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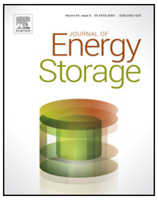

Modelling of current and temperature effects on supercapacitors ageing. Part I: Review of driving phenomenology

Dimitri Torregrossa*, Mario Paolone

Distributed Electrical System Laboratory, Swiss Federal Institute of Technology, Lausanne, Switzerland

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ABSTRACT

The paper proposes a study of the phenomenology driving the ageing mechanisms of electrochemical double layer supercapacitors (SCs) during their most common operating conditions. In particular, the paper focuses on the so-called life endurance (LE) and power cycling (PC) stresses. The paper first provides a description of the variables governing the SC behaviour at the microscopic scale (i.e., porosity of the electrode surface, diffusion and conductivity of the electrolyte). Then, the paper discusses the link between these variables and the ones describing the SC behaviour at the macroscopic scale (i.e., temperature of the electrolyte and delivered current). This analysis is applied to both LE and PC stresses and as well as to their combination. The discussions make reference to experimental results obtained at the Author's laboratory by means of a dedicated test bench.

1. Introduction

Electric double layer capacitors, also known as supercapacitors (SCs), are electrochemical energy storage devices characterized by relatively low values of energy density (in the order of few Wh/kg), high values of power density (above 10 kW/kg) and extremely high cycling capabilities (i.e., above half million cycles). These characteristics are typical for devices operating in nominal operating conditions, namely below the device rated current and within the rated operating temperatures [1].

As known, a SC is essentially composed by two electrodes confining an electrolyte generally composed by an organic liquid (typical electrolyte are tetraethyl ammonium tetrafluoroborate TEABF4 and triethyl methylammonium tetrafluoroborate TEMABF4). The SC uses the electric field of the electric double layer established at the electrode-electrolyte interface to store energy. The current delivered from the SC is extracted from this double layer at the electrode-electrolyte interface. The so-called *interactions losses* between the electrode and the electrolyte are the fundamental ageing mechanism occurring in the device [2,3].

From a macroscopic point of view, the SC is a device delivering energy to a load or receiving energy from a power generator. The external variables describing and influencing this energy transfer are: the voltage $v_{\mathrm{SC}}(t)$ across the SC, the external temperature$\tau_{\mathrm{SC}}(t)$ of the SC, the current $i_{\mathrm{SC}}(t)$delivered by the SC (or used to charge it). Macroscopically, the ageing process of a SC involves performances-fading associated to a decreased capability of storing (and delivering) a pre-defined amount of charge. In order to indirectly quantify the SC ageing process, a large part of the literature focused on the assessment of the so-called equivalent series resistance (ESR) and capacitance (C_{SC}) [1–15]. The types of stresses proposed in these papers can be grouped in two main categories, namely: (a) life endurance (LE) (also called life calendar tests) [1–11] and (b) power-cycling (PC) stresses [10–15].

During a LE test, the $v_{\mathrm{SC}}(t)$ and the $T_{\mathrm{SC}}(t)$ are controlled in a specific environment in order to analyse their effects on the performances fading of the device. During these tests the SC is not delivering any current.

During a PC tests the environment temperature is kept constant to the rated value and the SC is charged/discharged with an$i_{\mathrm{SC}}(t)$ of a given waveshape.

The results presented in the above works investigate the SC performances-fading with respect to $i_{\mathrm{SC}}(t)$ amplitudes comparable to the SC rated current and, to the best of the Authors knowledge, there are no contributions discussing the SC ageing with $i_{\mathrm{SC}}(t)$ amplitudes well beyond the SC rated values. Additionally, also the influence of high values of the environment temperature during combined PC and LE tests has not been addressed.

As known, from a microscopic point of view, a SC is an electrochemical device that stores charge using the double layer phenomenon [1]. At the interface between the electrode and the electrolyte, electrostatic interactions form a charge-layer around the electrode and, also, in the electrolyte. The current extraction from the electrode is based on the micro interaction between the

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* Corresponding author. Fax: +41 216934662.
E-mail address: dimitri.torregrossa@gmail.com (D. Torregrossa).

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porous electrode and the surrounding electrolyte. From this microscopic point of view, the ageing process is mainly related to the modification of the surface contact between the electrode and the electrolyte. The internal variables describing this surface interaction, and the consequent charge transfer, are: the porosity of the porous electrode Γ, the electrolyte conductivity k and the viscosity λ of the electrolyte, the charge diffusion coefficient D and the size of the micropore structure on the electrode surface. Then, at microscopic level, the ageing of the SC is basically related to the lower interaction between electrode and electrolyte due to changes in Γ,k and λ [2,3].

