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Analysis of the dynamic behavior changes of supercapacitors during calendar life test under several voltages and temperatures conditions

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ABSTRACT

Supercapacitors, also known as ultracapacitors are based on porous activated carbon electrodes and on electrostatic charge storage mechanisms. Carbon electrodes are supposed to be chemically and electrochemically inert and the electrostatic nature of the charge storage mechanism is highly reversible. These properties should assure that supercapacitors have an infinite shelf life. But in practice, supercapacitor cells exhibit performances fading when they are used for months. The purpose of this paper is to evaluate the performances fading of supercapacitors during calendar life test which correspond to lower current solicitations than power cycling test. In case of hybrid electric vehicle, which is a key application of ultracapacitors, this ageing test is useful because long rest periods represent a significant time of the vehicle real use. The degradation method of calendar life tests consists in maintaining the cells at high voltage and temperature. A periodic characterization based on impedance spectroscopy is done in order to quantify impedance changes. The obtained results confirm that impedance real part is increasing and the capacitance is decreasing.

1. Introduction

According to the nature of power demand in hybrid and electric vehicles in a broad sense, supercapacitors (SC) seem to be a very attractive option. They can be used in combination with another electrical source, like a battery or fuel cell. With a capacitances of nearly thousands of Farads/cell and very low serial resistance, the supercapacitors module can act as a booster device by supplying or accepting significant pulse power with high efficiency, while the primary source device works with a continuous rating. Thus, an improvement in the overall efficiency of the electrical source can be expected.

In real use, when they are involved in micro-hybrid architecture for instance, supercapacitors have to meet repetitive charge/discharge current levels of about a few hundred of amperes lasting approximately a few seconds. In other hand, this mission profile is also made of rest periods, from about few tens of seconds when included in the operation mode and up to few hours or several days when the vehicle is parked.

To ensure vehicle performances during its lifetime, supercapacitor reliability can be quantified by accelerated ageing tests. Among them, both power cycling tests and calendar life tests are useful since they address the real operating modes previously described, even if this is not done in a separate way. Therefore, the main goal of this paper is to study the impact the calendar life tests on supercapacitor performances by monitoring the parameters of a physical based model.

Supercapacitor cells are based on highly porous activated carbon electrodes [1–3]. These electrodes are characterized by a very high surface area which assures higher specific power (compared to batteries) and higher specific energy (compared to conventional capacitors). Thus, SC is able to fill the gap between batteries and conventional capacitors in terms of energy density, specific power and charge/discharge time [2]. The SC cells have a high cycle life of up to 500,000 cycles, according to the manufacturer, because of non faradic processes at the activated carbon electrodes.

But in the time scale of months, experience shows a performance fading of SC which consist in capacitance decrease and an equivalent series resistance increase [9,11–13]. These phenomena have widely been discussed by several authors in order to explain the observed performances changes. Azaïs et al. carried out some post-mortem analyses on aged cells [8]. They show changes of the atomic composition of the electrodes and asymmetric changes between the positive and the negative electrodes. They introduced also the presence of surface functionalities which accelerates the ageing. Kurzweil and Chwistek studied the chemical process of the electrolyte decomposition and observed that these unwanted chemical reactions leads to gas release (CO_2, H_2) [15].

The manufacturing process of porous carbon electrodes also has an important influence on the rate of the performance fading of the SC [10]. Indeed, this process uses water to wash the material, and traces of water are still present inside the porous structure, in spite of the drying phase. These water traces make electrolyte diffusion

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more difficult and play a role in the redox reactions responsible for degradations.

On the other hand, the polymer used for the activated electrode binding has a negative effect on SC shelf life because they contain a high amount of surface functionalities and thus, they contribute toward the acceleration of the performance fading [10]. All these processes lead to a deposition of some impurity molecules on the electrode surface and therefore, the access to a part of the porous structure is blocked.

In the first part of this paper, we present a generic impedance model for the SC. It is based on a physical description of both the porous electrode and the electrode–electrolyte interface. The model parameters are identified thanks to a characterization method based on impedance spectroscopy tests. The resulting model of a commercially available SC is validated on a wide frequency range [14].

Then, in the second part of this paper, the results of periodic characterization are used in order to monitor the evolution of the SC impedance and parameters. Finally the SC performance degradations are compared for several test conditions and for several cell technologies. The main goal is to link the model parameters to the physical and electrochemical change in the structure of the SC during ageing test.

2. Supercapacitors study

2.1. Impedance model

The porous nature of the electrodes is one of the main internal characteristics of ultracapacitors [1–3]. Because of the high porosity of such electrodes, internal kinetic effects differ from those observed in conventional planar electrodes and have a strong influence on the impedance. Thus, a simple RC series circuit is inappropriate for an accurate modelling of the ultracapacitor dynamic behavior in a wide frequency range.

