Supercapacitor Degradation and Reliability

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Abstract

Degradation of supercapacitor (SC) is analyzed by accelerated aging test. Evolution of SC parameters is determined before the aging test, and during up to 8×10^5 cycles of both 75% and 100% energy cycling. Capacitance fading, equivalent series resistance (ESR) increase, and leakage current trend are analyzed for off-the-shelf CapXX SC. Presented model consists of five parameters. These are Helmholtz and diffuse double layer capacitances, responsible for SC overall capacity. Next there is time dependent resistance in between Helmholtz and diffuse capacitances. And an ordinary ESR, and resistance responsible for SCs leakage current. Fading of both capacitances is modeled by exponential equation. Increase of ESR AC component is modeled by linear function.

Keywords

Supercapacitor, Aging test, Capacitance fading, Equivalent series resistance fading, Leakage current fading, Life-time

Introduction

This paper analyses the impact of aging modes on supercapacitor (SC) performance through the monitoring of several parameters of a physical-based five parameter equivalent circuit model. Here the SC is modeled by circuit, consisting of two ideal capacitors, two regular resistors, and one resistor with time dependent resistance value. Capacitors mentioned represent the capacitance of Helmholtz double layer C_1 and the increase of capacitance due to the diffusion of charges in the electrolyte C_2. The two ordinary resistors are the equivalent series resistance (ESR) R_1 and parallel leakage resistance R_L. The time dependent resistance $R_2(t)$ represents the impedance between C_1 and C_2. This resistance is time dependent, it increases with the square root of time of charging and covers the decreasing probability for another charge carriers' transport by diffusion. [1]. Diagram of this model is shown in Fig. 1. The utilization of this model helps in reliable estimation of sample's total capacitance, as it is not subjected to error caused by disregarding the diffusion capacitance.

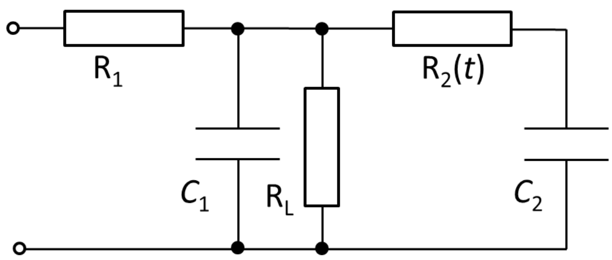

Fig. 1: basic two-branch equivalent circuit model with time dependent diffuse resistance [1]

In theory, SC is supposed to have infinite cycle life. This is due to the electrochemical inertness of both its main components, activated carbon electrodes and electrolyte. In practice though, substantial fading of SC parameters is observed. This fading is going on in the time scale of months, while under use, and consists of total capacitance decrease and ESR increase. [1-6]

Three kinds of aforementioned aging methods were implored for given SC samples. These are described in the remainder of the introduction. Parameters of a physical-based equivalent circuit were evaluated several times during the run of these aging tests. The time evolution of all the studied parameters serves as the indicator for the degradation sources determination. Next, the experiment is described, results are given and discussed, and lastly this paper is concluded.

CONTINUOUS ENERGY CYCLING TESTS

In order to artificially inflict the kind of damage SC sustains during its normal operation, two experimental continuous energy cycling methods were devised to test it. Both methods are based on SC basic work profile during its actual deployment. Namely they are referred to as "continuous 75% energy cycling" and "continuous 100% energy cycling" tests, where the percentage corresponds to the amount of SC energy, that is transferred in and out of the sample within every cycle.

Energy stored in conventional capacitor is given by first part of equation (1). By introducing the relation $dQ = C\,dV$, the second part of (1) may be extrapolated:

$$E = \int V\,dQ = \frac{1}{2} C V^2 \, , \tag{1}$$

where V is potential on SC terminals and C is its equivalent capacitance. [2]

These tests are based on periodic constant current charge pulses up to SC maximum operating voltage V_{op} during every aging cycle. It then must be discharged by constant current back to 0 V in order for 100% of the energy to shift in and out. Or (from (1)) back to ½ V_{op} to shift 75% of the energy in and out of the sample. The aim of these tests is to determine if the variable electric field and the induced self-heating could lead to degradation of capacitance, leakage current, and ESR of the device.

