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SUPERCAPACITOR DEGRADATION ASSESMENT BY POWER CYCLING AND CALENDAR LIFE TESTS

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Abstract

Degradation of *Supercapacitors* (SC) is quantified by accelerated ageing tests. Energy cycling tests and calendar life tests are used since they address the real operating modes. The periodic characterization is used to analyse evolution of the SC parameters as a whole, and its Helmholtz and diffusion capacitances. These parameters are determined before the ageing tests and during 3×10^5 cycles of both 75% and 100% energy cycling, respectively. Precise evaluation of the capacitance and *Equivalent Series Resistance* (ESR) is based on fitting the experimental data by an exponential function of voltage vs. time. The ESR increases linearly with the number (No) of cycles for both 75% and 100% energy cycling, whereas a super-linear increase of ESR vs. time of cycling is observed for the 100% energy cycling. A decrease of capacitance in time had been evaluated for 2000 hours of ageing of SC. A relative change of capacitance is $\Delta C/C_0$ = 16% for the 75% energy cycling test and $\Delta C/C_0$ = 20% for the 100% energy cycling test at temperature 25°C, while $\Delta C/C_0$ = 6% for the calendar test at temperature 22°C for a voltage bias V = 1.0 Vop. The energy cycling causes a greater decrease of capacitance in comparison with the calendar test; such results may be a consequence of increasing the temperature due to the Joule heat created in the SC structure. The charge/discharge current value is the same for both 75% and 100% energy cycling tests, so it is the Joule heat created on both the equivalent series resistance and time-dependent diffuse resistance that should be the source of degradation of the SC structure. The diffuse resistance reaches a value of up to 30 Ω within each 75% energy cycle and up to about 43 Ω within each 100% energy cycle.

Keywords: supercapacitor equivalent circuit, supercapacitor parameter evaluation, supercapacitor reliability, power cycling life test, calendar life test.

1. Introduction

This paper gives an analysis of the impact of ageing modes on SC performance by monitoring the parameters of a physical-based equivalent circuit model [1]. Here, a *Supercapacitor* (SC) is modelled by a circuit consisting of two ideal capacitors, two resistors and one resistor with a time-dependent resistance value. The two capacitors are representing the capacitance of Helmholtz double layer C_H and the increase of capacitance due to diffusion of charges in the electrolyte C_D. The resistors are representing the *Equivalent Series Resistance* R_1 (ESR) and parallel leakage resistance R_p. The resistor with a time-dependent resistance $R_2(t)$ represents the resistance between the Helmholtz and diffuse capacitances. This resistance increases with the square root of time and compensates the decreasing probability for another charge carriers' transport by diffusion [1].

The SC cells have a high life-cycle because of the chemical and electrochemical inertness of the activated carbon electrodes. However, in a time scale of months, experience shows

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a fading performance – decreasing capacitance and increasing ESR [1–6]. It is considered that the possible sources of these changes are mainly a decrease of the effective area of electrodes and/or a change of electrolyte conductivity.

Two experimental methods were used to examine SC ageing:

- The energy cycling tests – continuous 75% and 100% energy tests at temperature 25°C. An energy cycling test is based on applying periodic charge/discharge current pulses up to a maximum operating voltage (Vop). The aim is to determine if the variable electric field and the induced self-heating could lead to a degradation process of capacitance, leakage current [3, 7] and ESR. The charge/discharge current value was the same for both 75% and 100% energy cycling tests, hence the duration of one 100% energy cycle was about two times longer than one 75% energy cycle.
- The calendar life tests at different voltages and temperatures. In these tests, the stored energy of SC is sustained by maintaining the voltage at a constant value. We will present the results for temperatures $T = 22$°C and $T = 45$°C for a voltage bias of 0.8 Vop, 1.0 Vop and 1.2 Vop.

The parameters of a physical-based equivalent circuit model, as: Helmholtz and diffuse capacitances, equivalent series resistance and time-dependent diffuse resistance, were periodically evaluated during application of these ageing tests. The time evolution of the analyzed parameters serves as an indicator determining the degradation sources.

2. Experiment setting

The experiments were carried out on an HC SERIES ULTRACAPACITORS Maxwell part number BCAP0010P270T01 with a nominal capacitance of 10 F and the maximum operating voltage Vop = 2.7 V. The experimental data for a set of 9 samples are presented.

The voltage profile for the energy cycling tests is schematically shown in Fig. 1. The charging/discharging current value was 2.7 A for both 75% and 100% energy cycling tests. The duration of one cycle was approximately 20 seconds for the 100% energy cycle, and about 10 seconds for the 75% energy cycle. The real duration of the cycles depends on the capacitance of measured sample, which decreases as a result of cycling. We have recorded the total duration of each of 10^5 testing cycles. The samples examined in the 75% energy cycling tests are denoted as M23 to M25, whereas in the 100% energy cycling tests – as M17 to M19.

