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Constant power cycling for accelerated ageing of supercapacitors

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Keywords

«Supercapacitor», «Power cycling», «Lifetime», «Accelerated ageing», «Ageing law»

Abstract

This paper deals with the lifetime of supercapacitors used in transportation. Increasing onboard electrical devices require adapted storage elements like supercapacitors to supply all electrical systems. Reliability and lifetime are two major factors for electrical storage system. Based on accelerated ageing, some supercapacitors have been studied using a dedicated test bench. Temperature, voltage, current and power cycling are monitored since supercapacitor ageing are affected by these parameters. An ageing law suitable for a transport application is obtained and discussed.

1) Introduction

Electrical devices are more and more used in transport systems like trolleybus [1][2][3][4]. Nowadays, they are used for auxiliary part like air conditioning system or air cooling system... but traction motor will also be considered. However the development of electrical onboard systems requires an adapted energy storage component to ensure their power supply. In fact, during acceleration or braking, high current is respectively absorbed or provided by the trolley. Supercapacitors are very interesting for this kind of applications because high current can be considered for supercapacitor.

A 120 supercapacitors pack has been developed for an electrical bus. This pack must provide power spike up to 50kW. They are charged during the regenerative braking. Some studies have shown the feasibility of this approach [1][2][3][4][5][6]. Supercapacitors are new components and this paper will contribute to improve ageing data for the power application.

It is well known that supercapacitor ageing is significantly affected by temperature and applied voltage [7][8][9][10][11]. Ageing laws based on voltage and temperature have already been proposed [8][9][10][11][12][13][14]. These test conditions are far from the normal behaviour encountered in trolleybus application. In this application, constant power cycling is more appropriate. This paper establishes the behaviour of supercapacitor overstressed by constant power cycling. In this condition, reliability and lifetime are also affected. A dedicated test bench has been achieved for the power cycling of several supercapacitors. Then, two supercapacitor packs have been tested. Ageing law has been deduced from these tests.

Part II describes the test bench carried out for the power cycling. We start by a presentation of the supercapacitors. After that, a cycling description is given. Then, we describe the two devices used to the measurement. Part III presents criteria to quantify the state of health of supercapacitors and some individual supercapacitor results are presented. Then, experimental results for two supercapacitor packs are presented in section IV. Finally, ageing law obtained is explained and discussed in part V.

II) Hardware and software presentation

The test bench is composed by power supply load, acquisition data system and supercapacitors under test. Fig. 2(b) shows these different elements.

Supercapacitors under test

Four Maxwell supercapacitors connected in series were tested by the test bench. The rated voltage is 2.7V and capacitance is 3000F. Maxwell proposed two series of supercapacitor: Power and Energy. The difference appeared on the Equivalent Series Resistance (ESR) which is bigger for energy series (0.37mΩ). Our study is focussed on supercapacitor from energy series. Two packs composed by four capacitors were tested. In the first supercapacitor pack, components are named scE02; scE03; scE04; scE05 and in the second one, components are named scE07; scE08; scE09; scE10.

Fig. 1 shows two photos of supercapacitors under test.

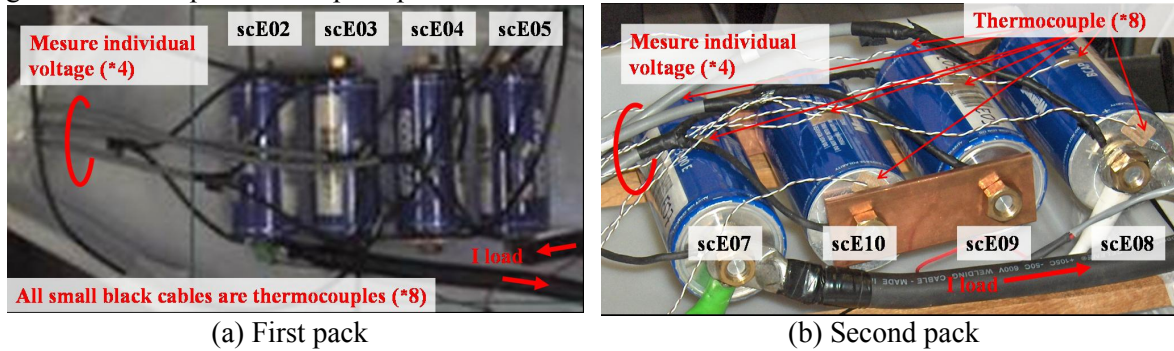


Fig. 1: Supercapacitors under test

Power cycling description

The power supply used is a BT2000-LNR-0V-30V-500A from ARBIN. This system can measure current and voltage across the supercapacitor pack terminals. The voltage value of each supercapacitor during the cycling change between $V_n/2$ and V_n ($V_n = 2.7V$). There are 4 supercapacitors linked in series. The maximum current value provided by this power supply can reach 500A. For a power constant cycle, the maximum current is reached when the output voltage of the supercapacitor pack is the lowest (5.4V pack voltage: 1.35V per component). Thus, for the four supercapacitors the maximum power value is 2700W. Considering a safety margin, power transfer during charge/discharge is chosen to be 2600W (phases 2 and 4 in fig. 2(a)). The release times (t_{break}) can also be changed in order to control the upper temperature. We can note that the charge/discharge times (t_c and t_d) depend on the power value, capacitance of the pack and the lower/upper voltage. Voltage and current of the power cycling profiles are illustrated in fig. 2(a).