It has been said that these tests require constant current pulses. Both charge and discharge currents are set to be equal and are calculated, using the basic relation $Q = I \cdot t$ to take short amount of time, usually within a minute. In addition it is customary to set the same current for both 75% and 100% energy tests, so that the effect of induced Joule heat is the same for both. [7] This has the consequence, that single cycle of 100% energy test takes twice as long on average as 75% energy test.

It is to be noted, that the required charge/discharge current is calculated in advance, using the nominal capacitance of brand new sample. Therefore the actual duration of single cycle shrinks as the aging progresses. This is due to both the sample total capacitance decrease, as it is capable of holding less charge while aged, and ESR increase (this effect is described later).

DISCONTINUOUS ENERGY CYCLING TEST

To simulate the sporadic load work profile of some applications, the discontinuous energy cycling test was devised. In this "discontinuous 75% energy cycling" test, the device is charged and discharged in the same fashion as for the analogous continuous test, with the single difference being an additional wait interval immediately after both charge and discharge segments. Note, that within the dead time period, the diffuse capacitance of sample gets charged or discharged gradually as the SC remains in open circuit condition.

The duration of the dead time interval is calculated to be equal to the charging and discharging times at the beginning of the aging. As SC parameters fade, the charging and discharging period shortens, but the dead time interval does not change. Therefore single dead time interval corresponds to ¼ of the cycle at the beginning of the aging and becomes larger in proportion to charge/discharge segments as the cycling progresses. It is important to notice that due to differing cycle duration the 8×10^5 cycles of 75% continuous test corresponds time wise to 4×10^5 cycles of the discontinuous one.

Experimental and Discussion

Off-the-shelf CapXX SC with stated nominal capacitance of 2.4 F and voltage of 2.75 V was used for all presented measurements. Experiments were performed within the facilities of EGGO Space s.r.o. company. The motivation for using an external company is the duration of the experiment, taking up to 215 days each. EGGO Space s.r.o is well suited for such large scale long term measurements of several samples in parallel.

The charging/discharging current value used was 0.66 A for all the 100% continuous, the 75% continuous, and the 75% discontinuous energy cycling tests. The duration (to start with) of single cycle was approximately 20 seconds, 10 seconds, and 20 seconds derived from equation (1), respectively. Actual duration of the cycle however depends on samples total capacitance (C_T) and ESR (R_1), which decrease and increase while the sample ages, respectively. Up to $8x10^5$ cycles of each test were implored. Batch of 3 brand new SCs was used for each test. The equivalent circuit parameters were evaluated after every 10^5 cycles, average values of studied parameters are presented.

Only $7x10^5$ cycles of 75% continuous test were performed, because one of studied samples went out of commission. In this moment the progression of both 75% experiments seized. Therefore only $4x10^5$ cycles of the discontinuous test were performed.

Equivalent Electrical Circuit Parameters Evaluation

The equivalent electrical circuit has five parameters: Helmholtz capacitance $C_1 = C_H$, diffuse capacitance $C_2 = C_D$, equivalent series resistance (ESR) R_1, leakage resistance R_L, and the time dependent resistance $R_2(t)$ between the Helmholtz and diffuse capacities [1]. The method for precise evaluation of these parameters values is described in [3].

As stated above, after every 10^5 cycles of each energy cycling test, the equivalent electrical model parameters of studied samples were evaluated. Following is the summary of the evaluation method and average values of studied parameters obtained from each batch. Even though the model has 5 parameters, only the total capacitance, ESR, and leakage current values are presented, as they seem to be the best indicator of SC state of health.

