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Supercapacitor equivalent electrical circuit model based on charges redistribution by diffusion

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HIGHLIGHTS

- New equivalent circuit model of supercapacitor was developed.
- Model consists of 2 capacitors & 3 resistors – one with time dependent resistance.
- Time dependent resistance characterizes the ability of charge to move by diffusion.
- The estimation of model parameters is fully described.
- Relative error between model and experiment is 5% in time interval 4000 s.

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ABSTRACT

A new method for the determination of parameters for an equivalent electrical circuit model of supercapacitors is proposed. The method is based on the evaluation of the time dependence of voltage measured on the supercapacitor terminals after its charging by a defined current pulse. The measured time dependence of the voltage is fitted by an exponential function, where the exponent is proportional to the square root of time. This term reflects the redistribution of charges by diffusion inside the supercapacitor structure. The equivalent electrical circuit of supercapacitors is described by five parameters – two capacitors and three resistors. One capacitor corresponds to the Helmholtz capacitance, which is charged immediately with the time constant in the order of hundreds milliseconds, while the second one represents the diffuse capacitance, which is charged with the time constant in the order of hundreds seconds. The two resistors in the equivalent circuit model represent the equivalent series resistance and the leakage resistance, respectively, while the third resistor describes the resistance for charge diffusion in the supercapacitor structure. This resistance is time dependent and a way for calculating its value is demonstrated.

1. Introduction

Supercapacitors (SCs) represent electrical energy storage devices, which offer high power density, short charging time, a high number of cycles, and long-life duration [1,2]. These devices are of particular interest in fast energy-storage applications, where highly dynamic charging and discharging profiles with high current rates are required [3]. Supercapacitors alone found applications in storing harvested energy for autonomous sensor nodes or in combination with rechargeable batteries [4]. Despite the fact that the concept of the double-layer capacitance was described firstly in 1853, a lack of understanding of their electrical behavior prevents to take advantage of the full potential of these devices. A supercapacitor model represents an important tool for evaluation and prediction using analytical methods or simulation e.g. Ref. [5] before practical deployments as well as to overcome a major obstacle for SCs applications: the charge loss due to self-discharge mechanisms, namely charge redistribution mechanisms [2,3,6,7].

The Helmholtz theory permits to explain the different physical phenomena that happen in the interface between an ionic

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electrolyte and an electronic electrode. The interface is modeled by two superficial distributions of charges, the first one as electronic for the electrode, and the second one as ionic of opposed sign for the electrolyte [8,9]. Gouy solved in 1910 the inability of Helmholtz's model to describe the voltage dependence of the electrical double-layer capacitance by introducing random thermal motion, which led him to consider a space distribution of the ionic charge in the electrolyte. This distribution is generally known as diffuse layer, which was mathematically formulated by Chapman in 1913. To improve the Gouy and Chapman's theory, Stern introduced in 1924 dimensions of ions and solvent molecules and also divided the space charge into a compact layer, constituted of adsorbed ions at electrode surface, and the diffused layer as defined Gouy and Chapman. Apparently, charge storage mechanism in a double-layer capacitor differs significantly from those that occur in conventional capacitors, thus traditional models used to describe capacitor behavior are inadequate in the case of electrochemical capacitors [8,10]. Models of various types have been proposed to predict or describe supercapacitors' behavior under numerous conditions in power storage applications. These types can be summarized into groups according to the way of identifications [2] (time-domain identification leading to RC-equivalent circuit model [2,4,6,9,11–16], frequency-domain identification by impedance spectroscopy model [8,17–21], and electrochemical thermal principal identification [7,22,23]), according to the degree of complexity (simple equivalent circuit e.g. [12], complex mathematical models e.g. [9], and robust models e.g. [23,24]), or according to the frequency range of applications (long-term applications e.g. Ref. [2], highly dynamic application e.g. Refs. [7,17,21]) etc.