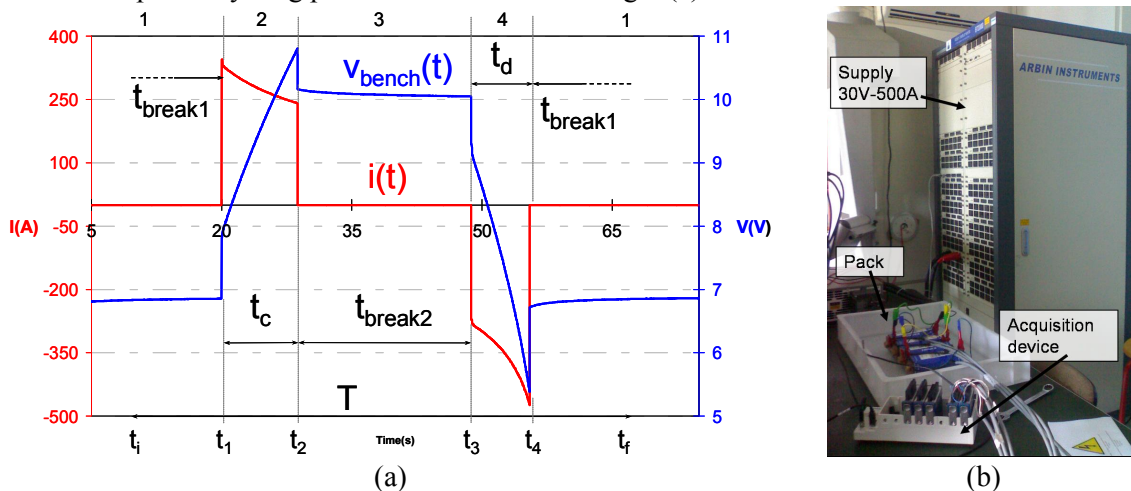


Fig. 2: Power cycling profile (a); Photo of the test bench (b);

Acquisition device and software

Since voltage and temperature are two significant factors for ageing, special care must be taken on these two represented quantities. Power cycling presented in fig. 2(a) has been achieved in order to stress the supercapacitor both in temperature and voltage. CompacDAQ device from National Instrument was used for data acquisition. The sampling frequency of this device can reach 100 kHz for the voltage measurement and 15 Hz for the temperature acquisition.

A labview program was developed for data acquisition. Each supercapacitor has two thermocouples, one paste on the middle spot of the case (named T_c) and the other on the positive terminal (fig. 1). Another thermal sensor measures the ambient temperature. From the current and voltage measurements, computation method of both ESR and capacitance during the cycling is detailed below.

Spectrometer

Several impedance spectroscopies were achieved during the power cycling to determine the state of health of the supercapacitor. The impedance analyser is an electrochemical workstation Zahner IM6 with a supplementary amplifier to increase current excitation. Impedance spectroscopy allows knowing the capacitance and the ESR values for a frequency range between 10mHz and 30kHz. Measurements and characterisation were accomplished for several bias voltages. However, this test method has two disturbances: the cycling must be stopped each time we want to realise impedance spectroscopy and the identification requires a lot of time (6h30).

III) Ageing factors

Introduction

Ageing factors are focussed on the variation of the equivalent series resistance (ESR) and capacitance. Supercapacitors are considered out of service when their equivalent series resistance increases two times above rated value [15]. 20% decrease of initial capacitance is considered as the limit [15].

In order to improve the lifetime, an aging law taking into account more significant parameters must be established. The ageing time is proportional to inverse of redox reaction rate [7][8][9][10]. The Arrhenius law is used to predict the reaction rate function of temperature [7][16]. Redox reaction rate in the supercapacitor is also affected by the voltage across the terminal of the electrode. Eyring law generalises the Arrhenius law to many factors as voltage [16]. In literature, Eyring law takes into account temperature and voltage value to predict the lifetime [8][9][10][12]. The current can induce a local temperature rise which must be taken into account. In hot spots, the redox reaction is accelerated. We proposed in this paper to consider RMS current, the temperature and the voltage in the Eyring law. The ageing mechanism leads to an increase of supercapacitors ESR and in the same time to a decrease of their capacitances. The rate of degradations of ESR and capacitance are used to determine the coefficient in the Eyring law. In next sections, two methods to determine the ESR and capacitance values are described.

