Microelectronics Reliability xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Microelectronics Reliability

journal homepage: www.elsevier.com/locate/microrel

Prediction of supercapacitors floating ageing with surface electrode interface based ageing law

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ARTICLE INFO

Article history:
Received 26 June 2014
Accepted 14 July 2014
Available online xxxx

Keywords:
Energy storage system
Supercapacitor
Ultracapacitor
Floating ageing
Ageing law

ABSTRACT

Supercapacitors (SC) are power devices used as transitory energy sources for peak power applications such as braking energy recovering in hybrid transports. They are subject to electrochemical ageing processes which affect their performances and reliability. Consequently, the main influence factors on SC ageing kinetic are temperature and voltage. Some ageing law based on experiment results have already been produced (for instance the Eyring law) but are not precisely related to physical considerations. In this article, we propose to use an ageing law which links ageing kinetic with the growth of an interface layer between the electrodes surface and electrolyte, called here SEI (Solid Electrode Interface) layer. In order to have a representative sample, 81 commercial supercapacitors coming from 3 different manufacturers will be tested through floating ageing tests at different voltage and temperature constraints. All presented components are manufactured with the most widespread SC technology (double layer SC using activated carbon for electrode and acetonitrile). The fitting of SC experimental ageing results and SEI ageing law is achieved. Then the effect of temperature and voltage on SEI ageing law parameters is performed.

1. Introduction

Supercapacitors [1] (SC) often called Electrochemical Double Layer Capacitors [2] (EDLC) or Ultracapacitors [3] (UC) are energy storage systems (ESS) based on the double layer effect. Double layer occurs when electric charges are facing with opposite ionic charges as shown in Fig. 1. The mechanism of energy storage is electrostatic thus highly reversible. This explains the higher lifespan of SC compared to electrochemical batteries (which use chemical transformations for energy storage). SC ageing phenomena are mainly related to the presence of chemical surface groups on electrode [4,5]. Those groups are reactive with electrolyte under SC voltage and temperature nominal conditions and lead to solids and gases products. Solids tend to reduce the capacitance of SC by laying on electrode conductive surface. This interface layer will be called Surface Electrolyte Interface (SEI). Some other SEI related ageing phenomena are present on literature with Li-ion batteries [6]. In this case the decrease of capacitance is proportional to the square root of time.

The aim of this article is to apply in a first time a SEI related ageing law to a representative sample of 81 SC coming from 3 manufacturers. That way we can verify the good fitting of the ageing law with capacitance decrease of double layer SC through ageing. In a second time it analyses the evolution of ageing law parameters as a function of constraints level. The improvement of such a method is that contrary to Eyring's ageing law (which can only predict the ageing time before an event such as a 20% loss of capacitance), we can predict the capacitance value at any time.

2. SC ageing

2.1. Characterization method principle

SCs are manufactured with simple components as shown in Fig. 1. Double layer is forming at the interface between electrode and electrolyte. To maximize the contact surface with electrolyte, electrodes are built with activated carbon [4,5] (a highly porous material capable of developing a contact surface around 2000 m^2/g). The electrodes are linked to electrical circuit by aluminum collectors and are protected from electric contact by a separator which is electric insulator but porous for ionic charges. Then the different components are sealed in a packaging.

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http://dx.doi.org/10.1016/j.microrel.2014.07.105
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Please cite this article in press as: German R et al. Prediction of supercapacitors floating ageing with surface electrode interface based ageing law. Microelectron Reliab (2014), http://dx.doi.org/10.1016/j.microrel.2014.07.105

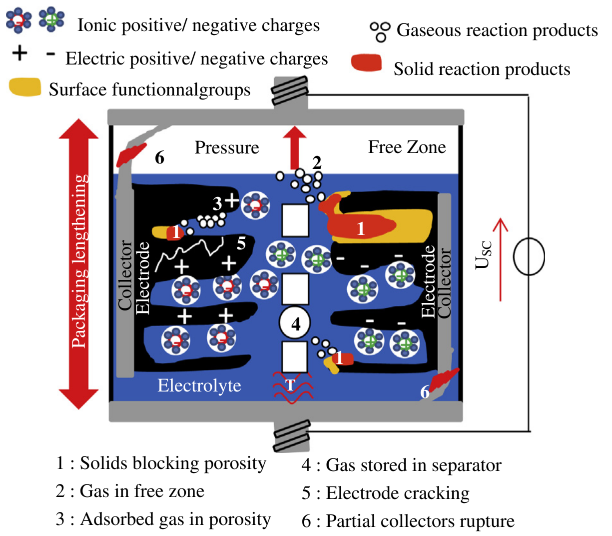

Fig. 1. SC working principle and ageing effects.

To obtain a porous electrode from carbon an operation called activation must be accomplished. Two types of activation exist (physical and chemical activation [7]).