In this respect, there are several works describing the micropore structure of the electrodes and its influence on the charge extraction (e.g., [2]) the temperature and voltage dependency with the conductivity and viscosity of the electrolyte (e.g., [14–16]). Although the analyses presented in these works are quite accurate, they are not framed in the context of SC applications. Indeed, they are not coupled with the high-power cycling that typically characterise the use of SCs. Consequently, the associated ageing mechanisms might be missed.

From this stand-point, the work presented in this paper aims at providing: (i) the phenomenological description of the ageing processes related to the most common categories of SC ageing stresses (i.e., LE and PC); (ii) the link between the local SC electrodes-electrolyte variables and the associated macroscopic ones during the ageing processes; (iii) the physical explanations supporting the time evolution of the SC external variables (ESR and C_{SC}) during combined PC and LE stresses.

Once the physical explanations of the ageing process are described and validated, we propose in part II to quantify the evolution of the performances-fading by a suitable model for the evaluation of the device State-of-Health in terms of decrease of C_{SC}.

The part I of the paper is structured as follows. Section 2 presents a short description of the physical processes driving the ageing mechanism of a SC; the links between local SC electrodes-electrolyte variables and external ones are proposed. Section 3 describes the ageing mechanisms driving the performances-fading during the targeted ageing tests; the quantification of the C_{SC} and ESR changes are supported by physical explanations. Conclusions summarize the contribution of the proposed work and introduce part II.

2. Base phenomenology of the SC ageing process

2.1. Summary about the SC charge storage mechanism

Before describing the SC ageing process, we here introduce the fundamental mechanisms that are used in these devices to store charges. This paragraph is intentionally introduced since we will use these concepts afterwards.

The modelling of the energy storage process associated to the double layer charge has been described in detail in [1]. As illustrated in [2,3], a SC is essentially composed by two carbon porous electrodes confining an electrolyte. The process of charge-transfer in a SC is composed by two sub-processes (see Fig. 1):

(a) the first one implies the ions diffusion within the electrolyte (electrolyte current);
(b) the second one refers to the electron diffusion within the electrodes toward the electric load connected to the SC itself (superficial electrode current).

Based on analysis given in Ref. [2], the superficial electrode current and the electrolyte one are given by the following equations derived from the local-form of the Ohm's law:

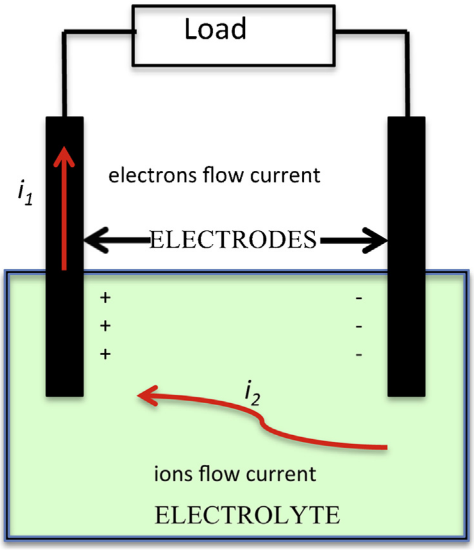

Fig. 1. Schematic representation of the charge transfer within a SC.

$$i_1 = -\sigma \frac{\partial \phi_1}{\partial x} \tag{1}$$

$$i_2 = -k \frac{\partial \phi_2}{\partial x} \tag{2}$$

where σ is the electrode conductivity, k is the electrolyte conductivity, $\phi_1$is the electrode potential, $\phi_2$is the solution potential, x is the coordinate associate with the width of the electrode or with the volume containing the electrolyte solution.

Eqs. (1) and (2) are derived from these hypotheses:

(a) the electrolyte concentration is uniform throughout the electrolyte itself.[1] The solvent evaporation takes place with a long time constant.
(b) Ohmic losses are the main source associated to the heating of the targeted device and the environment temperature is not close to the electrolyte boiling point (typically ranging from 351.5 K to 358.5 K).[2]
(c) the temperature is constant through the cell but it changes in time.[3]
(d) The capacitance of the SC, along with the physical properties of the electrolyte, are constant over the range of possible SC voltage. It is also assumed that the potential difference $\phi_1 - \phi_2$ is below the decomposition voltage of the electrolyte. As it will be explained later, the degradation phenomena associated to SC voltage values below the nominal one has a long time constant.

2.2. SC ageing processes description at microscopic level

By observing Eqs. (1) and (2), it is possible to state that, from a microscopic point of view, the ageing phenomena associated to the

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[1] This hypothesis is acceptable since, within the electrolyte of a SC, there are no redox reduction causing corrosion of the materials.

[2] Such hypothesis is necessary in order to avoid the presence of other degradation phenomena.

[3] The local over temperatures that can appear on the electrode electrolyte volume interface can be neglected.