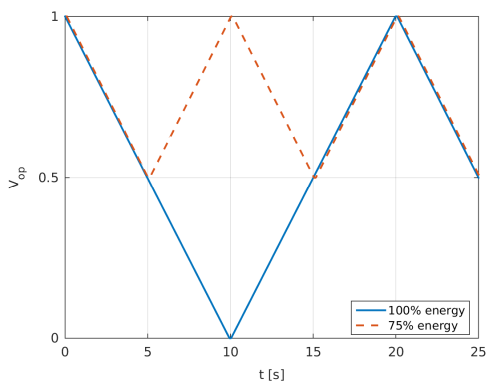

Fig. 1. A schematic voltage profile for the energy cycling tests: for the 100% test – blue solid line, for the 75% test – red dashed line (for the charge/discharge current 2.7 A).

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The calendar life tests are presented for samples: M27 (temperature 22°C, voltage bias 1.0 Vop), M32 (temperature 22°C, voltage bias 1.2 Vop), and M43 (temperature 45°C, voltage bias 0.8 Vop).

3. Evaluation of Equivalent Electrical Circuit parameters

The *Equivalent Electrical Circuit* (see Fig. 2) has five parameters: C_1 corresponding to the Helmholtz capacitance C_H, C_2 corresponding to the diffuse capacitance C_D, R_1 representing the ESR, R_p representing the leakage resistance, and $R_2(t)$ representing the time-dependent resistance between the Helmholtz and diffuse capacitances [1]. The experiment for precise evaluation of these parameter values is described in [1] and [3].

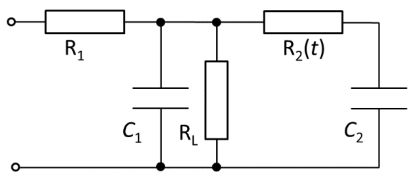

Fig. 2. The equivalent electrical circuit model of a supercapacitor [1].

An SC is charged with a defined current until the voltage at its terminals reaches the rated value of 2.7 V. It is assumed that the response to a controlled fast charging process is determined mainly by the Helmholtz capacitance parameters. The value of charging current must be as high as possible to provide the desired fast charging but a very high charging current is not recommended as it may thermally affect the capacitor parameters. We have used a charging current $I_C = 5$ A for SC Maxwell-10F/2.7V. The charging time Δt of SC is equal to about 5 seconds (see Fig. 3). After that period the terminal voltage is monitored for 2000 seconds (see Fig. 4).

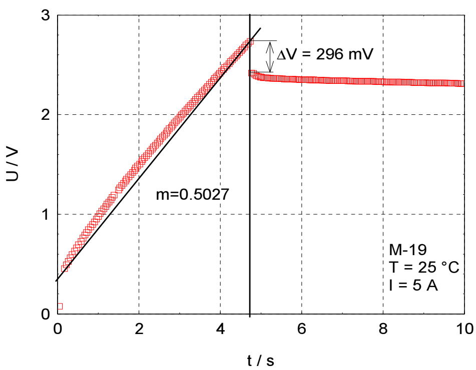

Fig. 3. The voltage at the SC terminals vs. time for the Maxwell M19 sample for a time interval from 0 to 10 s (charging current $I_C = 5$ A).

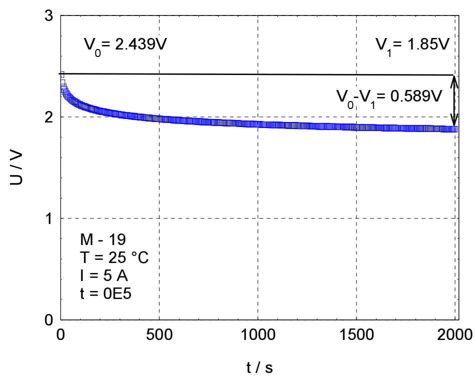

Fig. 4. The voltage at the SC terminals vs. time for the Maxwell M19 sample for a time interval from 0 to 2000 s.

Identification with a high accuracy requires minimization of the effect of measurement setup transient phenomena on the beginning and end of a current charging pulse. Therefore, we propose a method based on an analytical description of the SC terminal voltage [1].

3.1. Determination of voltage V_0 at the beginning of charging the diffuse capacitance

The voltage V_0 at the beginning of charging the diffuse capacitance (see Fig. 4) cannot be deduced from the sampled voltage value due to the transient phenomena of a step voltage change at SC terminals at the end of charging and due to the time delay between two successive measurements. Precise evaluation of the voltage V_0 at the beginning of charging the diffuse capacitance is based on fitting the experimental data by an exponential function of voltage vs. time in a time interval of 1 second, where the drift of charges in electric field is considered as the dominant charge carriers' transport mechanism:

$$V = V_{01} + \Delta V_{01} \exp(-t/\tau_0), \tag{1}$$

where: V_{01} is the value of voltage in infinity in the case when only the drift of charges is pronounced; ΔV_{01} is the voltage drop due to transfer of the charges by the drift only; and τ_0 is a time constant characterising redistribution of the charges by the drift in the SC structure.

