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Modeling and Simulations in Symmetrical Supercapacitors Using Time Domain Mathematical Expressions

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Abstract

This study presents the deduction of time domain mathematical equations to simulate the curve of the charging process of a symmetrical electrochemical supercapacitor with activated carbon electrodes fed by a source of constant electric potential in time ε and the curve of the discharge process through two fixed resistors. The first resistor R_{Co} is a control that aims to prevent sudden variations in the intensity of the electric current $i_1(t)$ present at the terminals of the electrochemical supercapacitor at the beginning of the charging process. The second resistor is the internal resistance R_A of the ammeter used in the calculation of the intensity of the electric current $i_1(t)$ over time in the charging and discharging processes. The mathematical equations generated were based on a $2R(C + kU_C(t))$ electrical circuit model and allowed to simulate the effects of the potential-dependent capacitance ($kU_C(t)$) on the charge and discharge curves and hence on the calculated values of the fixed capacitance C, the equivalent series resistance (ESR), the equivalent parallel resistance (EPR) and the electrical potential dependent capacitance index k.

Keywords

Symmetrical Supercapacitors, Electrical Circuit Modeling, Potential Dependent Capacitance, Simulation of Charge and Discharge Curves, Time Domain Mathematical Equations

1. Introduction

Recently, it has been shown that it is possible to simulate voltammogram curves of carbon-based with organic electrolyte symmetrical supercapacitors [1]. The inclusion of the potential dependency of the capacitance on the time domain

equations was essential to properly assess the experimental curves. This potential dependent capacitance implies that the capacitance changes as a function of the potential applied on the electrochemical supercapacitor and plays a crucial role in the time domain equations for the voltammetry simulations studies. More recently, it has also been shown that the capacitance dependent on the electrical potential becomes a factor that considerably increases the degree of difficulty in obtaining the time domain equations that aim to simulate galvanostatic curves of supercapacitors [2]. A straightforward electrical circuit was used and fed by a source of electric current of constant intensity in order to simulate the galvanostatic curves of the activated carbon-based supercapacitors.

Although modeling studies on electrochemical carbon-based supercapacitors have been carried out, the measurement techniques used dedicated apparatus such as potentiostat/galvanostat [1]-[14]. However, simpler setups can enable the collection of experimental data and assessment of proposed models. The present study uses a standard resistor for the discharge process and gives the analytical equations governing a straightforward theoretical equivalent circuit of an electrochemical symmetric supercapacitor. Charging has also been carried out employing a standard power supply operating at a constant potential mode. As in previous studies, the simulation of the curves for carbon-based supercapacitors with organic electrolytes also considered the effects of capacitance dependent on electric potential and the analysis was carried out in the time domain using a $2R(C + kU_C(t))$ model electric circuit [1] [2]. Analytical equations have been presented and comparisons between experimental and theoretical curves were made on a quantitative basis. The electric parameters have been determined using the equations and simulations with a straightforward but effective experimental setup.

The organizational structure of this paper has been divided into three main parts, namely: 1) obtaining the equations through which it is possible to simulate the experimental curves by means of the solution of non-linear and non-homogeneous first-order ODEs (obtained from the analysis in the time domain of an electrical circuit fed by a triangular electromotive force source with discharge through a resistor); 2) proof of the functionality of the deduced equations by comparing the experimental curves and the theoretical curves; 3) the conclusions of the work are presented, through which the functionality of the equations deduced in this study are observed. Experimental curves will be shown in black lines and the theoretical curves will be in dotted red.