The simplest and the most common model represents an equivalent electrical circuit which consists of a capacitor representing the SC capacitance, an equivalent series resistor (ESR) representing the ohmic losses and an equivalent parallel resistor (EPR) representing the SC self-discharge [10,12]. This model gives results for quick estimation, not for characterization the real SC, since it ignores important physical phenomena, such as charge redistribution and voltage dependence of SC capacitance. An evolution step represents an introduction of voltage-dependent capacitor in model described in Ref. [13], however, it is still insufficient for characterization of long-term behavior [1]. To model a 30-min behavior, Zubieta and Bonert [11] proposed an equivalent circuit of three parallel branches: the immediate branch, the delayed branch and long-term branch. Each branch of the equivalent circuit is formed by the series connection of a capacitor and a resistor, and has a different time constant to fit accurately experimentally observed behavior. The immediate branch contains a voltage-dependent capacitor. A parallel resistor connected to these branches represents current leakage [11]. Although the model accurately predicts the performance of SC in term of a half-hour, it fails in a description for SC self-discharging. The ladder model [14], transmission line model [9] or the four-branch model can overcome this failure for longer times. Nevertheless, these models are very difficult to implement because of a high number of components or unknown variables need to be identified in particular models.

Modeling a two-terminal device with more than two elements is always difficult, and requires additional assumptions, complicated test or sophisticated laboratory instruments [1,9,14], to define a useful circuit. Thus, Faranda et all [15]. proposed the simplified two-branch model, which describes the short-term behavior of the device with one branch, and the delay-term and long-term behavior with the other one. The model is popular among engineers since it is sufficient for prediction of SC behavior in minutes. For longer terms, Diab et al. [25] introduced a third RC-branch that models the nonlinear SC self-discharge, which is assumed to be caused by diffusion-controlled Faradic redox reactions. Zhang et all [4]. proposed to substitute a constant equivalent parallel resistance in Faranda's model for a variable leakage resistance, which takes into account the effects of various self-discharge mechanisms.

As is known, complete charging and discharging of SC require a long time in the order of several days [2,3,6]. Thus, a certain amount of charge always remains stored inside the SC, even after a long-term SC discharging [3]. An SC charging and SC relaxation are main examples when charge redistribution, or the redistribution of so-called “residual charge” plays a key role in a general SC behavior [2]. This charge redistribution is due to the limited ionic mobility and hence high resistance of ions moving in the vicinity of carbon electrodes [6]. Torregrossa et all [2]. accurately model the diffusion phenomenon of the supercapacitor residual charge through two current sources which they added to Zubieta's equivalent electrical circuit. Their model gives more accurate results compare to Zhang's model even for longer times. Graydon et all [6]. used a two-branch equivalent circuit model to explain a long-term rebound curve, which is caused by charge redistribution within a supercapacitor and not by leakage current.

This paper presents a new two-branch equivalent circuit and a new technique of parameters estimation that can be used to predict SC behavior in long time period of hours and days. The proposed model is built on physical phenomena at the interface electrode/electrolyte. Our model assumes that ions are not only adsorbed on electrodes as Stern pointed out [9] but also cover the ions diffusion in electrolyte in the vicinity of electrode/electrolyte interfaces. Ions redistribution by diffusion process leads to the time dependence of SC's capacitance after its charging, which become evident as the decrease of voltage on the supercapacitor's terminals.

The proposed identification process estimates particular parameters by evaluation of the voltage response on current pulses. Besides usage of traditional methodologies of parameter estimation [10]–[12], acquired voltage – time dependence is fitted by an exponential function, where the exponent is proportional to the square root of time, which covers the redistribution of charges by diffusion inside an SC's structure.

Three different types of commercially available supercapacitors: NessCap 10F/2.7 V (capacitance/rated voltage), Maxwell 10F/2.5 V, and CapXX 2.4F/2.75 V have been tested in the laboratory in order to verify our methodology. In this work, experimental data and simulation results of the proposed model are compared in order to validate the model performance.

2. Two-branch equivalent circuit with time dependent diffuse resistance

We propose for supercapacitor the equivalent electrical circuit, which has five parameters as shown in Fig. 1.

Here:

C_1 corresponds to Helmholtz capacitance C_H.
C_2 corresponds to diffuse capacitance C_D.
R_1 represents the equivalent series resistance (ESR).
R_L represents the leakage resistance.

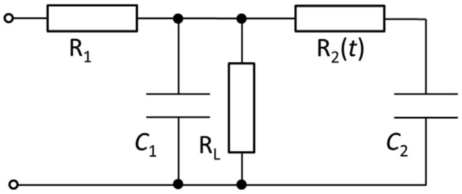

Fig. 1. Equivalent electrical circuit model for supercapacitor.