We will fit the data in a time interval from 0 to 1 s (see Fig. 5), where the drift current component is dominant for this type of SC [1].

For the M19 sample the voltage $V_0 = V_{01} + \Delta V_{01}$ at the beginning of charging the diffuse capacitance is $V_0 = 2.439$ V (see Fig. 5, measured at temperature $T = 25$°C for the charging current $I_C = 5$ A). The voltage drop ΔV, caused by switching off the charging current, depends on the charging current value and ESR (resistance R_1).

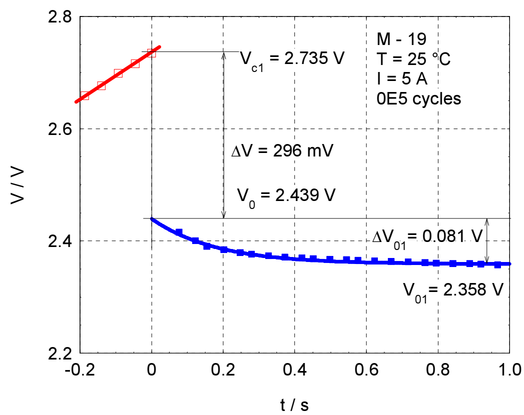

Fig. 5. The time dependence of the voltage at the SC terminals measured for the M19 sample before the energy cycling test at temperature $T = 25$°C (charging current $I_C = 5$ A).

The equivalent series resistance R_1 can be calculated as:

$$R_1 = \Delta V / I_C. \tag{2}$$

Considering the charging current $I_C = 5$ A and the voltage drop $\Delta V = V_{c1} - V_0 = 296$ mV, we obtain the value of $R_1 = 59.2$ mΩ prior to the ageing tests.

Similar estimation of SC parameters was performed after 1×10^5 cycles of the 100% energy cycling test. The voltage at the beginning of charging the diffuse capacitance was $V_0 = 2.402$ V and the voltage drop due to the switching off the charging current was $\Delta V = 376$ mV. Then the ESR $R_1 = 75.2$ mΩ. The equivalent series resistance R_1 increased by about 16 mΩ during 1×10^5 cycles of the 100% energy cycling test.

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3.2. Helmholtz, diffuse and total capacitances

Let us define the following parameters:

1. The Helmholtz capacitance C_H depends on the total charge Q_T delivered to the SC and on the voltage V_0 at the beginning of charging the diffuse capacitance :

$$C_H = Q_T/V_0. \tag{3}$$

2. The total capacitance C_T is given by the total charge Q_T and the voltage V_1 (see Fig. 3):

$$C_T = Q_T/V_1. \tag{4}$$

3. The diffuse capacitance is the difference between the total and Helmholtz capacitances:

$$C_D = C_T - C_H. \tag{5}$$

The value of voltage V_1, obtained from fitting the experimental data, can be with a sufficient accuracy substituted by the voltage value measured at the moment $t = 2000$ s. Then, the capacitances for the equivalent electrical circuit model can be calculated.

All parameters evaluated for the Maxwell M19 sample before the power cycling and after 1×10^5 cycles of the 100% energy cycling test are shown in Table 1.

Table 1. The constants evaluated from the experimental data and parameters of the equivalent electrical circuit model calculated for the Maxwell M19 sample before and after 1×10^5 cycles of the 100% energy cycling test.

No Cycles	V_0 / V	V_1 / V	Q_T / C	C_H / F	C_T / F	C_D / F	τ_2 / s	R_{D0} / $\Omega s^{-0.5}$
0	2.439	1.85	23.30	9.55	12.60	3.05	258	13.61
1×10^5	2.402	1.97	21.15	8.81	10.74	1.93	130	14.41

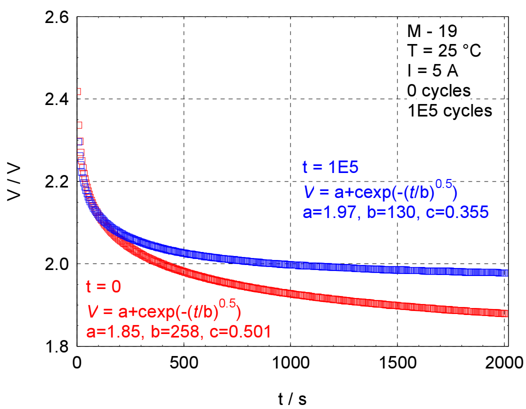

Fig. 6. The voltage at the SC terminals vs. time for the Maxwell M19 sample, experimental data and fitting equation, before (red) and after (blue) 1×10^5 cycles of the 100% energy cycling test.