Method

A spectroscopy and a temporal method are used to determine the state of health:

Impedance spectroscopy

In order to quantify the effect of ageing on the variation of the supercapacitor parameters and therefore on the lifetime, we realised an impedance spectroscopy test. To characterize supercapacitors, cycling test is stopped. Before the impedance spectroscopy impedance, supercapacitors were discharged and then short-circuited during at least 4 days.

The measurement was performed in 2 consecutive phases.

- Biasing stage: Firstly, the supercapacitors were biased by a voltage during 30 minutes. The voltage step was 0.54V from 0V to 2.7V.
- Complexes impedance measurement stage: After the biasing stage, a 10mV ripple was added to the DC voltage with a frequency from 10mHz to 30kHz. The spectrometer measured impedance phase and magnitude.

The impedance spectroscopy measurement was performed for two different temperatures (25°C and 60°C) in a climatic chamber. The result of spectroscopy test can be represented in a Nyquist plot.

The capacitance is deduced for impedance spectroscopy measurement by the following relation:

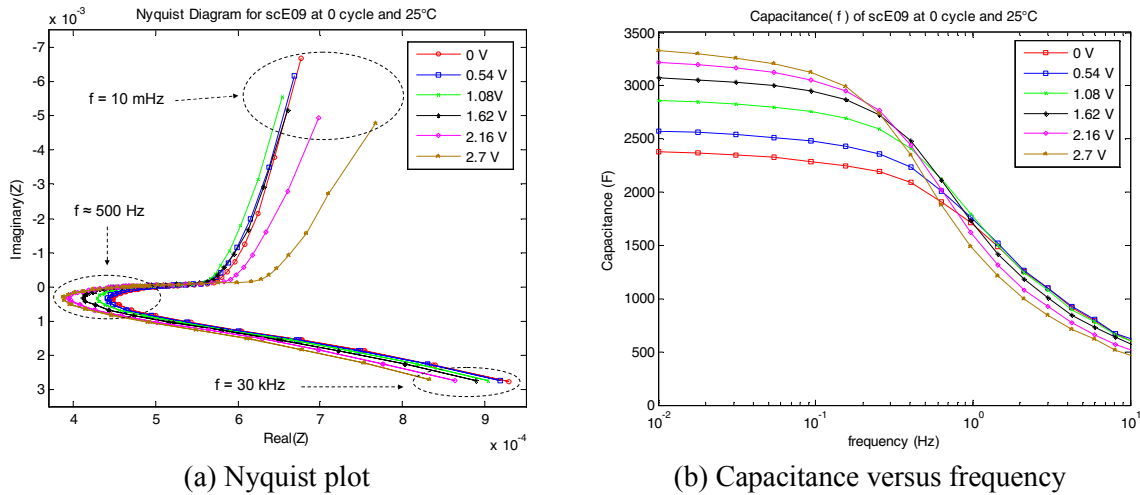
$$C_{spectro} = \frac{-1}{2\pi f \times \text{Im}(Z)} \quad [F] \quad (1)$$

The resistance is given by the relation:

$$ESR_{spectro} = \text{Re}(Z) \quad [\Omega] \quad (2)$$

where Z is the impedance of the supercapacitor at the frequency f .

In fig. 3, spectroscopy results are represented for scE09 at 25°C before the cycling test.



(a) Nyquist plot

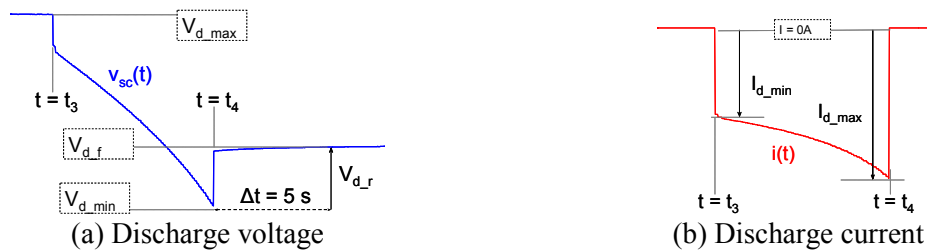
(b) Capacitance versus frequency

Fig. 3: Spectroscopy results for scE09 before cycling test and for several voltages at 25°C

The fig. 3 (a) shows all the results of one spectroscopy (for the scE09 component at 25°C and 0 cycle). The fig. 3 (b) exhibits the capacitance of the supercapacitor scE09 at 0 cycle, 25°C and for several voltages (1). Several spectroscopies at different temperatures and for several ageing state can be used to show the variation of the supercapacitor's parameters versus temperature and ageing [17][18].

The time domain method

This method uses the current and the voltage across the terminals of a supercapacitor during cycling to deduce the ESR and the capacitance. Maxwell uses the same method but with constant current cycles in spite of constant power cycles [13]. The method to evaluate the parameters is presented following.



(a) Discharge voltage

(b) Discharge current

Fig. 4: Definition of parameters during the discharge (as Maxwell method)

$v_{sc}(t)$ is the individual voltage of one supercapacitor of the considerate pack.

