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Capacitance recovery analysis and modelling of supercapacitors during cycling ageing tests

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ABSTRACT

During accelerated ageing tests of supercapacitors (SC), a decay in their performance is reflected by a decrease in capacitance and an increase in equivalent series resistance ESR. In power cycling, when electric solicitations of the SC are interrupted for the purposes of real use or characterisation, performance recovery is observed, mainly in terms of an increase in capacitance. This phenomenon is due to a redistribution of electrical charges, balancing of impurities inside the porous carbon electrodes, and the cell's return to thermodynamically steady-state conditions. A repetitive long rest period during cycling appears to slow down the ageing process, and to reduce the decay in performance. The impacts on capacitance recovery during rest time, of both cut-off voltage and temperature, are studied. A nonlinear analytical expression is used to predict the capacitance decay for several durations and test interruption periodicities; this is also used to model the capacitance during rest time, taking the cut-off voltage, rest time and temperature into account.

1. Introduction

In recent years, the electrochemical capacitor has been considered to be a very important electric storage device. As a consequence of their general operational principle, based on the formation of a electrochemical double layer at the interface between an electrolyte and a large surface area polarized electrode, SCs have a large capacitance and a very low series resistance, and therefore a high cycle lifetime [1,2].

Depending on the rapid charging process used, a SC can be an ideal additional feature for devices with a high specific energy, such as batteries or fuel cells. A SC module can act as a booster device by supplying or accepting significant pulse power with high efficiency, whereas the primary source operates at a continuous rating [3]. As an example, for a Mild-hybrid vehicle in a typical urban configuration, the SC module has to provide repetitive charge/discharge current pulses of several hundred amperes, over a period of typically a few seconds, in order to assist the internal combustion engine (ICE) at the vehicles start-up phase and to recuperate energy in the barking phase [4].

During power cycling tests, experience shows that the performance of the SC fades, with a decrease in capacitance and an increase in equivalent series resistance ESR [5]. The ageing process of SCs is driven mainly by temperature and cell voltage [6]. The failure mechanism during ageing is accompanied by a chemical process, which occurs on the electrodes and in the electrolyte. The release of gases (CO_2, H_2) is observed, which is related to the chemical process of the electrolyte decomposition on the activated surface [7–9]. In addition, residual traces of water are present inside the electrodes' pores, as a result of their manufacturing process, in which water is used to wash the material [10,11]. Thus, during the charge and discharge cycles, water electrolysis is initiated. This makes it more difficult for the electrolyte to diffuse, and plays a role in the redox reactions responsible for the degradation of SC performance.

A mission profile comprises also a rest periods which can be as short as a few seconds in the case of an urban driving cycle, and can last for as long as several hours or even several days when the vehicle is parked. Lajnef et al. show that the stop duration during power cycling has a strong influence on the performance of an SC. During this period, a recovery phenomenon is observed, which consists in a decrease in equivalent series resistance ESR and an increase in capacitance, i.e. the opposite effect to that which occurs during the cycling ageing tests [12–14].

In the present paper we are particularly interested in the recovery phenomenon in the context of SC performance degradation during power cycling tests.

In the first section, we present the results of cycling tests made on 650F SC cells. The cell's performance recovery is determined,

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and its impact on power cycling tests is discussed. The redistribution of ions inside the porous electrodes, and the cell's return to thermodynamically steady-state conditions have been cited as possible origins of the recovery phenomenon [15].

In the second section, the dynamics of capacitance recovery are analysed, in order to determine the influence on capacitance recovery of both ageing and rest time.

When the cycling test is interrupted, we record information related to the cut-off voltage and temperature during the interruption. Several tests were designed to study the impact of these parameters on the performance recovery and ageing process of SCs during rest time, by monitoring the capacitance and ESR using an online time domain characterisation method.

Finally, an original methodology for the modelling of SC ageing is proposed. The resulting ageing laws are validated, and allow the lifetime of SCs to be predicted whilst taking possible long periods of test interruption into account. This model is validated using several rest times and periodicities.

2. cycling tests and ageing trends

The testing of SC devices requires the use of expensive equipment, particularly for cycling tests with high current levels. Ageing tests are thus performed on a small number of samples under high temperature and high voltage conditions, but without exceeding the manufacturer's limits. It is thus reasonable to assume that the failure modes observed under these conditions are very close to those encountered in real-life use [16].

2.1. Profile specification

The SCs studied during cycling tests, were 650F-2.7V marketed cells, made with organic type of electrolyte (acetonitrile). Each cell was equipped with a thermocouple mounted onto the surface of the can. The cells were then placed in a forced-convection environmental chamber in order to control the test temperature conditions. An electrochemical workstation with a power booster was used to impose a dynamic current profile on the device under test (DUT), and to acquire the voltage and temperature on real time. The connection of the voltage sense to the terminals is made in such a way that the contact resistance between the terminals and the power bars had no influence on the voltage measurements.

