Study on specific effects of high frequency ripple currents and temperature on supercapacitors ageing

R. German a,⁎, A. Sari a, P. Venet a, O. Briat b, J.-M. Vinassa b

a Université de Lyon, Université Lyon 1, Laboratoire Ampère, UMR CNRS 5005, Villeurbanne F-69622, France

b Université de Bordeaux, IMS, UMR CNRS 5218, Talence F-33405, France

Article history:
Received 25 May 2015
Received in revised form 19 June 2015
Accepted 20 June 2015
Available online xxxx

Keywords:
Power devices
Energy storage systems
Supercapacitors
Reliability
Aging

A B S T R A C T
Although supercapacitors can store less energy than batteries, they are particularly appealing for hybrid vehicle applications (for example, for braking energy recovery, or stop and start systems supply). As power networks in hybrid vehicle experience high frequency ripple currents due to power electronics components such as static converters, experiments are done to study the impact of high frequency ripple currents on supercapacitor ageing. The results suggest that high frequency ripple currents do not create new ageing mechanisms. A complementary ageing test is also carried out to study the effect of temperature on supercapacitor ageing at very low voltage. It clearly shows that a significant part of increase in supercapacitor resistance is only linked to temperature, instead of the combined effect of temperature and voltage as assumed by literature for supercapacitor ageing. Whereas tests demonstrate that capacitance loss through time is linked (for the most part) to the combined effect of voltage and temperature. Hence, this paper shows that resistance increase is only partially linked to capacitance loss.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Supercapacitors (SCs) [1], also called Electrochemical Double Layer Capacitors [2] or Ultracapacitors [3,4] are energy storage systems (ESSs) capable of delivering higher power than batteries over a wider range of temperature [5], and with a longer lifetime, than batteries [6]. These characteristics make SCs desirable for high cyclability/high power applications in railway [7] and electrical traction systems, such as personal hybrid vehicles (HVs) [8], or as a supplement for batteries [9].

Power electronics in HVs power network (such as static converters) generate high frequency ripple currents. To understand their effect on SC ageing, tests are performed for representative frequencies existing in different applications. Selected for testing are commercial 3000-Farad SCs from 3 different manufacturers built with the most common technology (carbon/carbon electrodes and organic acetonitrile/TEABF4 electrolyte).

For most of the studied frequencies (except for 1 kHz test which has been perturbed by voltage regulation problems), HF ripple current does not influence SC ageing.

To demonstrate that 1 kHz should not be an exception to the observation above, a second test is performed, but at reduced voltage. In this test, HF 1 kHz ripple currents have no effect on SC ageing. This test also allows us to draw new conclusions. SC resistance increase appears to be only linked to temperature, which is different from capacitance loss mechanisms that need both voltage and temperature.

2. SC operational mode and ageing

SCs use electrostatic effect between ions and electric charges (double layer effect) to store energy (go to Fig. 7). The electrodes are porous to maximize the storage surface (thus the capacitance), and to minimize the equivalent series resistance (ESR). As the SCs use ions and porous electrodes for energy storage, they are only able to store energy at low frequency (LF) as shown in Fig. 1.

SC capacitance ($C_{100\text{mHz}}$) is calculated in Eq. (1) for a 100 mHz frequency and represents the energy stored in LF (at 100 mHz the capacitance is near the maximum as shown in Fig. 1). The 100 mHz ESR ($R_{100\text{mHz}}$), representing the cumulative effect of connections, conduction and porosity on current circulation, is calculated in Eq. (2).

$$C_{100\text{mHz}} = \frac{-1}{2 \cdot \pi \cdot f \cdot \text{Im}(Z_{sc})} \mid _{f=100\text{mHz}}$$

$$R_{100\text{mHz}} = \text{Re}(Z_{sc}(2 \cdot \pi \cdot f)) \mid _{f=100\text{mHz}}$$

Where $Z_{sc}$ is the SC impedance and $f$ the frequency of the electrical signal. Ageing phenomena for SCs lead to a decrease in capacitance and an increase in ESR. They are the result of reactions between parasitic chemical groups at the electrode surface [10] and electrolyte [11].
Literature considers that those reactions are accelerated by temperature, voltage and current rate (in the case of cycle ageing) [12].