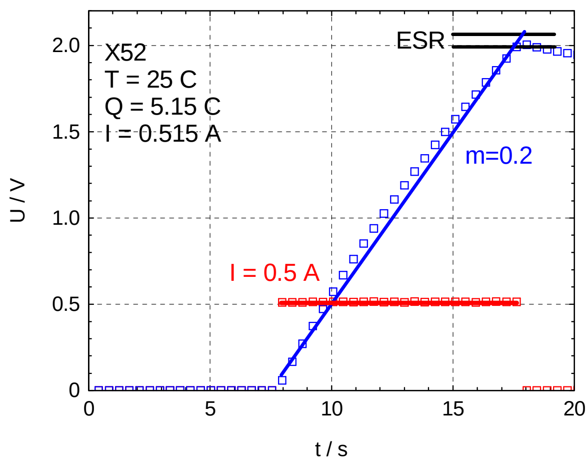

Fig. 2: Voltage on the SC terminals vs. time for sample CapXX X52 for time interval 0 to 20 s (charging current I_C = 0.5 A)

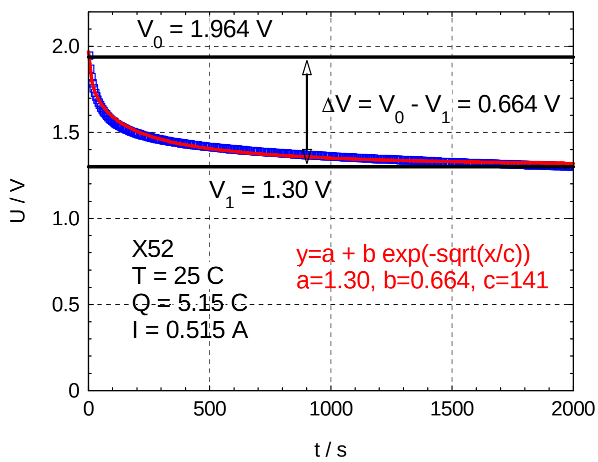

Fig. 3: Voltage on the SC terminals vs. time for sample CapXX X52 for time interval from 20 to 2000 s (charging current I_C = 0.5 A)

Firstly is the SC charged by defined current, until the voltage on its terminals reaches the rated value V_{op} = 2.75 V. It is assumed that the response to a fast controlled charging process is determined mainly by the parameters of the Helmholtz capacitance. 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 SC parameters. For these considerations, charging current I_C = 0.5 A was used. Time interval, needed to fully charge SC, is about 12 seconds (see Fig. 2). After which the terminal voltage is monitored for time interval of 2000 seconds (see Fig. 3).

Equivalent series resistance

Since the ESR effectively acts as resistor, connected in series with the rest of the model, it is responsible for a characteristic voltage step, when the magnitude of DC current changes. Such voltage drop (*ESR* in Fig. 2) may be used to determine the value of R_1, using the Ohm's law. Notable side effect of increasing ESR is shifted perception of SCs terminal voltage, while the current flows through. This means that while the SC is charged or discharged, the process is cutoff early, because the terminal voltage reaches the requested value sooner. This practically shortens the duration of single measurement cycle ever so slightly.

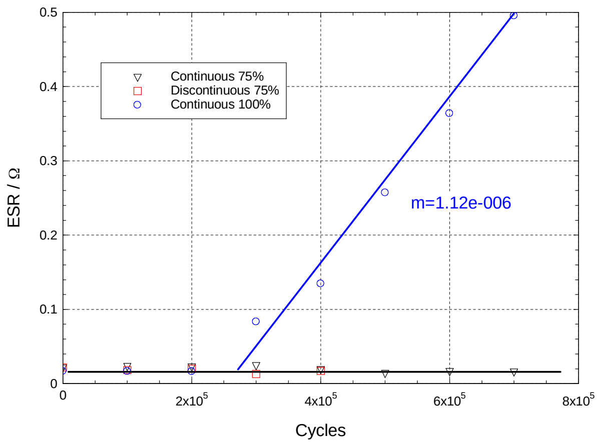

Fig. 4: Change of ESR for CapXX samples in relation to the number of endured cycles for different tests

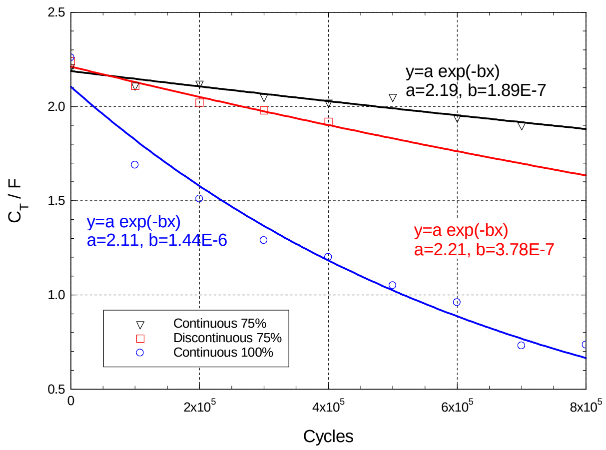

Fig. 5: Change of C_T for CapXX samples in relation to the number of endured cycles for different tests

