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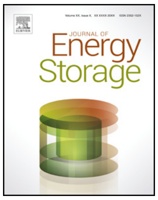

Modelling of current and temperature effects on supercapacitors ageing. Part II: State-of-Health assessment

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ABSTRACT

This second part of the paper proposes a model for predicting the State-of-Health (SOH) of electrochemical double layers supercapacitors (SCs) during combined high-pulsed power cycling and high-temperature life endurance stresses. The evolutions of the SC capacitance, C_{SC}, during these specific types of stresses have been discussed in part I and, based on the phenomenological observations we made, we here predict the C_{SC} evolution by means of a dedicated model. The inputs of the proposed model are the SC delivered charge and the duration of the temperature stress above the rated one; the output is the C_{SC}. The main virtue of the model is its capability to take into account the presence of the C_{SC} recovering and accelerated ageing that cannot be represented by other models available in the literature. The validation of the proposed SC ageing model is carried out by means of experimental results, other than those used to infer the model, obtained on a 365 F SC stressed by combined life-endurance and power-cycling stresses over a time window of 35 days.

1. Introduction

The assessment of the State-of-Health (SOH) of electrochemical double layer supercapacitor (SC) is of utmost importance for the correct design and operation of these storage devices. Indeed, along with the correct ageing prediction, it allows to accurately evaluate the cost associated to the future use of the device. The evaluation of the SOH also allows for identifying temporary degradations and, consequently, avoid major failures. Refs. [1–5] have discussed the use of the SOH of these devices for predicting the remaining lifetime and to define optimal energy management strategies.

From a macroscopic point of view, the ageing process of a SC involves the fading of its performances associated to a decreased capability of storing (and delivering) a given amount of charge. In order to quantify the ageing process, a large part of the literature has adopted as an indicator the so-called SC equivalent series resistance (ESR) and/or the SC capacitance (C_{SC}).

The first part of this work has already investigated the fading of these parameters during Life Endurance (LE), Power Cycling (PC) and combined LE and PC stresses. Additionally, the phenomenology describing the associated ageing processes has been described too.

From the best of the Authors' knowledge, even if there is a considerable amount of works discussing the SC ageing (i.e [6–10]), the literature concerning the computation of the SOH of these devices is quite scarce (to date, only [11] discusses this specific topic on a quantitative basis). On the contrary, major efforts have been focused on the SOH assessment of lithium cells [11–13].[1] However, the SOH estimation methods proposed in [11–13] present important drawbacks related to their computational complexity and/or need of large number of sensing devices.

In order to reduce the requirements associated to these drawbacks and focus on the specific case of SCs, this paper proposes a SOH estimator characterised by the following peculiarities:

1) it requires a limited number of sensing devices since it just relies on the measurement of the cell voltage, current and temperature;
2) it relies on a set of measurements that can be off-line performed on a sample SC cell;
3) it takes into account the effect of stresses associated to high-pulsed delivered current and, also, high temperatures;

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[1] These works might be of interest for the SOH assessment of SC's in view of the common ageing process between these two electrochemical storage systems (e.g., effects of current on the electrode, effects of temperature on the viscosity and conductivity of the electrolyte).

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4) it takes into account temporary performance changes due to the SC recovering phases (RPs) and accelerated ageing phases (APs) [14,15].

The part II of this work is structured as follows. Section 2 describes the elements of the physical process driving the ageing mechanism of a SC and that have been used to define the proposed SOH model. In this respect, a least square fitting is used to determine the parameters of the proposed SOH model during reference LE and PC stresses. The obtained SOH models are, then, integrated for predicting the C_{SC} evolution during combined PC and LE stresses. Section 3 illustrates how to modify the inputs of this look-up tables when the stress conditions differ from the reference one. We show that the obtained SOH model is capable to represent the accelerated ageing and recovering phases in a correct way. In this respect, a comprehensive experimental validation is illustrated in Section 4. In this section we made reference to a 365 F SC exposed to combined LE and PC stresses other than those used to infer the SOH model. In this section we also discuss the mismatch that we would obtain in case AP and RP are not accounted. The last section summarizes the main contributions and outlooks the methodology here discussed.

2. SOH mapping with respect to reference LE and PC stress conditions

The part I of the work has described the ageing processes driving the performances fading of SCs during PC, LE and stresses combining high-pulsed PC and high-temperature LE. The description of the main ageing mechanism has been presented in order to physically explain the trends of the C_{SC} and *ESR* experimentally observed during the considered types of stresses. It is possible to summarize the main findings as follows:

(a) during a LE stress, the average SC temperature (T_{SC}) and the time duration τ_D of the test (at T_{SC}) are the main ageing factors;
(b) during a combined LE and PC stress, the T_{SC} and delivered charge (*Ah*) are the main ageing factors.