In the end of discharge, the drop voltage value is considered equal to $ESR \times I$ value and is computed with this equation (cf. fig. 4) [13]:

$$V_{d_r} = |V_{d_min} - V_{d_f}| \quad [V] \quad (3)$$

with V_{d_f} the voltage value across the terminals of a supercapacitor after 5s to the end of discharge and V_{d_min} the minimum supercapacitor's voltage value during the discharge.

ESR_d is the ESR value computed during the end of discharge with the equation (cf. fig. 4):

$$ESR_d = \frac{V_{d_r}}{I_{d_max}} = \frac{|V_{d_min} - V_{d_f}|}{I_{d_max}} \quad [\Omega] \quad (4)$$

The discharge capacitance is given by (cf. fig. 4) [13]:

$$C_{d_m} = \frac{\int_{t_3}^{t_4} i(t) dt}{V(t_3) - V(t_4 + 5)} = \frac{Q_d}{V_{d_max} - V_{d_f}} \quad [F] \quad (5)$$

V_{d_max} is the maximum supercapacitor's voltage value during the discharge.
The discharge time and the period value are respectively equal to (cf. fig. 2):

$$t_d = t_4 - t_3 \quad [s] \quad T = t_c + t_d + t_{break1} + t_{break2} = t_f - t_i \quad [s] \quad (6)$$

with t_i and t_f are respectively the initial and the final time of the considered cycle. t_{break1} and t_{break2} are considered to be equal and they are defined in fig. 2. We also compute the RMS current and the mean voltage value:

$$I_{RMS} = \sqrt{\frac{1}{T} \int_{t_i}^{t_f} (i(t))^2 dt} \quad [A] \quad \langle V_{sc} \rangle = \frac{1}{T} \int_{t_i}^{t_f} v_{sc}(t) dt \quad [V] \quad (7)$$

IV) Results

Two packs with four supercapacitors were cycled with a constant charge/discharge power at 2600W. To have two different cycle profiles, the t_{break} time for the first cycle profile is chosen to be smaller than the t_{break} of the second cycle profile. Thus, in the first case, the RMS current and the case temperature of supercapacitors were bigger and the lifetime was smaller. The ambient temperature (T_a) was 24°C for the two tests.

First pack

The first pack was composed of four supercapacitors Maxwell 3000F-2,7V energy series named scE02; scE03; scE04; scE05. At the beginning, the t_{break} time is set to 15 seconds and after 100 cycles, the t_{break} time is set to 22s. We have realised only 1500 cycles on this pack because the temperature has reached the critical value and an acetonitrile leakage was feared (cf. Table II).

Fig. 5 shows applied voltage on the four supercapacitors at the beginning and after 1500 cycles.

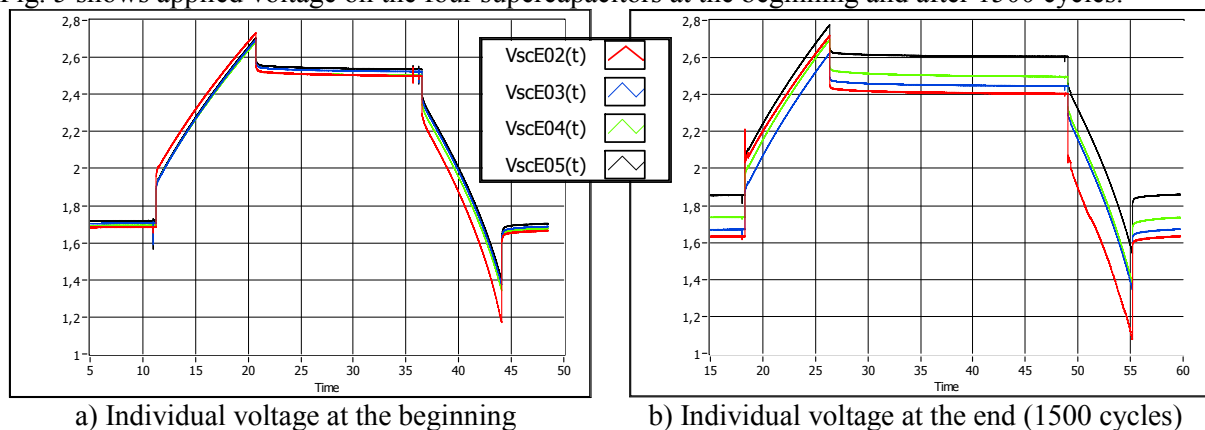


Fig. 5: Supercapacitor voltage during power cycling

Three major modifications can be observed in the fig. 5:

- ESR increase affect voltage steps at the beginning/end of the charge/discharge
- The capacitance degradation affects the duration of the charge/discharge (t_c and t_d).
- Ageing process and temperature affect the voltage distribution of the supercapacitors in series

A charge balancing can be implemented to decrease the voltage dispersion and thus to increase the lifetime of the pack [11][12]. With the time domain method, the values of the parameters at the beginning and after 1500 cycles are given in the next table:

Table I: Parameters at the beginning and the end of cycling computed with time method