2. Equivalent Circuits and Equations

As demonstrated in previous studies, a symmetrical carbon-based supercapacitor can be represented by the electric circuit $2R(C + kU_C(t))$ (inside the rectangle made with dashed lines), as shown schematically in **Figure 1** [1] [2]. The circuit used to charge and control the initial electric current flowing through a supercapacitor is composed of a source of constant potential in time ε, the control resistor R_{Co} used in order to avoid overloads in the ammeter with internal electrical

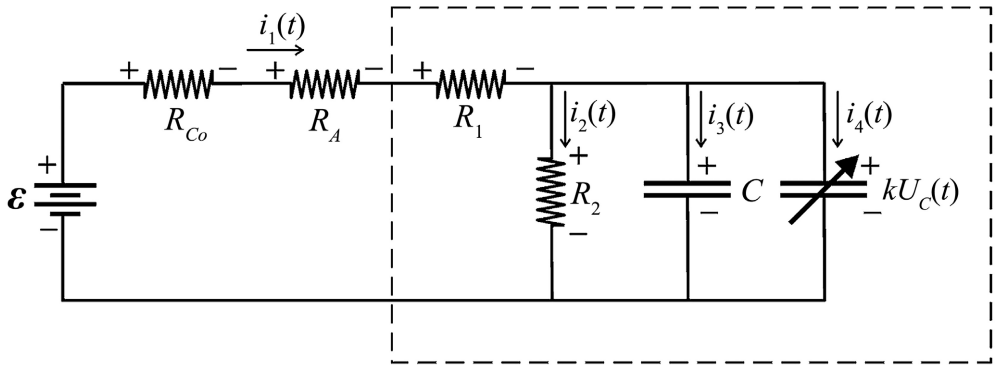

Figure 1. Schematic of the charging process of an electrochemical supercapacitor by a source of constant electric potential ε considering that it can be represented by the electrical circuit $2R(C + kU_C(t))$ fed by a source ε in series with a control resistance R_{Co} and with the internal resistance R_A of an ammeter used to determine the values of $i_1(t)$.

resistance R_A and the equivalent $2R(C + kU_C(t))$ supercapacitor circuit (enclosed in dashed line). The charging process of the capacitor of fixed capacitance C is carried out by the source of constant potential and the discharging process is controlled by resistors. In the circuit, the equivalent series resistance (*ESR*) is represented by the electrical resistance R_1, the equivalent parallel resistance (*EPR*) by the electrical resistance R_2 and the electric potential-dependent capacitance by the electric potential-dependent variable capacitance capacitor $kU_C(t)$. By the analysis of the circuit shown in Figure 1, an equation can be obtained so that it is possible to calculate the theoretical values of t as a function of the experimental values of the electric current $i_1(t)$ at the terminals of the electrochemical supercapacitor with electrodes of activated carbon material and organic electrolyte for its charging process.

In accordance with the circuit $2R(C + kU_C(t))$ shown in Figure 1 for the charging process of the fixed capacitance capacitor C, it is verified that:

$$-\varepsilon + \left(R_{Co} + R_A + R_1\right) i_1(t) + U_C(t) = 0, \tag{1}$$

as well as:

$$i_1(t) = i_2(t) + i_3(t) + i_4(t), \tag{2}$$

therefore:

$$-\varepsilon + \left(R_{Co} + R_A + R_1\right)\left(i_2(t) + i_3(t) + i_4(t)\right) + U_C(t) = 0. \tag{3}$$

It turns out that:

$$i_2(t) = \frac{1}{R_2} U_C(t), \tag{4}$$

$$i_3(t) = C\frac{\mathrm{d}}{\mathrm{d}t} U_C(t), \tag{5}$$

$$i_4(t) = kU_C(t)\frac{\mathrm{d}}{\mathrm{d}t} U_C(t). \tag{6}$$

which implies:

$$-\varepsilon+\left(R_{Co}+R_A+R_1\right)\left(\frac{1}{R_2}U_C(t)+C\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+kU_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)\right)+U_C(t)=0, \quad (7)$$

$$\left(R_{Co}+R_A+R_1\right)\left(\frac{1}{R_2}U_C(t)+C\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+kU_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)\right)+U_C(t)=\varepsilon, \quad (8)$$

$$kU_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+C\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{1}{R_2}U_C(t)+\frac{U_C(t)}{R_{Co}+R_A+R_1}=\frac{\varepsilon}{R_{Co}+R_A+R_1}, \quad (9)$$