3. Experiment setup

Fig. 2 presents the test bench developed for SC ageing tests. The floating (i.e. constant) constraints (USC, T) are applied by independent DC power supplies and a temperature chamber. The ripple current (IAC) is applied to the stacked SCs by a programmable AC current supply and the DC supplies are protected from ripple current by coils (L1,…,L6). The temperature of SCs during ageing is monitored by a thermocouple placed on the middle of the component packaging (see Fig. 3).

We tested 33 SCs from three manufacturers (A, B, C) to get a representative sample of commercial high capacitance ACN/TEABF4 SCs [13]. The tested SCs are equivalent in terms of technology and performances as shown in Table 1.

The tested SCs are high capacitance (3000 F), high power (ESR <0.29 mΩ), and low voltage elements (≤2.8 V to minimize the solvent decomposition rate), which are typically designed for hybrid vehicle use. As presented in Table 2, three components of each manufacturer are aged at 2.8 V, 60 °C floating constraints (i.e. constant voltage and temperature).

For a second batch of SCs (from manufacturers A, B and C), sinewave ripple currents are added to the floating constraints on two SCs by manufacturer and by investigated ripple current (see Table 2). Three particular frequencies are investigated for 2.8 V, 60 °C floating constraints (i.e. constant voltage and temperature).

For a second batch of SCs (from manufacturers A, B and C), sinewave ripple currents are added to the floating constraints on two SCs by manufacturer and by investigated ripple current (see Table 2). Three particular frequencies are investigated for 2.8 V, 60 °C floating constraints (i.e. constant voltage and temperature).

After observing the result from the above test, a second ageing test is performed for 1 kHz ripple current at 0.1 V.

At regular intervals, SCs are disconnected from the DC and AC supplies and an impedance spectroscopy is carried out on each component from 10 kHz to 10 mHz.

4. Results

4.1. Effect of ripple current frequency [14,15]

Fig. 4 presents the evolution of C100mHz and R100mHz as a function of ageing time. The ageing tests take up to 6600 h (9 months) and lead to a minimum capacitance decrease of 30%. As SCs are considered not usable after 20% for capacitance drop [13], the results are very representative of SCs lifetime.

For 100 Hz and 10 kHz, the impact of ripple current on SCs is not evidently different from the (2.8 V, 60 °C) floating ageing results. The frequency also seems not to be a significant ageing acceleration factor, as the results are the same for 100 Hz and 10 kHz ripple current. The ripple current does not contribute to an increase of SC temperature as shown in Fig. 5. This is because the SCs are high current components [see Table 1] designed for a 15 °C joule effect self-heating when a 130 Amax Current is applied [16]. As the self-heating is proportional to the square of the current, the self-heating from 12 ARMS current should be negligible.

Fig. 5 presents the evolution of SCs temperature during ageing tests. For 100 Hz and 10 kHz ripple current, the temperature does not increase at all before 5000 h. The slight increase of temperature (<1.5 °C) observed for manufacturers A and B between 5000 h and 7000 h (for 10 kHz ageing test) can be related to the change in slope of the SC R100mHz parameter after 5000 h for 10 kHz ageing test (see Fig. 4) possibly indicating an effect of overageing on connections (at this stage the SCs are in extreme capacitance loss state (>−20%)). This negligible rise of temperature is a confirmation of the results presented in

![Figure 1. Evolution of SC capacitance with frequency.](image1)

![Figure 2. Scheme of the experimental test bench.](image2)

![Figure 3. Thermocouple location on the SC package.](image3)

![Figure 4. Effect of ripple current on SC capacitance and resistance.](image4)

![Figure 5. Evolution of SCs temperature during ageing tests.](image5)

Please cite this article as: German R, et al, Study on specific effects of high frequency ripple currents and temperature on supercapacitors ageing, Microelectronics Reliability (2015), http://dx.doi.org/10.1016/j.microrel.2015.06.026
It tends to show that the HF current ripples are not a factor causing ageing acceleration for SCs.