As shown in Fig. 1, the micro-cycle was defined in terms of a pulse width, peak pulse level, and rest time. It led to an RMS current of 62 A (close to the RMS value limit given by the manufacturers) and a cycle period of approximately 40 s. The voltage variation range is [U_n, 1 V], where Un is the rated voltage.

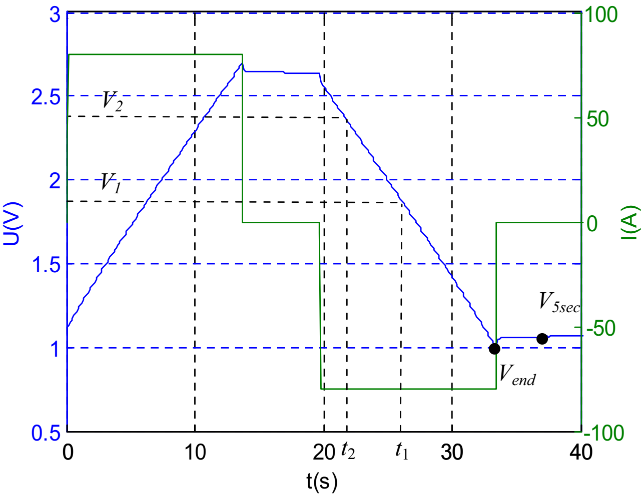

Fig. 1. Current profile and voltage response of a 650F-2.7V cell.

The quantification of the SC's ageing was based on an online time domain characterisation applied to each of the DUTs, and based on the IEC standard [17].

As shown by Eq. (1), the cell capacitance C is determined by measuring the depleted charge $I \cdot \Delta t$ when the cell voltage decreases from V_2 to V_1 during a constant current discharge at 80 A.

$$C = \frac{I \cdot \Delta t}{\Delta V} = \frac{I \cdot (t_2 - t_1)}{V_2 - V_1} \quad (1)$$

In order to avoid calculating the intersection of the tangent of the discharge with starting voltage at constant current (IEC), the equivalent series resistance ESR is defined according to Eq. (2). It can thus be calculated from the voltage change occurring after current switch-off, and is based on the recovery voltage (V_{5s}) measured 5 s after the end of the discharge at which the voltage is given by V_{end} [18,19]. This method of ESR determination is commonly used by SC manufacturers for the qualification of their products (as it permits good internal redistribution of charges), and is compatible with on-line determination even with slow sampling.

$$ESR = \frac{\Delta V}{I} = \frac{V_{5sec} - V_{end}}{I_{end}} \quad (2)$$

where $V_2 = 0.9U_n$ at t_2, $V_1 = 0.7U_n$ at t_1 and I_{end} is the cut-off current at the end of discharge.

2.2. Results from online characterisation

Fig. 2(a) illustrates the online variation of both the capacitance C and the equivalent series resistance ESR for SC1, tested at 50 °C using the current profile describe above, with no long rest time. These results show that the performance fades during the cycling ageing test, corresponding to a decrease in capacitance and an increase in ESR [20].

In terms of variations in ageing rate, the decrease in capacitance during nonstop cycling test is faster than the increase in resistance [21]. Thus, after 300 h of continuous cycles, the relative decrease in capacitance is approximately 14.4%, whereas the relative increase in resistance is approximately 12%. As showing in Fig. 2(b), with the extrapolation of both capacitance and resistance evolution, the criteria of end of life in terms of capacitance loss (20% loss of the initial capacitance) is reach before the duplication of the equivalent series resistance (100% increase).

Regarding Fig. 2, only the capacitance exhibits a fast decay at the beginning of the ageing test. The first point of the capacitance vs. time plot in Fig. 2 has been obtained after a rest time during which the cell voltage was set to zero by a short circuit. This condition is a particular case that leads to a high capacitance initial value that depends on the previous cut-off voltage value, as it will be discussed in Section 4.1, paragraph 5. So, in this figure, the capacitance difference between the first and the second point is important, leading to a high $\Delta C/\Delta t$ at the beginning of the ageing test.

Electrochemical reactions can be explaining the performances degradation. Indeed, The main source for ageing are the degradation of the electrolyte in contact with the electrodes by redox reactions, the electrolyte is decomposed during ageing and gives rise to several species (which are not present in the new state) as fluorine, nitrogen or boron [7]. Also, chemical analyzes indicate a decrease in the amount of oxygen (from traces of water) and surface groups for aged electrodes. Indeed, these chemical species decompose during ageing and give rise to gases such as H_2, O_2, CO_2. So the species formation in electrode pores will reduce the specific area and as consequence a performance fading. Oxygen is formed more