$$\begin{aligned}&U_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{C}{k}\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{1}{kR_2}U_C(t)+\frac{U_C(t)}{k\left(R_{Co}+R_A+R_1\right)}\\&=\frac{\varepsilon}{k\left(R_{Co}+R_A+R_1\right)},\end{aligned} \quad (10)$$

$$U_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{C}{k}\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{R_{Co}+R_A+R_1+R_2}{kR_2\left(R_{Co}+R_A+R_1\right)}U_C(t)=\frac{\varepsilon}{k\left(R_{Co}+R_A+R_1\right)}. \quad (11)$$

which results:

$$\int\frac{C+kU_C(t)}{\varepsilon R_2-\left(R_{Co}+R_A+R_1+R_2\right)U_C(t)}\mathrm{d}U_C(t)=\frac{1}{R_2\left(R_{Co}+R_A+R_1\right)}\int\mathrm{d}t. \quad (12)$$

$$\begin{aligned}c_1=&\left[C\left(R_{Co}+R_A+R_1+R_2\right)+k\varepsilon R_2\right]\ln\left[\varepsilon R_2-\left(R_{Co}+R_A+R_1+R_2\right)U_C(t)\right]\\&-k\left[\varepsilon R_2-\left(R_{Co}+R_A+R_1+R_2\right)U_C(t)\right]+\frac{\left(R_{Co}+R_A+R_1+R_2\right)^2}{R_2\left(R_{Co}+R_A+R_1\right)}t.\end{aligned} \quad (13)$$

To obtain the expression of the constant c_1, it is considered that the beginning of the charging process of the fixed capacitance capacitor occurs at $t = t_{(iPC)}$ and that at such instant $U_C(t) = U_C(t_{(iPC)})$. In this way, it can be seen that:

$$\begin{aligned}c_1=&\left[k\varepsilon R_2+C\left(R_{Co}+R_A+R_1+R_2\right)\right]\ln\left[\varepsilon R_2-\left(R_{Co}+R_A+R_1+R_2\right)U_C\left(t_{(iPC)}\right)\right]\\&-k\left[\varepsilon R_2-\left(R_{Co}+R_A+R_1+R_2\right)U_C\left(t_{(iPC)}\right)\right]+\frac{\left(R_{Co}+R_A+R_1+R_2\right)^2}{R_2\left(R_{Co}+R_A+R_1\right)}t_{(iPC)}.\end{aligned} \quad (14)$$

Substituting the term to the right of Equation (14) in Equation (13) one has that:

$$\begin{aligned}t=t_{(iPC)}-&\frac{R_2\left(R_{Co}+R_A+R_1\right)}{R_{Co}+R_A+R_1+R_2}\left\{\left(C+\frac{k\varepsilon R_2}{R_{Co}+R_A+R_1+R_2}\right)\right.\\&\left.\times\ln\left[\frac{\varepsilon R_2-\left(R_{Co}+R_A+R_1+R_2\right)U_C(t)}{\varepsilon R_2-\left(R_{Co}+R_A+R_1+R_2\right)U_C\left(t_{(iPC)}\right)}\right]+k\left(U_C(t)-U_C\left(t_{(iPC)}\right)\right)\right\}.\end{aligned} \quad (15)$$

Referring to Equation (15), it is not possible to obtain the solution analysis of the same for $U_C(t)$ because it is an electrical parameter that cannot be measured directly in an electrochemical supercapacitor, be it symmetrical or not ($U_C(t)$ is the electrical potential between the terminals of an ideal capacitor used to build an electrical circuit that represents a real supercapacitor). However, it is possible to obtain the analytical solution for the theoretical values of t taking as reference the experimental values of the current $i_1(t)$ present in the branch that connects

an electrochemical supercapacitor to the source of constant electric potential in time ε. Thus, considering the charging process of the fixed capacitance capacitor C contained in the electrical circuit $2R(C+kU_C(t))$, it is verified that:

$$-\varepsilon+\left(R_{Co}+R_A+R_1\right)i_1(t)+U_C(t)=0. \tag{16}$$

It is also observed for the charging process of the fixed capacitance capacitor C that:

$$U_C(t)=\varepsilon-\left(R_{Co}+R_A+R_1\right)i_1(t), \tag{17}$$

as well as:

$$U_C\left(t_{(iPC)}\right)=\varepsilon-\left(R_{Co}+R_A+R_1\right)i_1\left(t_{(iPC)}\right). \tag{18}$$