Average value of SC's ESR measured in relation to the number of endured cycles is shown in Fig. 4. Contrary to other experiments, the ESR value of CapXX 2.4F/2.75V SC does not significantly change for neither 75% energy cycling method. For the 100% continuous energy cycling test the value of ESR steeps significantly after $2x10^5$ endured cycles. The rate of ESR increase is (as expected) linear. This discrepancy may be linked to the fact, that measurement cycles of different methods have different duration, and therefore the electric field is applied for varying amount of time. Hence for neither 75% energy cycling test the SCs measured sustained enough damage for their value of ESR to increase.

Helmholtz and diffuse capacitance

In order to determine the Helmholtz and diffuse capacitance values, capacitor needs to be charged by constant DC current I for specified time interval, during which the voltage on capacitor is measured. Total charge Q_T = 5.15 C (see Fig. 2) stored in SC may be inferred by integration of applied current. The maximum voltage reached after the charging has ended is denoted V_0. It follows that the value of Helmholtz capacitance is:

$$C_H = C_1 = Q_T / V_0 \tag{2}$$

After the charging interval, the voltage drop (during which the diffuse capacitance is being charged) on SC's terminals is monitored. Since the diffuse current component is dominant in this kind of SC, this voltage characteristic is fitted by function:

$$V = V_1 + \Delta V e^{-\sqrt{t/\tau_D}} \tag{3}$$

Where the voltage V_1 is the open circuit voltage value at infinity, ΔV is voltage drop due to the diffuse capacitance charging ($V_0 = V_1 + \Delta V$). And τ_D is the time constant of diffuse capacitance charging.

The diffuse capacitance

$$C_D = C_2 = C_T - C_H = Q_T / V_1 - Q_T / V_0 \ . \tag{4}$$

Knowing the value of both the diffuse and the Helmholtz capacitance allows for the accurate determination of total capacitance from (4). This result is not burdened by the intermediate charging error. This error of total capacitance estimation results from the diffuse capacitance being slightly charged prior to the evaluation process.

The degradation of total capacitance may be fitted by basic exponential equation, as shown in Fig. 5. From this extrapolation it becomes obvious, that the total capacitance fades due to both the duration of applied electric field and the amount of charge passing through the SC.

The fading of capacitance for the 100% test is the most remarkable. By the time the measurement has finished, the average capacitance of SCs under the test had dropped five fold. The degradation of capacitance inflicted by both 75% tests is disproportionately smaller within the same time frame.

The capacitance degradation of both 75% tests differs by the ratio of 2 in exponent. This is due to the fact that the $4x10^5$ cycles of discontinuous test last roughly the same time as $8x10^5$ cycles of 75% continuous test. From this it follows, that the fading effect on capacitance in time is the same for both continuous and discontinuous tests, and that the only the duration for which the electric field is applied matters. In addition for both 75% tests the fitting shows extremely accurately the value of original capacitance.

Leakage resistance

The leakage resistance (R_L) of the equivalent circuit model is directly proportional to SC's leakage current and the applied voltage. As shown in Table 1, the leakage current of fully charged sample is quite minuscule. Even though the measurement is burdened with significant error, linear trend of leakage current decline is observed. The slope of leakage current decline is also shown in the aforementioned table.

First thing to notice is that the decline caused by discontinuous test is twice as large as one caused by continuous test for the same energy cycling. This is again due to the fact, that the discontinuous test lasts twice as long. It therefore follows, that were there both results plotted in time scale, both slopes would match. The effect of both 75% tests is the same, from which it follows, that the effect of sustaining electric field produces the drop in leakage current. Also, while the field is applied for longer time, the narrowing of effective electrode distance occurs.