When charging is switched off, the voltage at the SC terminals decreases over the monitored time interval of 2000 s from value V_0 (see Fig. 3) due to charging of the diffuse capacitance.

The time dependence of voltage at the capacitor terminals is described by [1]:

$$V = V_1 + V_2 \exp(-\sqrt{t/\tau_2}), \tag{6}$$

where: the voltage V_1 is the voltage value at infinity; V_2 is the voltage drop due to charging the capacitance, and τ_2 is a time constant of diffusion process.

Figure 6 shows the experimental data of the time dependence of voltage at the SC terminals (before the power cycling and after 1×10^5 cycles of the 100% energy cycling test, respectively). These data are fitted by a function given in (6). The constants from the data fit are included in Table 1.

3.3. Resistance R_D between Helmholtz and diffuse capacitances

The resistance R_D between Helmholtz and diffuse capacitances is given by (see [1]):

$$R_D = 2\frac{V_0 \cdot \sqrt{\tau_2}}{C_D \cdot V_1}\sqrt{t} = R_{D0}\sqrt{t}\,, \tag{7}$$

where: V_0 is the voltage at the beginning of charging the diffuse capacitance; τ_2 is a time constant of diffusion process; V_1 is an expected value of voltage at infinity; C_D is the diffuse capacitance, and R_{D0} is the diffuse resistance parameter which is equal to the resistance R_D value at the moment $t = 1$ s.

The value of resistance R_D between Helmholtz and diffuse capacitances is proportional to the root of time. The diffuse resistance parameter R_{D0} is given by:

$$R_{D0} = 2\frac{V_0 \cdot \sqrt{\tau_2}}{C_D \cdot V_1}. \tag{8}$$

The value of diffuse resistance parameter R_{D0} depends on the parameters of equivalent circuit and time constant τ_2 of ions diffusion. The diffuse resistance R_D vs. time calculated for data from Table 1 is shown in Fig. 7 for the Maxwell M19 sample before the cycling test and after 1×10^5 cycles of the 100% energy cycling test, respectively.

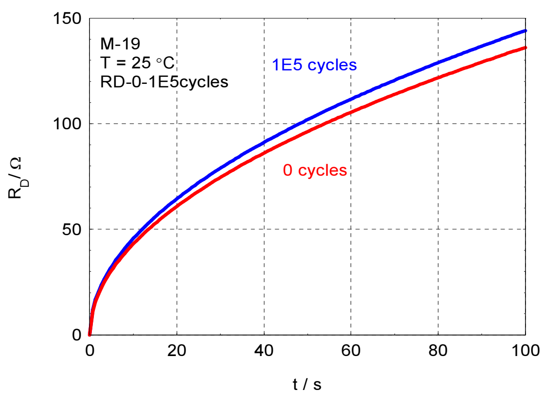

Fig. 7. The resistance R_D between Helmholtz and diffuse capacitances vs. time calculated for the Maxwell M19 sample before (red) and after (blue) 1×10^5 cycles of the 100% energy cycling test, the determined values of diffuse resistance parameter are: $R_{D0} = 13.61\ \Omega s^{-0.5}$ (before) and $R_{D0} = 14.41\ \Omega s^{-0.5}$ (after) 1×10^5 cycles of the 100% energy cycling test.

Ageing of SC with an energy cycling test induces the increase of the value of resistance R_D between Helmholtz and diffuse capacitances. However, the effect is small, because both the diffuse capacitance and time constant τ_2 of diffusion process decrease during ageing.

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3.4. Differential capacitance

A voltage-dependent value of capacitance is determined by the SC physical construction. We identify the capacitance from the charge vs. voltage curve determined for the charging or discharging with a constant current I_C (see Fig. 8). The charge is calculated as $Q = I_C \cdot t$, where t is the duration of charging.

The dependence of the stored electric charge Q on voltage (see Fig. 8) can be approximated by the 2nd order function:

$$Q = C_{H0}V + \tfrac{1}{2}C_{H1}V^2, \tag{9}$$

where: C_{H0} is the Helmholtz or immediate capacitance and C_{H1} is a constant which characterizes the voltage dependence of SC capacitance.

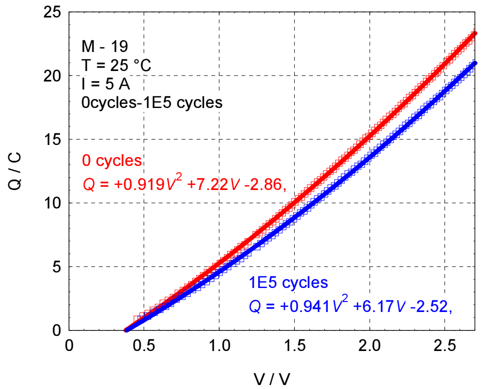

Fig. 8. The electric charge Q vs. voltage for the Maxwell M19 sample for charging with a constant current I_C = 5 A before (red) and after (blue)1 × 10^5 cycles of the 100% energy cycling test.