Substituting the expression to the right of Equations (17) and (18) in Equation (15) it is verified that:

$$\begin{aligned} t=t_{(iPC)}&-\frac{R_2\left(R_{Co}+R_A+R_1\right)}{R_{Co}+R_A+R_1+R_2}\Bigg\{k\left(R_{Co}+R_A+R_1\right)\left(i_1\left(t_{(iPC)}\right)-i_1(t)\right)\\ &+\left(C+\frac{k\varepsilon R_2}{R_{Co}+R_A+R_1+R_2}\right)\\ &\times\ln\left\{\frac{\varepsilon R_2-\left(R_{Co}+R_A+R_1+R_2\right)\left[\varepsilon-\left(R_{Co}+R_A+R_1\right)i_1(t)\right]}{\varepsilon R_2-\left(R_{Co}+R_A+R_1+R_2\right)\left[\varepsilon-\left(R_{Co}+R_A+R_1\right)i_1\left(t_{(iPC)}\right)\right]}\right\}\Bigg\} \end{aligned} \tag{19}$$

By using Equation (19), it is possible to calculate the theoretical values of t as a function of the experimental values of $i_1(t)$ collected during the charging process of a supercapacitor evaluated during its charging carried out through a source of constant electric potential in time ε considering that it can be represented by the electric circuit $2R(C+kU_C(t))$. Although the value of the electric potential ε is adjusted in the source of constant potential so that the supercapacitor nominal value is not exceeded (causing decomposition of the electrolyte), the electrical control resistor R_{Co} must be used.

Although the value of the electric potential ε can be adjusted in the source of constant potential so that the maximum value of this parameter recommended by the manufacturer of the electrochemical supercapacitor is not exceeded (higher potential will cause decomposition of the electrolyte) the electrical control resistor R_{Co} must be used. Considering that a symmetric supercapacitor can be represented by the electrical circuit $2R(C+kU_C(t))$, an equation must be obtained by means of which it is possible to calculate the theoretical values of t as a function of the experimental values of $i_1(t)$ collected during the process of discharging the supercapacitor through the resistors R_{Co} and R_A (when its evaluation by the technique of charge at constant electric potential and discharge through resistors). To obtain this equation, **Figure 2** is taken as a reference, so that, the process of discharging the fixed capacitance capacitor C of the $2R(C+kU_C(t))$ electrical circuit through resistors R_{Co} and R_A is carried out.

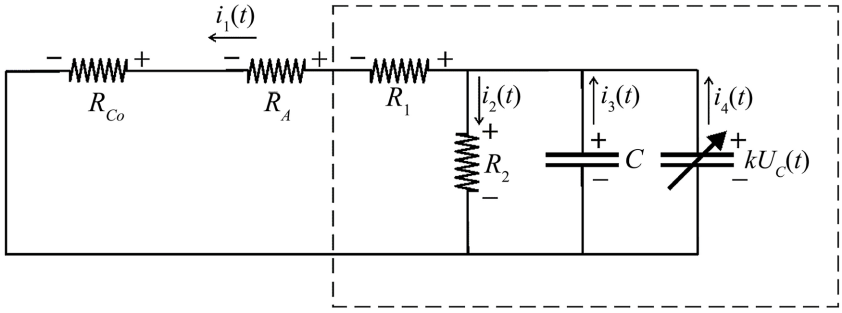

Figure 2. Discharge process of the fixed capacitance capacitor C contained in the electrical circuit $2R(C+kU_C(t))$ through resistors R_A and R_{Co}.

