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THE INFLUENCE OF DIELECTRIC RELAXATION PHENOMENA ON THE SUPERCAPACITORS CAPACITY MEASUREMENT RESULTS

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Abstract
Supercapacitors properties based on the electrostatic double layer and consequently the dielectric relaxation phenomena should be taken into account. The paper concerns the problem of the measurements of capacitance and dynamic properties of the supercapacitors. Some practical conclusions related to the description of parameters of supercapacitors are presented.

1. Introduction

The scope of applications of the supercapacitors dynamically rises e.g. in the field of energy saving. Supercapacitors properties based on the electrostatic double layer and consequently the dielectric relaxation phenomena should be taken into account. The paper concerns the problem of the measurements of capacitance and dynamic properties of the supercapacitors. Some practical conclusions related to the description of parameters of supercapacitors are presented.

2. Supercapacitors impedance models

The impedance of a capacitor is often described by the scheme presented in Fig. 1. The equivalent circuit consists of series resistance R_c, parallel leakage resistance R_u and series inductance L. For typical capacitor the capacitance in Fig. 1 can be regarded as a constant function of frequency. Due to dielectric relaxation phenomena, while describing supercapacitor impedance one should take into account the variability of this parameter as a function of frequency.

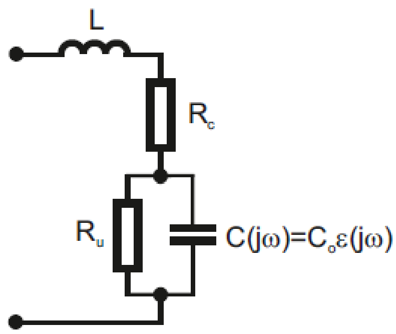

Fig.1. Supercapacitor equivalent circuit.

2. Train movement simulator

In cases of analysis of the signals which range of the frequency spectrum is limited to 10 kHz, the inductance L can be omitted. This paper concerns the case, it focuses on the impact of the ion relaxation phenomena in supercapacitors. Typical relaxation time constants for the elements range from several to several tens of seconds [1]. Due to that, the significant effect of relaxation phenomena on impedance frequency characteristics occurs in a range of 0.001 Hz to tens Hz.

For the ideal case the relaxation phenomena is described by Debye model. In practice, experimental modifications to the model are introduced [2]. General model of the complex value is described by Haviliak-Negami. Due to the generally available computational procedures for a fractional transfer function it is more convenient to apply the Cole-Cole equation in a simpler form

$$\varepsilon_{CC}(j\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+(j\omega T)^\delta} \quad 0 < \delta \le 1 \qquad (1)$$

where

ε_∞ – dielectric constant for high frequencies,

ε_s – static dielectric constant,

T– typical relaxation time constant.

Coefficient δ is specified experimentally.

According to the circuit of Fig. 1, the supercapacitor impedance can be described by

$$Z(j\omega) = R_c + \frac{R_u \frac{1}{j\omega C(j\omega)}}{R_u + \frac{1}{j\omega C(j\omega)}} \quad (2)$$

wherein the capacitance complex value C(jω) is proportional to the dielectric constant described by (1). The inductance L is neglected. This impedance can be treated as the transfer function with current signal at the input and voltage signal at the output. By replacing the Fourier transform with Laplace transformation the impedance model of Cole-Cole can be presented as a transfer function.

$$G_{CC}(s) = \frac{\left(1+\frac{R_c}{R_u}\right) + s^{\delta}\left(1+\frac{R_c}{R_u}\right)T^{\delta} + sR_cC}{\frac{1}{R_u} + s^{\delta}\frac{T^{\delta}}{R_u} + sC} \quad (3)$$

Expression (3) can be presented in a general form [2]

$$G(s) = \frac{b_0 s^{\beta_0} + b_1 s^{\beta_1} + \cdots + b_{m-1}s^{\beta_{m-1}} + b_m s^{\beta_m}}{a_0 s^{\alpha_0} + a_1 s^{\alpha_1} + \cdots + a_{n-1}s^{\beta_{n-1}} + a_n s^{\alpha_n}} \quad (4)$$

Transfer function (4) exponents are both integer numbers and fractional. As a result the description is associated with differential-integral calculus of fractional orders [3]. For the calculation of transfer function of systems containing supercapacitors which impedance is described by (3) one can use specialized computational packages, e.g. FOTF [4], developed as a complement to Matlab software.