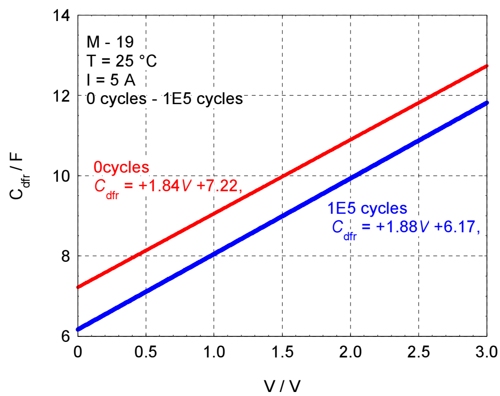

Fig. 9. The differential capacitance C_{dfr} vs. voltage bias V for the Maxwell M19 sample for charging with a constant current I_C = 5 A before (red) and after (blue) 1 × 10^5 cycles of the 100% energy cycling test.

The differential capacitance C_{dfr} increases linearly with the voltage bias V and it decreases after the energy cycling test (see Fig. 9). We have derived the dependence of the differential capacitance on the voltage bias before and after 1 × 10^5 cycles of the 100% energy cycling test as:

– before cycling – 0 cycles $\qquad C_{dfr} = 7.22 + 1.84\ V$;

– after 1×10^5 cycles of 100% energy cycling test $C_{dfr} = 6.17 + 1.88\ V$.

The differential capacitance C_{dfr} decreases during an energy cycling test, whereas its first derivative vs. voltage is approximately constant, as shown in Fig. 9.

4. Results of ageing tests

We will give the obtained values of SC equivalent circuit parameters as changes (during ageing) of: equivalent series resistance R_1, total C_T, Helmholtz C_H, and diffuse C_D capacitances, and resistance R_D between Helmholtz and diffuse capacitances.

4.1. Equivalent Series Resistance R_1

The *Equivalent Series Resistance* R_1 is one of the most important parameters due to the losses of SC energy represented by the Joule heat created on R_1. In Fig. 10-left it is shown that the average value of ESR R_{1aver} calculated for samples M17 to M19 and samples M23 to M25, respectively, increases with No of cycles linearly with slopes: $s_{100} = 1.17 \times 10^{-4}$ mΩ/cycle for the100% cycling test and $s_{75} = 5.25 \times 10^{-5}$ mΩ/cycle in 3×10^5 cycles for the 75% cycling test.

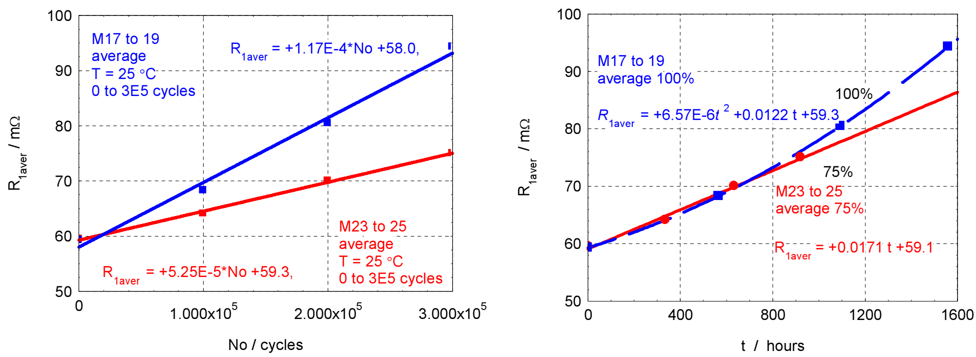

Fig. 10. The average value of ESR R_{1aver} vs. number of cycles (left) and vs. time (right) for the 75% energy cycling test (samples M23 to M25) and 100% energy cycling test (samples M17 to M19).

As mentioned before, the duration of one cycle was approximately 20 seconds for the 100% energy cycle, and about 10 seconds for the 75% energy cycle. However, the real duration of a cycle decreases in time due to decreasing the capacitance value. The capacitance decrease within the 75% energy cycling test is smaller in comparison with the 100% energy cycling test, because the duration of 1×10^5 cycles of 100% energy cycling test is 566 hours while the duration of 1×10^5 cycles of 75% energy cycling test is about 316 hours. The dependence of the average value of equivalent series resistance R_{1aver} on the duration of cycling tests is shown in Fig. 10-right. We can see that the ESR increases linearly with time of cycling for the 75% energy cycling test, while a super-linear increase of ESR vs. time of cycling is observed for the 100% energy cycling test.