Start	$t_c = 9.5s$	$t_d = 7.6s$	$I_{RMS} = 188 A$	End	$t_c = 8s$	$t_d = 6.2s$	$I_{RMS} = 155A$	
	$C_d(F)$	$ESR_d(m\Omega)$	$\langle V_{sc}(t) \rangle (V)$	$C_d(F)$	$\Delta C_d(\%)$	$ESR_d(m\Omega)$	$\Delta ESR_d(\%)$	$\langle V_{sc}(t) \rangle (V)$
scE02	2810	1.01	2.10	2510	-10.8	1.14	13.5	2.03
scE03	2810	0.639	2.13	2490	-11.2	0.675	5.63	2.07
scE04	2850	0.682	2.11	2530	-10.9	0.744	9.10	2.13
scE05	2820	0.614	2.14	2590	-8.03	0.652	6.19	2.24

Except changing the t_{break} time at the 100th cycle, RMS current decrease is explained by the charge/discharge time decrease. Some mean values obtained during the entire cycling test are given in

the table II. In this next table, an infrared picture for the four supercapacitors (fig. 6) exhibits hot spots on the supercapacitor which has the biggest ESR (c.f. table I).

Table II: Mean values of some parameters and an infrared photo (top view)

element	Mean values during cycling test				Mean value
	scE02	scE03	scE04	scE05	
T_c (°C)	70	69	65	50	64
$\langle V_{sc} \rangle$ (V)	2.06	2.07	2.11	2.23	2.11
Other mean value during the cycling					
$\langle T_a \rangle = 24$ °C	$\langle I_{RMS} \rangle = 159$ A		$\langle t_{break} \rangle = 22.4$ s		
$\langle t_c \rangle = 8.38$ s	$\langle t_d \rangle = 6.57$ s		$\langle T \rangle = 59.75$ s		

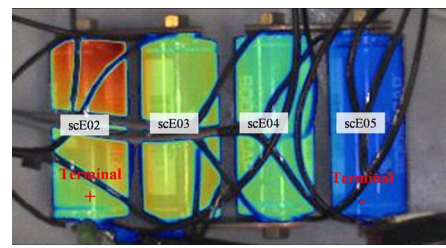


Fig. 6: Infrared picture of the first pack

Two spectroscopy measurements were realised for all supercapacitors of this pack (one at the beginning and one after 1500 cycles). These characterisations have been carried out at 25°C, 2.16V voltage bias and 10mHz. The decrease of the mean value of 4 individual spectroscopies, $C_{spectro}$, is represented in the fig. 6.

In the fig. 6, we can see also the variation of $C_{d,m}$ during 1500 cycles. The capacitance $C_{d,m}$ is the mean value of the four supercapacitors computed from measurements. A linear extrapolation, $C_{d,extrapol}$, is realised from the last measured cycle (1500 cycles) up to 6300 cycles by using a least square method [15]. Then, we have interpolated the entire data (measured and extrapolated data) versus cycle number (cycle) by the following equation:

$$C_d(\text{cycle}) = 190,8 \times e^{-\frac{\text{cycle}}{100}} - 0,0601 \times \text{cycle} + 2628,2 \quad (8)$$

20% decrease is obtained for the 6210th cycle. The equivalence number cycle/time gives a following lifetime:

$$6210 \times \langle T \rangle = 103 h \quad (9)$$

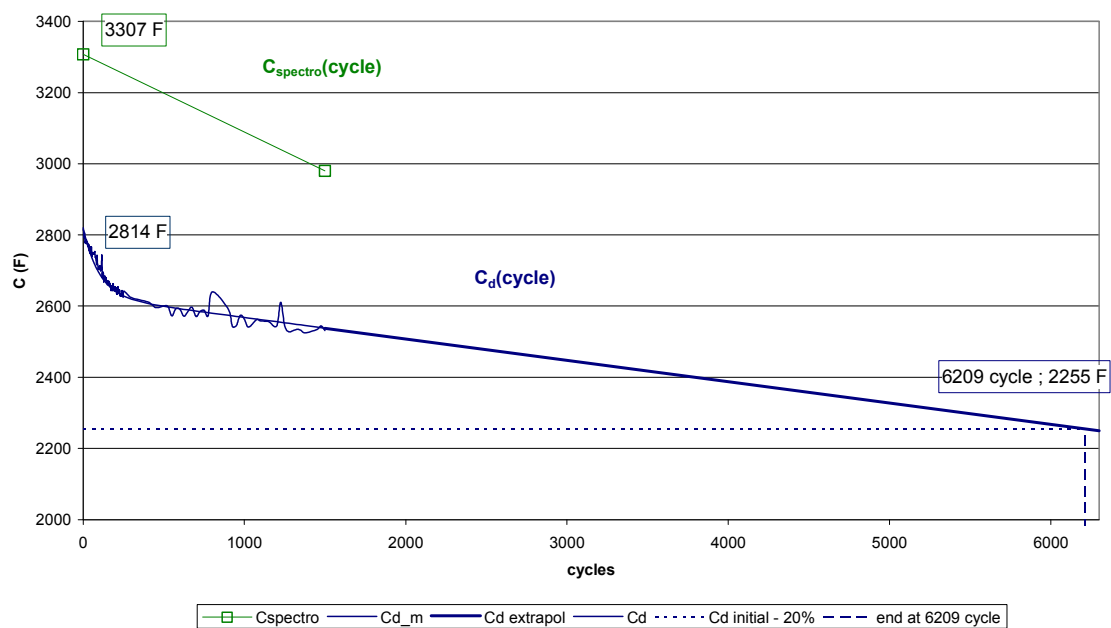


Fig. 6: Mean capacitance value of 4 supercapacitors of the pack

Second pack

The second pack is composed of four supercapacitors of 3000F 2.7V energy series named scE07; scE08; scE09; scE10. The t_{break} time is set at 40 seconds. This pack have made 25000 power cycles. Some mean values obtained during the entire cycling test are given in the table III. In this next table, an infrared picture for the four supercapacitors (fig. 7) shows that the two supercapacitors in the centre are a little bit hotter than the others.

Table III: Mean values of some parameters and an infrared photo (top view)

element	Mean value during all cyclage				Mean Value
	scE07	scE08	scE09	scE10	
T_c (°C)	39	38	43	42	40
$\langle V_{sc} \rangle$ (V)	2.13	2.17	2.09	2.06	2.11
Other mean value during all cyclage					
$\langle T_a \rangle = 24$ °C	$\langle I_{RMS} \rangle = 122$ A		$\langle t_{break} \rangle = 40.5$ s		
$\langle t_c \rangle = 7,81$ s	$\langle t_d \rangle = 6.13$ s		$\langle T \rangle = 95.4$ s		

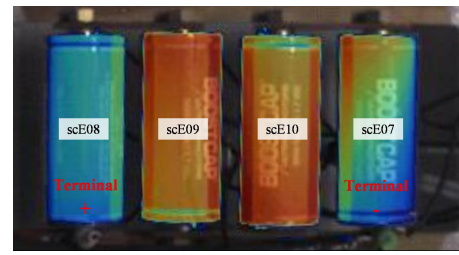


Fig. 7: Infrared picture for the second pack

Four spectroscopies measurements were realised for all the components of this pack (one at the beginning, the second after 300 cycles, the third after 10000 cycles, and the last after 25000 cycles). These characterisations have been carried out at 25°C, 2.16V voltage bias and 10mHz. The decrease of the mean value of 4 individual spectroscopies, $C_{spectro}$, is represented in the fig. 7.

In the fig. 7, we can see also the variation of $C_{d,m}$ during 25000 cycles. The capacitance $C_{d,m}$ is the mean value of the four supercapacitors computed from measurements. A linear extrapolation, $C_{d,extrapol}$, of this variation is given up to 38000 cycles by using a least square method [15].

Then, we have interpolated the entire data (measurement and extrapolated data) by the following equation:

$$C_d(\text{cycle}) = 360 \times e^{-\frac{\text{cycle}}{2500}} - 0,006 \times \text{cycle} + 2480 \quad (10)$$

20% decrease is obtained for the 34800th cycle. The equivalence number cycle/time gives a following lifetime:

$$34800 \times \langle T \rangle = 923 \text{ h} \quad (11)$$

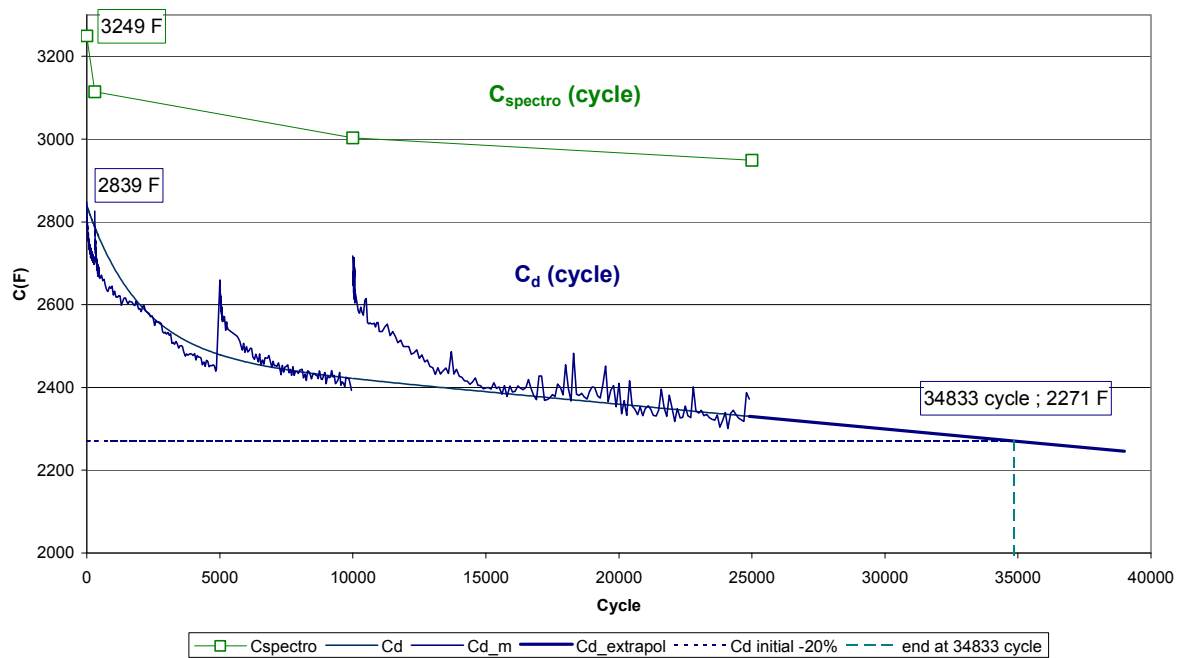


Fig. 7: Mean capacitance of 4 supercapacitors

During the cycling process, the redox reaction of the electrolyte induces impurities in the activated carbon [8]. This implies a capacitance decrease and an ESR increase. Regeneration of the capacitance is observed at each cycling off [15]. Two phenomena can explain that:

- impurity redistribution inside the pores since there impurities are thermodynamic instable [18]
- inverse redox reaction comes and a regeneration of ions in the electrolyte operates [19].

V) Discussion & ageing laws

Manufacturer data are used to quantify the lifetime. These data used are given by a floating test. The floating test consists in studying electrical parameter of supercapacitor for several voltage biases in a

climatic chamber. This method is used to quantify both temperature and voltage on the lifetime. In floating test, the climatic chamber temperature is equal to the case temperature of supercapacitor (T_c). These data are used in life prediction equation when the RMS current is null. An interpolation and extrapolation of the Maxwell datasheet for the floating test give the table IV [13]:

Table IV: Interpolation/extrapolation of manufacturer data

	Maxwell Data	Linear interpolation	Maxwell Data	Linear extrapolation
Voltage across the supercapacitor terminals:	2.7 V	2.7 V	2.5 V	2.5 V
Reduction of the rated capacitance for:	30%	20%	15%	20%
With $T_c = 65^\circ\text{C}$, the necessary time is:	5500 h	3670 h	5500 h	7330 h
With $T_c = 55^\circ\text{C}$, the necessary time is:	11000 h	7330 h	11000 h	14700 h
With $T_c = 45^\circ\text{C}$, the necessary time is:	22000 h	14700 h	22000 h	29300 h
With $T_c = 35^\circ\text{C}$, the necessary time is:	44000 h	2930 h	44000 h	58700 h
With $T_c = 25^\circ\text{C}$, the necessary time is:	88000 h	58700 h	88000 h	117300 h

The table IV illustrates the effect of both temperature and voltage bias on the lifetime. We can note 50% reduction of the lifetime for an increase of 10°C or for an increase of 0.2V on the applied voltage [13][14]. Assuming this trend faithful, we can establish a lifetime equation function of voltage and temperature [12]:

$$\tau_s(T_c; V) = 3,85 \times 10^9 \times e^{-(0,1 \ln(2) T_c + 5 \ln(2) V)} \quad [h] \quad (12)$$

τ_s is the lifetime in hours, V is the constant voltage value across the supercapacitor terminals and T_c is the case temperature in Celsius.

For constant value of the voltage and temperature, the redox reaction rate is considered as constant. For a dynamic voltage, the rate of the redox reaction is not constant and the mean value of the reaction rate must be used. Considered the lifetime directly proportional to inverse of reaction rate, with a dynamic voltage and temperature, the lifetime equation to use becomes [12]:

$$\tau_d(T_c(t); v(t)) = \frac{t_{end} - t_{init}}{\int_{t_{init}}^{t_{end}} \left(\frac{1}{\tau_s(T_c(t); v(t))} \right) dt} \quad [h] \quad (13)$$

t_{init} and t_{end} are respectively the beginning time and the end time of the entire test.

The constant value of the temperature and the periodical variation of the voltage enable to use one cycle to determine the mean reaction rate. In reality, the temperature is not constant because the ESR value increases during cycling and thus the temperature increase to. The low increases of temperature are neglected and the mean temperature value is used. That why, the mean rate of the reaction is computed with a cycle which has the same voltage characteristic of the mean value found during the entire test.

The lifetime equation (13) computed for a static temperature and one cycle voltage considerate becomes:

$$\tau_{d2}(T_c; v(t)) = 3,85 \times 10^9 \times e^{-0,1 \ln(2) T_c} \times \frac{T}{\int_{t_i}^{t_f} \left(\frac{1}{e^{-5 \ln(2) v(t)}} \right) dt} \quad [h] \quad (14)$$

T, t_i and t_f are respectively the period, the beginning time and the end time of one cycle.

