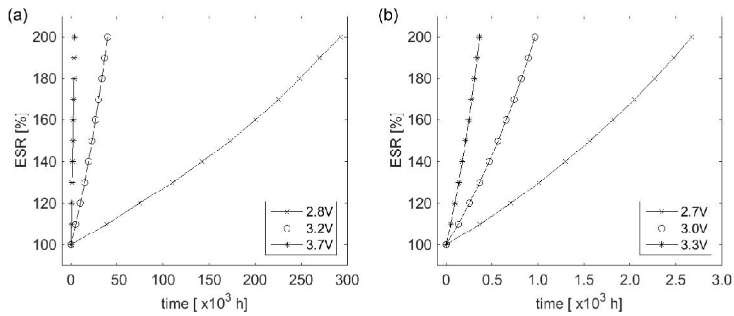

Fig. 9. Simulated relative changes in series resistance *ESR* of supercapacitor over time for tested supercapacitor: C_N= 10 F, U_N = 2.7 V (a) and C_N= 10 F, U_N = 2.5 V (b). Model parameters calculated based on measured changes in *ESR* during degradation procedures

5. Conclusions

The lifetime of supercapacitors can be defined based on the observation of changes of two its parameters: capacitance and equivalent series resistance. Over time these parameters undergo degradation, i.e. capacitance decreases and resistance increases. The results, presented in this article, of the lifetime estimation with the use of accelerated ageing tests were based only on the changes in series resistance. The time was determined by measuring the progressing degradation processes at their beginning, under accelerated conditions, and then their continuation was estimated by means of the simulation. Following this procedure for a few voltages allowed for the determination of the value of the coefficient accelerating the ageing process. As a result, the estimation of the lifetime under rated conditions was possible. The mathematical model called the geometric Brownian motion was introduced. The time to failure was determined as the time for the resistance value to reach 200% of the initial value, whereas multiple simulations allowed for the determination of the distribution of density and reliability functions.

The lifetime of capacitor 1 under nominal conditions was estimated to be 50 years, which exceeds the period of at least 10 years guaranteed by the producer. However, this results was obtained for a short observation period and is of comparatively high uncertainty. On the other hand, the lifetime estimated in the same way for supercapacitor 2 was only 2 years. This result was obtained on the basis of a 40–hour testing (over 2 thousand charging and discharging cycles).

The results confirm the possibility of using the suggested method to estimate the distribution of the reliability function under normal conditions. However, they require much longer observations in the initial period. In addition, the results concerning the changes in capacitance should also be considered in the estimation. Parallel to increasing voltage, changes in operating temperature may also be implemented as a factor accelerating the ageing process.

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