4.2. Total capacitance variation with energy cycling test

The dependences of the average value of total capacitance C_T on the number of cycles and on the duration of cycling, for the 75% and 100% energy cycling tests are shown in Fig. 11.

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We suppose that the mathematical law which describes the process of ageing is an exponential function of square root of time which well fits with our previous SC degradation analyzes [8].

The dependence of total capacitance C_T on the number of cycles for both 75% and 100% energy cycling tests (see Fig. 11-left) can be fitted by an exponential function of square root of number of cycles as:

$$C_T = C_{T1} + C_{T2}\exp\left(-\sqrt{x/\tau_C}\right), \tag{10}$$

where: x is the number of cycles; C_{T1} is the capacitance value for the number of cycles at infinity; C_{T2} is the capacitance decrease factor; and τ_C is a time constant of the energy cycling degradation process given in the number of cycles. The values of these parameters obtained from the experimental data fits are shown in Table 2.

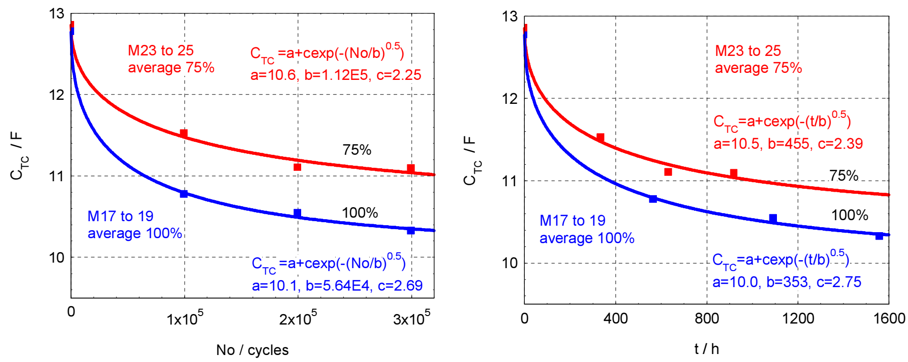

Fig. 11. The average value of total capacitance C_T vs. number of cycles (left) and vs. time (right) for the 75% energy cycling test (samples M23 to M25) and 100% energy cycling test (samples M17 to M19).

Table 2. The constants evaluated from the experimental data fit of average value of total capacitance C_T vs. number of cycles – for the 75% (samples M23 to M25) and 100% (samples M17 to M19) energy cycling tests.

Cycling test	C_T (t = 0 s) / F	C_{T1} / F	C_{T2} / F	τ_C / cycles	C_{T1} / C_T (t = 0 s)
75% energy	12.85	10.6	2.25	1.12×10^5	0.825
100% energy	12.79	10.1	2.69	5.64×10^4	0.790

The value of constant τ_C of the energy cycling degradation process depends on the amount of energy changed in one cycle. For the 75% energy cycling test it is about twice smaller than for the 100% energy cycling test.

The dependence of total capacitance C_T on time of ageing for 75% and 100% energy cycling tests (see Fig. 11 right) can be fitted by an exponential function of square root of time:

$$C_T = C_{T1} + C_{T2}\exp\left(-\sqrt{t/\tau_h}\right), \tag{11}$$

where: t is time in hours; C_{T1} is the capacitance value for the time of ageing at infinity; C_{T2} is the capacitance decrease due to cycling; and τ_h is a time constant of the energy cycling degradation process in hours. The values of these parameters obtained from the experimental data fits are shown in Table 3.

Table 3. Constants evaluated from the experimental data fit of average value of total capacitance C_T vs. time of cycling – for the 75% (samples M23 to M25) and 100% (samples M17 to M19) energy cycling tests.

Cycling test	C_T (t = 0 s) / F	C_{T1} / F	C_{T2} / F	τ_h / hour	C_{T1} / C_T (t = 0 s)
75% energy	12.89	10.5	2.39	455	0.815
100% energy	12.75	10.0	2.75	353	0.784

The value of constant τ_h of the energy cycling degradation process depends on the amount of energy dissipated in a sample volume within one hour. For the 75% energy cycling test it is by about 30% higher than for the 100% energy cycling test. Fig. 10-right shows that the ESR value is comparable in time for the samples subjected both to 75% and to 100% energy cycling tests. We suppose that the additional energy dissipation occurs on the diffuse resistance R_D. The diffuse resistance is time-dependent and it reaches the value of up to 30 Ω within each 75% energy cycle, and to about 43 Ω within each 100% energy cycle.

4.3. Helmholtz capacitance C_H variation with energy cycling test

The mean values of Helmholtz capacitance C_H determined within 3×10^5 cycles of 100% energy cycling test (samples M17 to M19), and 75% energy cycling test (samples M23 to M25), respectively, are given in Table 4. The relative change of Helmholtz capacitance with respect to the initial C_H value before cycling is also calculated.