Table 1: CapXX leakage current in relation to the number of endured cycles for different tests

Cycles x 10^5	1	2	3	4	5	6	7	8	Slope
Test	[μA]	[μA]	[μA]	[μA]	[μA]	[μA]	[μA]	[μA]	[pA/cycle]
100% Continuous	1.28	0.70	0.81	0.62	0.74	0.72	0.59	0.78	-0.50
75% Continuous	1.38	1.38	1.37	0.95	0.47	0.44	0.62	–	-1.79
75% Discontinuous	1.44	0.79	0.75	0.24	–	–	–	–	-3.64

The degree of degradation for 100% cycling test is the least of all three methods. This is because residual conductive paths within the electrolyte are not completely broken by the applied electric field. This may be linked to the fact, that unlike 75% methods, the 100% method actually discharges the Helmholtz capacitance completely, reaching 0 V.

Conclusion

Off-the-shelf CapXX 2.4F/2.75V SCs were evaluated. Evolution of several equivalent circuit model parameters was analyzed. These parameters are:

1. **Equivalent Series Resistance** is low, in the order of 10 mΩ, in the beginning for all tests. It remains constant for both 75% energy cycling methods. ESR vs. time of ageing can be approximated by linear function. For 100% continuous test linear increase is observed within $3x10^5$ cycles. This increase reaches roughly 0.4 Ω in $6x10^5$ cycles.

2. **Total capacitance**, which sustains the largest degradation by 100% energy cycling test. The capacitance fading vs number of endured aging cycles was modeled by exponential function with time constant in the order of 10^5 cycles. During the experiment total capacitance decreases to 0.6 F for 100% method. The extrapolation of 75% discontinuous and 75% continuous energy cycling tests to $8x10^5$ cycles shows only drop to 1.6 F and 1.9 F, respectively. Both 75% energy cycling tests have the same impact in relation to the duration of applied electric field. The difference in change of capacitance between 75% cycling and 100% cycling is the impact of current cycling on the SC structure.

3. **Leakage Resistance**, which is proportional to the measured leakage current. The evaluation of change in leakage current shows, that (for studied CapXX samples) the increase in leakage is inversely proportional to

damage inflicted by aging. For 100% energy cycling the leakage current decreases with slope of 0.5 pA/cycle. While for 75% energy the decline is larger and would be the same if transformed into time space. The leakage resistance increases by aging. Unlike other parameters, that actually worsen under the harsher aging procedure, the leakage current behaves inversely. The value of this parameter is therefore a good indicator of SC state of health.

The discontinuous cycling has no real impact on the sample life time in comparison to the same type of continuous method. The only discrepancies arise from different duration for each 75% cycling method. The 100% energy cycling test has great impact on all studied parameters. Such kind of working profile is detrimental to sample's life and should be avoided for this type of SC.

Acknowledgment

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References

[1] Sedlakova V, Sikula J, Majzner J, Sedlak P, Kuparowitz T, Buergler B and Vasina P 2015 Supercapacitor equivalent electrical circuit model based on charges redistribution by diffusion J. Power Sources 286 58–65

[2] Kuparowitz T, Sedláková V, Szewczyk A, Hasse L and Smulko J 2014 Charge Redistribution and Restoring voltage of Supercapacitors Electroscope 2014 1–7

[3] Sedlakova V, J. Sikula, J. Valsa, J. Majzner, P. Dvorak, "Supercapacitor Charge and Self-discharge Analysis" in Proceedings of Conference Passive Space Component Days, ESA/ESTEC, Noordwijk, The Netherlands, Sept. 24e26, 2013.

[4] Zubieta L and Bonert R 2000 Characterization of double-layer capacitors for power electronics applications IEEE Trans. Ind. Appl. 36 199–205

[5] Graydon J W, Panjehshahi M and Kirk D W 2014 Charge redistribution and ionic mobility in the micropores of supercapacitors J. Power Sources 245 822–9

[6] Faranda R 2010 A new parameters identification procedure for simplified double layer capacitor two-branch model Electr. Power Syst. Res. 80 363–71

[7] Sikula J., Sedlakova V., Majzner J., "Technical note 10, WP500 Super-Capacitor Electrical Characteristics Modeling, R6. Equivalent Electrical Circuit Model", ESA project No. 4000105661/12/NL/NR - Evaluation of Supercapacitors and Impact at System Level. March 20, 2014, pp. 1 – 90.