Most of the time activation is chemical [7], which means that corrosive activation species are used to create the porosity during carbonization. After carbonization, electrodes are washed to remove activation species. However, washing process is not perfect. Thus, there are still some remaining species on the activated carbon electrodes [5]. These species are called functional groups. Functional groups are highly reactive with electrolyte under the nominal constraints (voltage U_{SC} and temperature T) of the SC [4]. When they react with electrolyte, there are both solid and gaseous reaction products. The solid products are slowly blocking the porosity of electrodes (zone 1 of Fig. 1) and reducing the contact surface between electrode and electrolyte [4]. The produced gases have multiple possible destinations and impacts on SC ageing. The produced gases can indeed reach the free zone and thus contribute to the increase of the SC internal pressure (zone 2). Gases produced in SC porosity can also be adsorbed on electrode surface (zone 3) and possibly reducing contact surface between electrode and electrolyte. As those gases are in adsorbed state they do not contribute to internal pressure increase (the phenomenon of pressure is associated with the thermal agitation of gas which is characteristic of free gas, whereas adsorption corresponds to a static state). Gas can also be stored in the separator and block the circulation of ionic charges (zone 4). The increase of internal pressure can cause electrode cracks (zone 5) and SC packaging lengthening which damages collectors (zone 6).

Thus, we can conclude that the ageing phenomena are reducing the contact surface between electrode and electrolyte, lowering the quality of contacts by electrode cracking and reducing the movement of ions. Thus, the capacitance (which is dependent on the contact surface between electrode and electrolyte) and the Equivalent Series Resistance (ESR is dependent on contacts and charges movement) are affected by SC ageing. Thus impedance of the SC is a good indicator of SC ageing [8]. Fig. 2 presents evolution of SC impedance (Z_{SC}) spectrum with time for 2.8 V, 60 °C floating ageing constraints.

The increase of ESR is visible with the increase of Z_{SC} real part and the decrease of capacitance with the increase of Z_{SC} imaginary part in low frequency. As a matter of fact:

$$C(\omega) = \frac{-1}{\omega.\mathrm{Im}(Z_{SC}(\omega))} \tag{1}$$

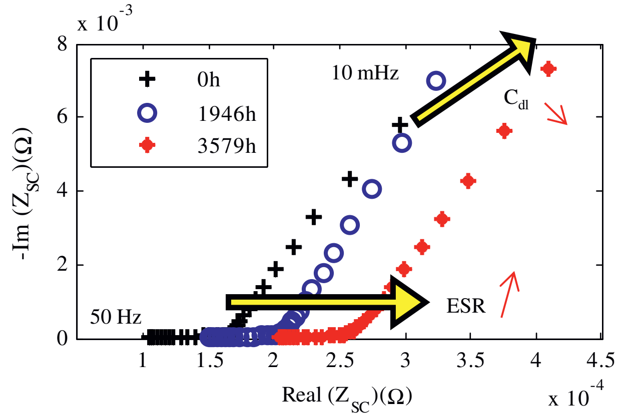

Fig. 2. Evolution of SC impedance spectrum with ageing.

2.2. Solid Electrolyte Interface (SEI) ageing law

SC floating ageing is mainly irreversible contrary to cycling ageing [9]. That means that after an ageing interruption, the regeneration effect (capacitance increase and ESR decrease), is negligible. This suggests that a permanent structure such as a solid layer is mainly responsible of the capacitance fading. Gases adsorption seems to be negligible for capacitance fading as it would lead to reversible ageing (because gases adsorption on a surface, especially physisorption is mainly reversible). During floating ageing charges are equally spread along the pore length [10] leading to a steady formation of SEI. SC pores are represented cylindrical and their length is supposed more important than their diameter (de Levie hypothesis [11]). Some information on the chemical species present in the SEI can be found in [4].

The growing of interface layer thickness (ΔZ) is often represented by a law proportional to the square root of time (t).

$$\Delta Z(t) = A_Z \cdot \sqrt{t} \tag{2}$$

This model is quite well known for describing batteries ageing [6,12] but remains rarely used for SC [13]. Fig. 3 presents the SEI growth into the porosity.

The loss of electrode surface ($\Delta S(t)$) is proportional to SEI growth.

$$\Delta S(t) = -2 \cdot \pi \cdot l_{pore} \cdot A_Z \cdot \sqrt{t} \tag{3}$$

where l_{pore} is the length of the pore. The thickness of SEI called d (that means the distance between opposite sign charges) is considered to be constant. That supposes that the SEI layer is conductive

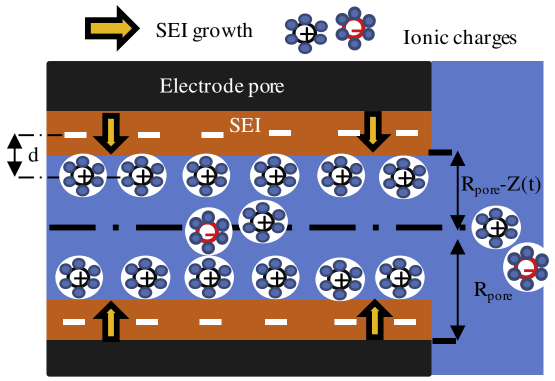

Fig. 3. SEI growth in a SC pore.

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