3. Dynamic characteristic of supercapacitor

Expression (3), describing supercapacitor impedance can be usually presented in a simpler form [5]

$$G_{CC}(s) = \frac{1 + s^{\delta}T^{\delta} + sR_cC}{\frac{1}{R_u} + sC} = \frac{1 + b_1 s^{\delta} + b_2 s}{a_0 + a_2 s} \quad (5)$$

which can be spread into simple fractions

$$G_{cc}(s) = \frac{1 + b_1 s^{\delta} + b_2 s}{a_0 + a_2 s} \quad (6)$$

where

$$G_{cc1}(s) = R_c \quad (7)$$

corresponds to the equivalent series resistance of the capacitor. Component

$$G_{cc2}(s) = \frac{R_u}{1 + sR_uC} \quad (8)$$

describes the ideal capacity with parallel leakage resistance, and component

$$G_{cc3}(s) = \frac{s^{\partial}T^{\partial}R_u}{1 + sR_uC} \quad (9)$$

is associated with the phenomenon of dielectric relaxation.

Fig. 2 shows the modules of each component of the transfer function (7)-(9). They are asymptotes of the transfer function (6) It is possible to approximate the slope of N(ω) logarithmic plot using those asymptotes, where

$$N_{cc}(\omega) = \frac{d\left(log(|G_{cc}(\omega)|)\right)}{d\left(log(\omega)\right)} \quad (10)$$

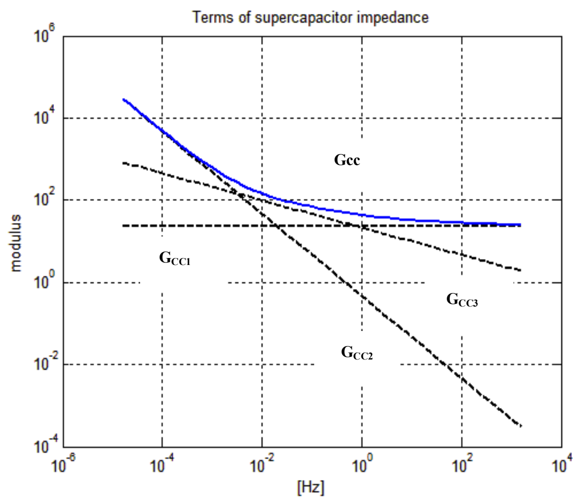

Fig.2. Modules of components of the transfer function (6) for supercapacitor 0.33 F.

The slope of the asymptotes equals - 20dB/decade with increasing frequency excluding a very low values, and equals - 20*(1-δ) dB/decade in the medium range of frequencies. For the range of higher frequencies the characteristic is constant and corresponds to capacitor series resistance R_c (Fig. 1).

Frequency range in which the frequency response characteristic is strongly dependent on dielectric relaxation phenomena is related to the production technology of supercapacitors. In some supercapacitors the relaxation phenomenon is dominated by the impact of electrodes resistance. In such cases the intersection point of horizontal asymptote G_{CC1} and G_{CC2} (Fig. 2) is higher than the intersection point of G_{CC2} and G_{CC3} asymptotes on modules characteristic.

The influence of dielectric relaxation phenomena manifested among others by the non-linearity of current step response of supercapacitor. The responses of transfer function components (6) and their sum for 0.33 F supercapacitor are shown in Fig. 3. This issue is discussed in more detail in [6]. The relation between fractional order dynamic model of supercapacitor impedance and its response to step current is discussed i. a. in [7].

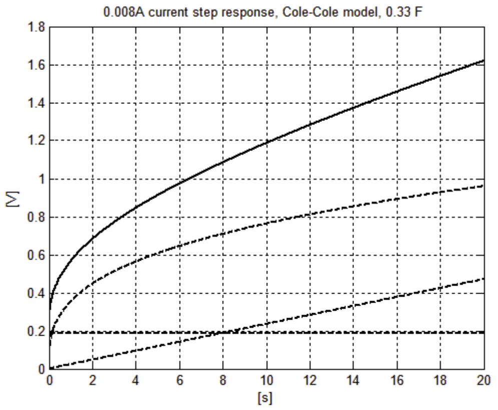

Fig. 3. Current step response of supercapacitor of 0.33 F

Fig. 4 shows experimental 0.47 F supercapacitor response on square current wave with an amplitude of 0.2 A. Voltage step changes match the value of voltage drop on supercapacitor series resistance. The slope of the response after the step is variable and far exceeds the slope, corresponding to the charging of the ideal capacitor with a capacity of 0.47 F with current 0.2 A, which is 0.4 V / s.