We are interesting of the voltage acceleration factor identify by the equation (14) as:

$$A_{v1} = \frac{T}{\int_{t_i}^{t_f} \left(\frac{1}{e^{-5 \ln(2) v(t)}} \right) dt} \quad (15)$$

If the voltage is assumed to be constant during the t_{break} time and if the charge/discharge phase is neglected, the voltage accelerate factor becomes:

$$A_{v2} = \frac{2}{\exp(-5 \ln(2) \langle V_{tbreak1} \rangle) + \exp(-5 \ln(2) \langle V_{tbreak2} \rangle)} \quad (16)$$

This equation is given with $t_{break1} = t_{break2}$ and with $\langle V_{tbreak1} \rangle$ and $\langle V_{tbreak2} \rangle$ respectively the mean voltages during the t_{break1} and the t_{break2} . If $\langle V \rangle$, the mean value of voltage during a cycle, is utilised, the voltage acceleration factor becomes the same as the equation (12):

$$A_{v3} = e^{-5\ln(2)\langle V \rangle} \quad (17)$$

The next table shows the results of voltage acceleration factor versus the computed method (15), (16), (17).

Table V: Voltage acceleration factor value versus computed method

	A_{v1} (15)	A_{v2} (16)	A_{v3} (17)
	$\frac{T}{\int_{t_i}^{t_f} \left(\frac{1}{e^{-5\ln(2)v(t)}} \right) dt}$	$\frac{2}{e^{(-5\ln(2)\langle V_{break1} \rangle)} + e^{(-5\ln(2)\langle V_{break2} \rangle)}}$	$e^{(-5\ln(2)\langle V \rangle)}$
The 775 th cycle of the first pack	0,000317	0,000313	0,000649
The 15200 th cycle of the second pack	0,000334	0,000336	0,000660

The integer method provides in theory the more accurate result (A_{v1}). But we can see that the method neglecting the charge/discharge gives a good approximate result (A_{v2}). However, used the mean voltage value to computed this acceleration factor introduce an error of a factor two (A_{v3}).

The equation (14), with the mean temperature value and a representative cycle of the two packs, gives:

- For the first pack:

$$\tau_{d2}(64; v(t)) = 14800 \quad h \quad (18)$$

- For the second pack:

$$\tau_{d2}(40; v(t)) = 78500 \quad h \quad (19)$$

These results are better than those obtained by the cycling test because they do not take into account the influence of the current.

An Eyring type stresses is added to overcome this default by introducing the RMS current in the lifetime. The equation (14) becomes:

$$\tau_{d3}(T; v(t); I_{eff}) = 3,85 \times 10^9 \times \exp(-0,1 \ln(2)T) \times \frac{T}{\int_{t_i}^{t_f} \left(\frac{1}{\exp(-5 \ln(2)v(t))} \right) dt} \times \exp\left(\left(B + \frac{C}{T} \right) I_{RMS} \right) \quad (20)$$

The ratio of two differently lifetime with the same voltage and temperature values gives:

$$\frac{\tau_{d3}(T; v(t); I_{eff})}{\tau_{d3}(T; v(t); 0)} = \exp\left[\left(B + \frac{C}{T} \right) I_{RMS} \right] \quad (21)$$

We must identify the two constants B and C. The results (18) and (19) are identifying equal to $\tau_{d3}(T; v(t); 0)$ in the above equation. The two tests (“first pack” and “second pack”) give two another points (9)(11). With these data, two differently ratios are determined in order to identify the two constants. After a numerical application, we find:

$$B = -0,02234 \quad \text{and} \quad C = -0,567 \quad (22)$$

In finality, the lifetime equation becomes:

$$\tau_{d3}(T; v(t); I_{eff}) = 3,85 \times 10^9 \times \exp\left[- \left(0,1 \ln(2)T + \left(0,0224 + \frac{0,567}{T} \right) I_{RMS} \right) \right] \times \frac{T}{\int_{t_i}^{t_f} \left(\frac{1}{\exp(-5 \ln(2)v(t))} \right) dt} \quad (23)$$

This equation is in good agreement with data provided by floating and for the result described in this publication. Other test must be doing to validate or to optimise the manufacturer data and this law. A possible evolution of this law is to take into account only the ambient temperature and not the case temperature. In fact, the case temperature can be deduced from the ambient temperature, the RMS current and the ESR value. The difficulty is to determinate the ESR variation law according to the RMS current and the ambient temperature.

VI) Conclusions

This paper described the process developed to study the ageing of supercapacitors. It is based on capacitance computation. A method to determine ageing factors are proposed and explained. Measurements required to determine the capacitance are obtained from a dedicated test bench. During the cycling process, supercapacitors ageing can be observed based on voltage and impedances measurements. Thermal analysis (thermocouple and infrared camera) complete the study and allow us

to deduce (with voltage data) ageing laws. This study will be useful for the integration of supercapacitor pack in transportation system. Two packs are cycled, in order to determine the Eyring stress constant

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