Table 4. The mean values of Helmholtz capacitance C_H and the calculated relative change of Helmholtz capacitance ΔC_H with respect to the initial C_H value before cycling – for the 75% (samples M23 to M25) and 100% (samples M17 to M19) energy cycling tests.

Number of cycles	C_H / F		ΔC_H /%	
	100% energy	C75% energy	100% energy	75% energy
0	9.54	9.74	100	100
1×10^5	8.97	9.43	94.0	96.8
2×10^5	8.52	9.13	89.3	93.7
3×10^5	8.31	9.04	87.1	92.8

The Helmholtz capacitance C_H decreases with the number of cycles for both 75% and 100% energy cycling tests. The average value of Helmholtz capacitance decreases by about 7% for the 75% energy cycling test and by about 13% for the 100% energy cycling test within 3×10^5 cycles.

4.4. Diffuse capacitance C_D variation with energy cycling test

The mean values of diffuse capacitance C_D determined within 3×10^5 cycles of the 100% energy cycling test (samples M17 to M19), and the 75% energy cycling test (samples M23 to M25), respectively, are given in Table 5. The relative change of diffuse capacitance with respect to the initial C_D value before cycling is also calculated.

The average value of diffuse capacitance C_D before the ageing tests was about 3 F, dropping to about 2 F after 1×10^5 cycles for both 75% and 100% energy cycling tests. Thus, it remains approximately stable with additional cycling (see Table 5).

The relative value of lowering the diffuse capacitance is about 30% within 1×10^5 cycles, whereas the Helmholtz capacitance C_H lowers by only about 6%. It follows from this result that lowering the total capacitance cannot be caused only by the change of the effective area of SC electrodes, but another process (like lowering concentration of electrolyte ions)

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is probably involved. The decrease of electrolyte conductivity is in good correlation with the increase of ESR R_1 value during the cycling tests.

Table 5. The mean values of diffuse capacitance C_D and the calculated relative change of diffuse capacitance ΔC_D with respect to the initial C_D value before cycling – for the 75% (samples M23 to M25) and 100% (samples M17 to M19) energy cycling tests.

Number of cycles	C_D / F		ΔC_D /%	
	100% energy	C75% energy	100% energy	75% energy
0	3.08	3.19	100	100
1×10^5	2.09	1.90	67.9	59.6
2×10^5	1.97	1.96	64.0	61.4
3×10^5	2.05	2.05	66.6	64.3

5. Degradation due to calendar life tests

In these tests, the stored energy of SC is sustained by maintaining a constant value of voltage. During the whole experiment, a dedicated floating test bench is capable to measure such SC parameters as: its leakage current, DC capacitance, equivalent series resistance R_1 and AC parameters. The calendar life tests have been performed at different voltages and temperatures. The results of periodic characterization of capacitance have been used to monitor evolution of the SC parameters.

5.1. Effect of electric field and temperature on degradation of capacitance during calendar life test

The results of calendar life test experiments performed during 2000 hours at temperature 25°C for voltage 1.0 Vop = 2.7 V (red curve), and voltage 1.2 Vop = 3.24 V (blue curve) and at temperature 45°C for voltage 0.8 Vop = 2.16 V (black curve) are shown in Fig. 12.

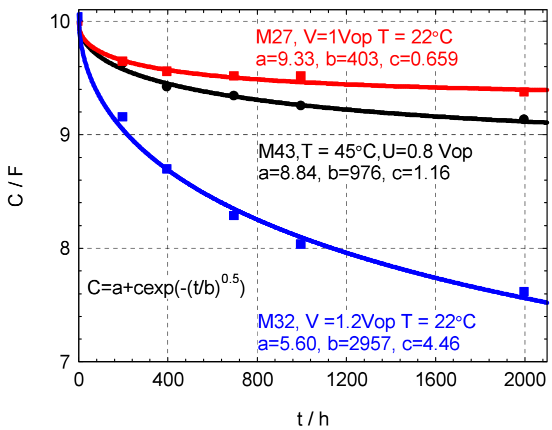

Fig. 12. The capacitance C vs. time of ageing for the samples: M27 at T = 22°C and V = 2.7 V – red curve, M32 at T = 22°C and V = 3.24 V – blue curve, and M43 at T = 45°C and V = 2.16 V – black curve.

The capacitance C vs. time of ageing can be fitted by an exponential function of square root of time:

$$C = C_1 + C_2 \exp\left(-\sqrt{t/\tau_h}\right), \tag{12}$$

where: t is time in hours; C_1 is the capacitance value for time of ageing at infinity; C_2 is the capacitance decrease due to the calendar life test and τ_h is a time constant of the capacitance degradation process. The values of these parameters obtained from the experimental data fits are shown in Table 6. Increasing both the electric field and temperature accelerates the decrease of capacitance value. The increase in voltage and temperature accelerates the electrochemical reactions responsible for degradation of capacitance.