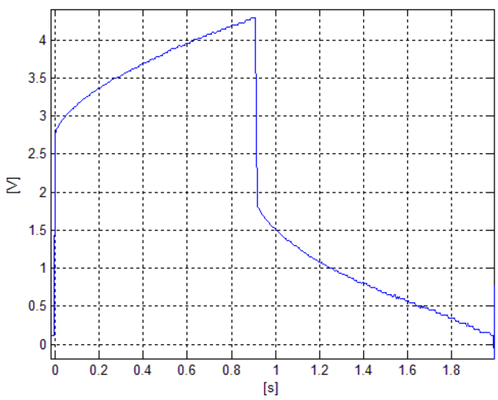

Fig. 4. Experimental 0.47F supercapacitor response on square current wave with an amplitude of 0.2 A.

4. Supercapacitor capacity measurement

International standard IEC 62391-1:2006 [8] and national standards provides measurement of capacity of fixed electric double-layer capacitors for use in electronic equipment named supercapacitors or ultracapacitors on the basis of voltage drop during constant current discharge.

The method described in the standard assumes that the voltage changes during supercapacitor discharge with constant current I_0 are similar to the voltage changes during discharge of ideal capacitor. The voltage is a linear function in time and the capacity equals [8]

$$C_0 = I_0 \frac{t_2 - t_1}{u(t_1) - u(t_2)} \tag{11}$$

where I_0 is discharge current and $u(t_x)$ is voltage after time t_x.

In reality the method of the measurement does not give accurate value of capacity. The first reason is the capacity of the supercapacitors dependence on voltage, and second is nonlinearity of the voltage response on step current associated with dielectric relaxation phenomenon.

To demonstrate the influence of the both mentioned factors the experimental research was carried out. The point was to determine the capacity basing on the slope of the charge and discharge curves for the case when $\Delta t = t_2 - t_1 \rightarrow 0$. Wanted expression is

$$C(u) = -\frac{I_0}{\frac{du}{dt}} \tag{12}$$

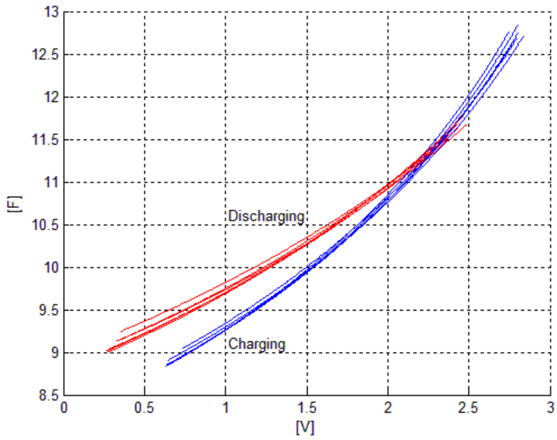

Fig. 5. Determination of the capacity basing on the slope of the constant current charging and discharging curves

The research confirmed that there is significant relation between the capacity and the voltage value. The differences in the capacity in the range of operating voltages for the examined supercapacitor are ±20% [10].

The results differ for the charging and discharging process. The differences in the results depend also on the value of I_0, it means that it depends on charging and discharging rate. That shows, that besides the static nonlinearity resulting from C(u), the measurement result is also influenced by the dynamic phenomena, related to dielectric relaxation.

Conclusions

On the basis of the study it can be concluded that the measurement method of supercapacitors capacity specified by IEC 62391-1: 2006 allows only approximate determination of the capacity of these elements. For accurate modeling of static parameters of these elements should be paid attention to the relationship between voltage and capacity described in the literature.

For accurate measurement of capacity and description of the work of supercapacitors in dynamic conditions it is necessary to take into account dielectric relaxation phenomena.

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