In comparison, the results obtained for 1 kHz current ripple are slightly different from the floating ageing results (for capacitance $C_{100mHz}$) and even more different for $R_{100mHz}$ [15]. Those results could be due to a particular effect of 1 kHz frequency on gas production during ageing such as suggested in [17] or to the ageing test disturbance caused by two voltage breakdowns (during the 1 kHz test the voltage regulation system broke down twice as shown in Fig. 4).

During the breakdowns voltage was uncontrolled and unrecorded leading to a succession of overvoltage and undervoltage for several hours. Before the first breakdown the SCs aged at 1 kHz are strictly ageing in the same way as floating ageing test. Manufacturer C elements were stopped because they started to leak. The second breakdown is accompanied by a sudden increase in $R_{100mHz}$. The temperature also increases significantly by 3 °C.

The increase of $R_{100mHz}$ cannot explain the temperature increase by joule effect (see manufacturer data on selfheating [16]). That seems to indicate that the voltage breakdowns lead to a modification of electrolyte and creates a few exoenergetic reactions in the electrolyte.

To be sure that the differences observed between the 1 kHz and the floating ageing tests are caused by the two breakdowns but not the particular effect of 1 kHz current ripple, we decide to observe the effect, of the 1 kHz current ripple again, but this time at very low voltage to minimize ageing related to floating constraints.

4.2. Effect of temperature on SC ageing (at low voltage)

To test the effect of ripple current at 1 kHz, a second ageing test of one year (8700 h) is carried out. The SCs of the three manufacturers are placed at 60 °C in a thermal oven and maintained at very low voltage (+0.1 V to avoid negative voltage). As it is commonly noted by manufacturer, and verified in literature [8], an increase of the SC voltage by 200 mV results in an increase of ageing kinetic by a factor 2.

Thus, at 100 mV, the ageing kinetic due to voltage is negligible (10^4 factors smaller compared to a 2.8 V ageing at the same temperature condition). Thus, the capacitance loss and the ESR gain must be very small.

The test consists of two phases as shown in Fig. 6. For phase 1, 1 kHz/12 ARMS ripple current is applied to the SCs. Then, for phase 2 (just before 6000 h), the ripple current is stopped. Then, during phase 2, SCs are only subjected to 0.1 V, 60 °C floating conditions. Fig. 6 presents the evolution of $C_{100mHz}$ and $R_{100mHz}$ for this test. We can notice that the capacitance and the resistance evolution are not affected by the 1 kHz current ripple again, but this time at very low voltage to minimize ageing related to floating constraints.

$C_{100mHz}$ is hardly (2%) affected by the 1 year (8700 h) ageing test at 0.1 V. Thus, storing short-circuited SCs, even at high temperature, will have a very small impact on their capacitance.

The evolution of $R_{100mHz}$ is quite different. At 6000 h, by comparing with the $R_{100mHz}$ increase with 2.8 V, 60 °C floating ageing results, we notice that the components of the manufacturer A and B gain respectively +40% and +10% for $R_{100mHz}$ at 6000 h for 0.1 V, 60 °C, which represents 50% and 25% of the increase of $R_{100mHz}$ (@6000 h for 2.8 V, 60 °C). From that, we can conclude that temperature plays an important part in causing resistance increase (even when voltage is negligible).

---

**Fig. 4.** Evolution of $C_{100mHz}$ and $R_{100mHz}$ with ageing time.
This phenomenon is independent of the 1 kHz ripple current, as an important increase of $R_{100 \text{mHz}}$ happens with, and without, ripple current (see Fig. 6).

