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Modelling of degradation and a soft failure moment during the operation of a supercapacitor applying selected diffusion processes

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ABSTRACT

An important requirement imposed on storage batteries nowadays is to have sufficient capacity. At the same time a high level of availability, reliability and safety is required as well. Our intention is to determine a capacity degradation threshold and the moment the soft failure of a graphite supercapacitor (SC) occurs. If we do not take into account the idle state, the functioning of the supercapacitor might be expressed by charging and discharging processes under different operating conditions given by the allowed extent of SC design. When looking for the degradation threshold and the moment of soft failure occurrence we performed the experimental part of measuring in the climatic chamber. We performed and recorded the processes of SC charges and discharges at different temperatures: 40 °C, 25 °C and −42 °C and at different charging and discharging currents: 2A, 4A, 6A and 8A. The experimental results were used to model mathematically the SC discharge process. Appropriate tools used for SC discharge are diffusion processes. In this case we apply a Wiener process with drift and an Itô process.

1. Introduction

When it comes to the quality of a product, ensuring dependability of technical objects is of great importance. If we are to ensure system functionality, it is necessary to have steady electric energy supply. Therefore, dependability – availability, reliability and capability of accumulators is essential nowadays.

We focus on the discharging process of a supercapacitor with respect to temperature and discharge current. We presume that the course of SC discharge is a stochastic process $U(t)$ which depends on environmental conditions. First we want to estimate the distribution of the first hitting time (FHT). The FHT (also known as the first passage time) is the time when, in general, a stochastic process first encounters a given (critical) threshold. We speak about the time when a supercapacitor is no longer able to provide a sufficient amount of voltage. The time when the voltage hits the critical threshold for the first time is also the time of a soft failure. Therefore, we try investigating the distribution of FHT and in all following instances the FHT means also time of a soft failure

Abbreviations: SC, supercapacitor; FHT, first hitting time; LRM, linear regression model; K-L divergence, Kullback-Leibler divergence; WP, Wiener process IP Itô process; $D(P\|Q)$, Kullback-Leibler divergence of Q from P; $H(X)$, differential entropy of continuous random variable; t_{FHT}, first hitting time; $U(t)$, voltage; U_{TR}, threshold voltage; $W(t)$, Wiener process

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occurrence. In our case it can be written as $t_{\mathrm{FHT}} = \min\{t > 0 : U(t) > U_{\mathrm{TR}}\}$, where U_{TR} is a predefined threshold of the supercapacitor voltage. In our case $U_{\mathrm{TR}} = 50\ \%$ of the maximum allowable voltage which is 7V. The FHT is the time of SC capacity degradation threshold and during repeated discharge processes it is also the time of getting a soft failure. In order to model the SC discharge, we selected a specific stochastic diffusion process.

During an SC technical life there are hundreds of thousands of charging and discharging cycles under standard operating conditions. The experiment, we designed and performed, served to measure a few tens of charging and discharging cycles. The experiments were performed at operating temperatures recommended for SC design. The selection of temperature levels in the experiment was based on the statistical evaluation of meteorological measurements. The experiment was designed to fit the highest and lowest recorded temperature levels in central Europe at which the operated system with SC can be found.

From the reliability point of view, a distribution of the FHT is an important feature since it is possible to derive a number of other availability, capability and reliability indicators – e.g. mean up-time, time of soft failure occurrence, mean life time. Moreover, it provides an overview of a random variable as such.

2. State of the art

When analysing the state of the art, we focused on the works which dealt with SC mainly from the following points of view: i) accelerated tests of SC, ii) SC failure occurrence, and iii) the exploration of SC degradation. However, we did not address physicochemical SC processes as they have been examined abundantly. We did not take into account the publications dealing with SC design either.

In [1], authors studied the time to failure of a supercapacitor and developed a model of an expected useful life of supercapacitors which is related to the properties of electrodes and depends also on operational voltage and temperature. However, they concentrated on the overall life-time of supercapacitors. Similarly, supercapacitor aging is studied in [2], where authors measured and analysed variations of the supercapacitor characteristics such as equivalent series resistance and equivalent capacitance. Also in [3,4], the aging of a supercapacitor was examined; particularly they showed the impact of calendar aging and the thermal [3] or power [4] cycling aging. They focused on changes in supercapacitor capacitance and effective series resistance, and compared the respective degradation changes.

Mathematical models of supercapacitor behaviour can be found, e.g. in [5,6] – both articles deal with supercapacitors used in vehicles. Patel and Salameh [5] developed a model for calculating the energy requirement. Although they used different charging and discharging currents, they ran the test at the same ambient temperature. Rafik et al. [6] described supercapacitor behaviour as a function of frequency, voltage and temperature. They compared the model and experimental data and found good correlation between simulation results with the proposed model and experimental ones for temperature range between -20 °C and 60 °C and the voltage range between 0V and 2.5V.

The influence of different levels of temperature has been also studied, for example in [7], where an electrical model of supercapacitor was covered. The authors proposed an experimental method to determine effective series resistance and compared its variation with respect to the temperature of the device and its environment. As for [8], supercapacitors were studied from an electrochemical point of view. The authors performed tests for different mixtures of electrolyte selected because of their low melting temperature.

The efficiency of supercapacitors is widely studied with respect to the material of a supercapacitor, see e.g. [9–12]. Nevertheless, as far to our knowledge, the efficiency of a supercapacitor in terms of providing voltage during one cycle is neither studied nor modelled in the literature.

After we had studied the relevant literature, we found out that the assessment of operating conditions affecting availability, capability and reliability is not sufficient and therefore it is necessary to fill this gap.

3. Data description

The data used in this article was obtained by measuring the discharge of SC placed in the climatic chamber Vötsch VC^{3}7034 the temperature of which was kept at a constant level. The measuring device recorded time, SC voltage and SC current. The time intervals between measures were not the same, but they were of random length having not very large dispersion. The measurement was performed at constant temperatures of 40 °C, -42 °C and 25 °C. These temperatures were based on empirical meteorological data collected from central Europe and they represent maximum and minimum temperatures measured. As an illustration, the temperature 25 °C is a common room temperature. The SC was kept in the climatic chamber for some time to take the ambient temperature in its full extent. Each of the SC was discharged by four different current levels 2A, 4A, 6A and 8A. They are standard operation discharging currents. A few tens of charge and discharge cycles were performed for each temperature level, a current level and every piece of the tested SC. The sample of the data obtained is put in Table 1 and the course of SC discharging is shown in Figs. 1 and 2. In the next part of our article we selected the temperature -42 °C and the discharging current 6A to demonstrate the procedure.

4. Design and theoretical description of SC model

The proposed model of SC discharge course is shown in Fig. 3. The respective steps of the model are described in subsequent sections.