As known, ageing tests on electrochemical storage systems are usually time-consuming activities since the goal is to estimate the conditions for which the C_{SC} decreases to (typically) 80% of its initial value. An alternative to the brute-force testing to assess the ageing of the SC is to extrapolate the C_{SC} trend by means of a data fitting performed on a limited data set of a representative given stressing condition.

Two data fitting of the C_{SC} trends have been inferred for each type of the considered stresses: the first one links the C_{SC} (at constant temperature) and τ_D for the LE stress, and a second one linking the C_{SC} with the SC delivered charge (at constant temperature) for the PC stress.

The following subsections describe the criteria used for the fitting equations for each type of test.

2.1. Life endurance ageing

In the first part of the work, it has been already illustrated that during LE stresses, the main reason of the C_{SC} degradation are the changes in: (i) the viscosity and in the conductivity of the electrolyte and; (ii) the electrode porosity. These changes are mainly due to the impurities into the electrolyte generated during its manufacturing and those produced during the SC usage.

It has already illustrated that the degradation of the conductivity and viscosity of the electrolyte vs the temperature are described by exponential functions (e.g., [17–20]). In this respect, part I has experimentally observed that the associated degradation process of the C_{SC} is represented by two time constants. In the first 150 h of LE stress, it is possible to observe a quite fast C_{SC} degradation of 7%. Then, for the next 1000 h, the C_{SC} degradation is of 3% and, finally, it evolves towards a quasi-linear time trend. Indeed, both the impurities production and their active filling of the electrode pores are more important at the beginning of the stress. Then, they become relatively less important during the SC usage.

Table 1
Summary of the inferred parameters of Eq. (1) for the mapping of the LE ageing.

Parameter	Value
A	29.35
a	17.5×10^{-6}
B	13.06
b	27.1×10^{-6}
$C_{LE\infty}$	307 F

Additionally, it is worth noting that once the quasi-linear C_{SC} degradation is reached, the C_{SC} will tend to an asymptotic value depending on the type of stress. This value is in the range of 70–80% of the starting C_{SC} if the V_{SC} and the T_{SC} are within the rated values.[2]

For the above reasons, the model adopted for mapping the C_{SC} degradation evolution during a LE is composed by two exponential functions and a constant value (see Eq. (1)).

The C_{SC} evolution,[3] called C^*_{SC}, is then estimated during a LE stress test using the following model:

$$C^*_{SC,LE}(\tau_D) = Ae^{-a\tau_D(t)} + Be^{-b\tau_D(t)} + C_{LE\infty} \tag{1}$$

where:

- $Ae^{-a\tau_{D(t)}}$,$Be^{-b\tau_{D(t)}}$, are the two exponential functions taking into account the two time constants of the LE ageing process evolution before described.
- $C_{LE\infty}$ is the value of the C_{SC} defined by the SC manufactures as the life-time expectation of the device.

The following least square fitting problem has been defined for inferring the above model parameters:

$$\underset{A,a,B,b,,C_{SC\infty}}{argmin} \left\{ C_{SCM}(t) - Ae^{-a\tau_{D(t)}} - Be^{-b\tau_{D(t)}} - C_{LE\infty} \right\}^2 \tag{2}$$

where $C_{SCM}(t)$ is the measuredC_{SC} each 24 h.

The parameters that have been inferred from Eq. (1) are reported in Table 1.

The blue curve in Fig. 1 shows the measured evolution of the C_{SC} during a LE test performed for 60 days at 328.15 K. The C_{SC} has been evaluated each 24 h by the experimental procedure described in [19]. The red curve shows the C^*_{SC} using the above model. The obtained root mean square error is equal to 0.997.

2.2. Power cycling ageing

In part I, we have already discussed the fact that the main mechanisms driving the C_{SC} degradation during a PC cycling are similar the ones associated to the LE stress (i.e., viscosity and conductivity of the electrolyte and electrode porosity). The main difference between LE and PC stress is that the latter amplifies the degradation of the electrolyte and the production of impurities since it is associated to the current extraction (the so-called

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[2] If the boiling point of the electrolyte (78 °C) and/or its decomposition voltage (3.5 V) are reached, other degradations, that are out of scope of the work here presented, take place and involve more important C_{SC} fading [15].

[3] We remind that this fitting refers to a LE stress obtained at constant average T_{SC}.