Table 6. The constants evaluated from the experimental data fit of capacitance C vs. time of ageing for the calendar life test on samples M27, M32, and M43.

Cycling test	$C(t = 0$ s$)$ / F	C_1 / F	C_2 / F	τ_h / hour	$C_1 / C(t = 0$ s$)$
M27 (22°C/1.0 V_{op})	9.989	9.33	0.659	403	0.934
M32 (22°C/1.2 V_{op})	10.06	5.60	4.46	2957	0.557
M43 (45°C/0.8 V_{op})	10.00	8.84	1.16	976	0.884

5.2. Effect of self-heating and variable electric field on degradation of capacitance

We will compare the effect of power cycling tests with that of calendar life tests in order to determine if the induced self-heating could lead to different degradation processes. In both cases, the voltage and temperature have a major impact on ageing, which can be caused by parasitic reactions due to the intrinsic impurities of materials.

It was observed that the induced self-heating increases temperature of SC by about 20°C. If temperature was the only source of degradation, the SC capacitance vs. time of ageing for the calendar life test at 45°C would be very close to the dependences for 75% and 100% energy cycling tests.

The relative values of capacitance C/C_0 vs. time of ageing are shown in Fig. 13, where the red curve corresponds to the mean value of total capacitance determined for samples M23 to M25 (75% energy cycling test), the blue curve corresponds to the mean value of total capacitance determined for samples M17 to M19 (100% energy cycling test), and the black curve corresponds to the capacitance measured during the calendar life test for sample M43 (45°C/0.8 Vop).

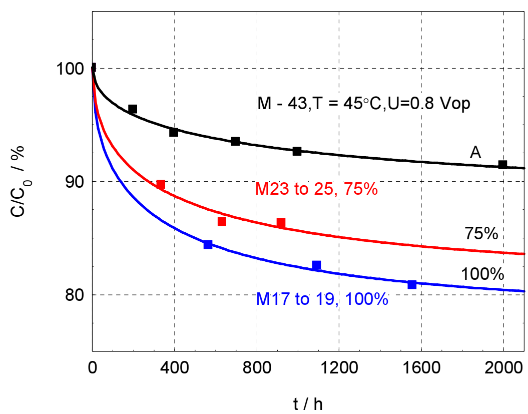

Fig. 13. The relative values of C/C_0 capacitance vs. time of ageing, where the red curve corresponds to the 75% and the blue curve to 100% energy cycling tests at temperature $T = 25$°C, and the black curve – to the calendar test at temperature $T = 45$°C and voltage $V = 0.8$ Vop.

The capacitance decrease during initial 2000 hrs of ageing is:

- C(2000h)/C_0 = 9% for calendar test 45°C/0.8 Vop;
- C(2000h)/C_0 = 16.3% for 75% energy cycling test;
- C(2000h)/C_0 = 19.5% for 100% energy cycling test.

We can see that the impact of elevated temperature 45°C on the capacitance decrease is not equal to the impact of the temperature increase due to the current cycling. The impact of the variable electric field must be taken into account as an additional source of degradation.

6. Conclusion

Ageing of SC with energy cycling tests has a higher effect on the diffuse capacitance which decreases after 1×10^5 ageing cycles by about 30%, while the Helmholtz capacitance C_H decreases by only about 6%. It follows from this results that lowering the total capacitance cannot be caused only by changing the effective area of SC electrodes, but another process, like lowering concentration of electrolyte ions, is probably involved.

Ageing SC with energy cycling tests induces the increase of the value of resistance R_D between the Helmholtz and diffuse capacitances. However, this effect is small because during the ageing both the diffuse capacitance and time constant τ_2 of the diffusion process decrease.

The equivalent series resistance R_1 increases linearly with No of cycles for both types of cycling tests. The ESR increases linearly with time of cycling for 3×10^5 cycles of the 75% energy cycling test, while a super-linear increase of ESR vs. time of cycling is observed for 3×10^5 cycles of the 100% energy cycling test. The decrease of electrolyte conductivity is in good correlation with degradation of the equivalent series resistance R_1.

The degradation process in SC structure depends on the amount of energy dissipated in a sample volume. The capacitance decrease in time is by about 30 % lower for the 75% energy cycling test than for the 100% energy cycling test. The ESR value is comparable – within a period of initial 1000 hours – for samples subjected to both cycling tests.

We suppose that the additional energy dissipation occurs on the diffuse resistance R_D. The diffuse resistance is time-dependent and it reaches a value of up to 30 Ω within each 75% energy cycle, while to about 43 Ω within each 100% energy cycle.

The results from the calendar life tests show that increasing both the electric field and temperature accelerate decreasing the capacitance value.

There are at least three sources of degradation of SC parameters: (i) decreasing the capacitor area, (ii) lowering the electrolyte conductivity and (iii) the impact of variable electric field.

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