Among the equivalent electrical models proposed in the literature, we have focused on a physical description of the current path through the cell [14]. This model leads to the equivalent electrical model of Fig. 1 for the SC behavior.

The resistance R_s represents the resistance of the terminals, of the current collectors and of the separator. It is mainly impacted by the collector and the terminals conductivity, but also by the properties of the binding agent that composes the electrode structure.

The resistance R_{el} depends on the electrolyte conductivity and represents the ions mobility inside the porous structure. This resistance mainly depends on the electrolyte conductivity and on the pores size and number.

The equivalent circuit includes a series of n RC parallel branches which correspond to a series expansion of the transmission line model [5]. They represent the charge diffusion into the porous structure. This expansion leads also to a series capacitor to represent the effect of the double layer capacitor. However, the double layer charge process corresponds to an imperfect capacitor that can be modelled by a constant phase element (CPE) [4]. The impedance of the CPE is expressed as $1/[M(j\omega)^{\alpha}]$ where M is the magnitude of the CPE, α is the CPE exponent which is a parameter whose value ranges from 0 to 1 [6]. The phase of this impedance is always $-\alpha \cdot \pi/2$. The value of $\alpha = 1$ correspond to an ideal capacitor and $\alpha = 0$ to a pure resistor. We use the CPE exponent to quantify the behavior drift compared to an ideal capacitor, so we use the exponent $1-\gamma$ instead of α.

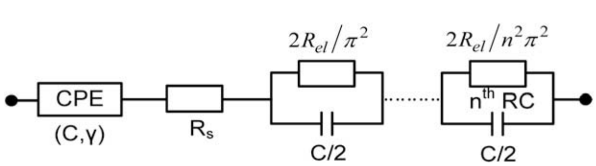

Fig. 1. Electrical equivalent model of supercapacitor cell.

The CPE is used to take the surface roughness and the dispersion of pore sizes into account [4]. The C unit depends on γ values and can be expressed as $F \cdot s^{-\gamma}$. In practice, as the γ value is very low (10^{-3} to 50×10^{-3}), the total capacitance of the cell is close to the C value.

At low frequencies, the equivalent electric circuit of the series RC branches is a resistor $R_{el}/3$ for an infinite number of branches n. Therefore, the SC impedance can be expressed by Eq. (1) and by Eq. (3) to highlight the real and the imaginary parts.

$$Z = R_s + \frac{R_{el}}{3} + \frac{1}{(j\omega)^{1-\gamma}C} \quad (1)$$

$$Z = ESR - j\frac{e^{j\gamma\pi/2}}{\omega^{1-\gamma}C} \quad (2)$$

$$Z = ESR + \frac{\sin(\gamma\pi/2)}{\omega^{1-\gamma}C} - j\frac{\cos(\gamma\pi/2)}{\omega^{1-\gamma}C} \quad (3)$$

where $ESR = R_s + R_{el}/3$ correspond to the cell equivalent series resistance.

2.2. Impedance spectroscopy and model validation

The impedance analyser used for spectroscopy tests allows the investigation of the cells behavior in a wide frequency range from mHz and even few μHz to MHz [7]. As the impedance of SC large cells is very low, this analyser is associated with a power booster (±80 A) to improve the measurement accuracy.

The experimental frequency response of a 2600 F/2.7 V element is given in Fig. 2 where real and imaginary parts are given in the frequency range of [4 mHz–1 kHz]. The parameter identification procedure is based on several impedance plots, as illustrated in Fig. 2, for a 2600 F element at U = 2.5 V (bias voltage) and T = 20 °C.

The resistive parameters R_s and R are both identified using the Nyquist plot. Indeed, R_s corresponds to the minimum impedance real part and using Eq. (2), R_{el} is proportional to the difference between the impedance real part at medium and high frequencies. Then, the γ parameter is linked to the slope d of the Nyquist plot at low frequency by $\gamma = 2a\tan(d^{-1})/\pi$. Finally, C corresponds to the maximum capacitance observed in the capacitance versus frequency plot.

Fig. 2 represents a comparison between measured and simulated real and imaginary parts for a bias voltage of 2.5 V. The good match between experimental and calculated impedances validates the proposed model throughout the entire frequency range investigated. But due to voltage parameters dependency, an investigation for all the voltage range is needed.

2.3. Supercapacitor electrochemical characteristics and self discharge

The electrostatic charge storage mechanism for SC is based on the electric double layer formed at the interface between the electrolyte and the electrode. But, due to parasitic redox reactions, some of the charge is stored by electrochemical process [1,3]. Thus electrochemical phenomena cannot be avoided because of the presence of some heteroatom in the surface of the activated carbon electrodes. The amount of these chemical species depends on the manufacturing process used for electrodes fabrication. To highlight the pseudo-capacitive effect, we use the cyclic voltammetry test [16].

The leakage current due to SC self discharge, representing the charge leakage trough the activated carbon electrode, is a key issue for the study of the supercapacitor reliability [17]. It is due to the