This significant increase cannot be explained by the acceleration factor observed on the capacitance loss. Consequently, we can deduce that the increase of $R_{100 \text{mHz}}$ is caused by several mechanisms: A part of the increase of $R_{100 \text{mHz}}$ is influenced by the chemical reactions linked with the capacitance decrease (i.e. gas creation caused by reaction between parasitic surface group and surface group and electrolyte). Another part of the $R_{100 \text{mHz}}$ increase is linked with totally different phenomenon linked only to temperature. As this part of resistance increase is not linked to voltage, which is required for capacitance ageing, we can conclude that the supplementary effects causing $R_{100 \text{mHz}}$ increase are not linked with capacitance ageing (thus they probably take place outside the electrodes porosity).

We can also notice that the supplementary mechanisms for $R_{100 \text{mHz}}$ ageing are not necessarily present for all SCs manufacturers. For example, for manufacturer C, $R_{100 \text{mHz}}$ stays constant for the low voltage ageing test. It indicates that the increase of resistance is mainly linked to the capacitance loss for manufacturer C.

Thus, the supplementary causes of $R_{100 \text{mHz}}$ increase, are linked with porosity engineering factors, which tend to reduce the charge flow, without any relation to electrode storage surface. The first possible cause can be the degradation of the binding agent that sticks active carbon electrode and collector together. This makes the contact area smaller. The second possible cause could be that some parasitic chemicals inside the electrolyte dislocate without other reactant (zero order reaction), or react together with temperature effect leading to a degradation of electrolyte conductivity. Finally, the separator itself can also become less conductive for ions due to ageing, because of fouling and/or slow decomposition mechanisms (the SCs separator is just simply built of paper).

4.3. Interpretation of HF ripple current transparency

A physical interpretation is given in Fig. 7. As described in part 2, SCs are relatively low frequency ESSs. At the ageing test frequencies (between 100 Hz and 10 kHz), we can deduce that ions are not fast enough to compensate the supplementary electric charges from the AC current (the capacitance is close to 0 F for this frequency range as shown in Fig. 1). Supplementary electric charges from one electrode negate with the supplementary charges from the other electrode. Thus, there is no supplementary formation of double layer and thus no supplementary ageing reactions between electrolyte and electrodes. This explains why SCs are not affected by high frequency current ripples.

5. Conclusion

This article presents the possible effect of HF current ripple and the particular effect of temperature on SC ageing kinetic. 33 SCs from 3 different manufacturers are aged up to 12 months with or without ripple current. Three frequencies (100 Hz, 1 kHz and 10 kHz) are investigated. As these SCs are designed for around 120 A_{RMS} current use and as the maximum ripple induced by DC–DC converters is estimated to be 10% of the mean current, the current ripple for one component is fixed to 12 A_{RMS}.
The evolution of the electric parameters of SCs (C_{100mHz} and R_{100mHz}) is monitored with regular impedance spectroscopies. The temperature of SCs is also monitored during ageing.

The tests reveal that HF current ripples do not have any significant effect on SC ageing. Consequently, we can conclude that the supplementary electric charges from AC current do not participate in double layer formation, because the frequency is too high for ions, to compensate the supplementary charges brought by ripple current. Thus, HF ripple currents do not impact SCs, because no new zone of double layer ageing is created.

These conclusions have a great appeal to SC integrators, as they won't have to use costly coils to protect SCs from HF ripple currents (from domestic appliance (~100 Hz) to high frequency static converters (~10 kHz)).

The complementary test shows that SC capacitance is hardly affected under low voltage/high temperature ageing test whereas their resistance can increase a lot. That shows that the ageing mechanisms affecting SC capacitance and SC ESR are not identical.

Acknowledgement

French national research agency (ANR) is supporting these research works which are part of the Supercal project. Supercal is a project held by IMS Bordeaux which combines three academic laboratories (Ampère (Lyon), IMS (Bordeaux), French institute of sciences and technology for transport, development and networks (IFSTTAR)) and manufacturers from transportation and energy storage devices sectors (PSA Peugeot Citroën, Valeo, Batscap).

References