In accordance with the circuit $2R(C+kU_C(t))$ for the charging process of the fixed capacitance capacitor C, it is verified that:

$$-\left(R_{Co}+R_A+R_1\right)i_1(t)+U_C(t)=0, \tag{20}$$

as well as:

$$i_1(t)=-i_2(t)+i_3(t)+i_4(t), \tag{21}$$

therefore:

$$-\left(R_{Co}+R_A+R_1\right)\left(-i_2(t)+i_3(t)+i_4(t)\right)+U_C(t)=0. \tag{22}$$

It occurs for the fixed capacitance capacitor discharge process that:

$$i_2(t)=\frac{1}{R_2}U_C(t), \tag{23}$$

$$i_3(t)=-C\frac{\mathrm{d}}{\mathrm{d}t}U_C(t), \tag{24}$$

$$i_4(t)=-kU_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t). \tag{25}$$

which implies:

$$\left(R_{Co}+R_A+R_1\right)\left(\frac{1}{R_2}U_C(t)+C\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+kU_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)\right)+U_C(t)=0, \tag{26}$$

$$\left(R_{Co}+R_A+R_1\right)\left(\frac{1}{R_2}U_C(t)+C\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+kU_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)\right)+U_C(t)=0, \tag{27}$$

$$\frac{1}{R_2}U_C(t)+C\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+kU_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{1}{R_{Co}+R_A+R_1}U_C(t)=0, \tag{28}$$

$$U_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{C}{k}\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{1}{k}\left(\frac{1}{R_{Co}+R_A+R_1}+\frac{1}{R_2}\right)U_C(t)=0, \tag{29}$$

$$U_C(t)\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{C}{k}\frac{\mathrm{d}}{\mathrm{d}t}U_C(t)+\frac{R_{Co}+R_A+R_1+R_2}{kR_2\left(R_{Co}+R_A+R_1\right)}U_C(t)=0. \tag{30}$$

what results:

$$C\int\frac{\mathrm{d}U_C(t)}{U_C(t)}+k\int\mathrm{d}U_C(t)=-\frac{R_2+R_{Co}+R_A+R_1}{R_2\left(R_{Co}+R_A+R_1\right)}\int\mathrm{d}t, \tag{31}$$

$$c_2 = C\ln\left(U_C(t)\right) + kU_C(t) + \frac{R_2 + R_{Co} + R_A + R_1}{R_2\left(R_{Co} + R_A + R_1\right)}t. \tag{32}$$

Considering that the beginning of the discharge process of the capacitor C contained in the electrical circuit $2R(C + kU_C(t))$ occurs immediately at the end of the charging process, it results that $t_{(iPD)}$ is equal to $t_{(fPC)}$, just as $U_C(t_{(iPD)})$ is equal to $U_C(t_{(fPC)})$.

In this way it can be seen that:

$$c_2 = C\ln\left(U_C\left(t_{(iPD)}\right)\right) + kU_C\left(t_{(iPD)}\right) + \frac{R_2 + R_{Co} + R_A + R_1}{R_2\left(R_{Co} + R_A + R_1\right)}t_{(iPD)}. \tag{33}$$

Substituting the term to the right of Equation (33) in Equation (32):

$$t = t_{(iPD)} - \frac{R_2\left(R_{Co} + R_A + R_1\right)}{R_2 + R_{Co} + R_A + R_1}\left[C\ln\left(\frac{U_C(t)}{U_C\left(t_{(iPD)}\right)}\right) + k\left(U_C(t) - U_C\left(t_{(iPD)}\right)\right)\right]. \tag{34}$$

It turns out that it is not possible to evaluate the electrical potential $U_C(t)$ of a supercapacitor (whether symmetrical or not), but it is perfectly possible to assess the intensity of the electric current $i_1(t)$ present in the terminals of the same terminal using an ammeter. Thus, considering the discharge process of the fixed capacitance capacitor C contained in the electrical circuit $2R(C + kU_C(t))$, it is verified that:

$$U_C(t) = -\left(R_{Co} + R_A + R_1\right)i_1(t), \tag{35}$$

which implies:

$$U_C\left(t_{(iPD)}\right) = -\left(R_{Co} + R_A + R_1\right)i_1\left(t_{(iPD)}\right). \tag{36}$$

Replacing the term to the right of Equations (35) and (36) in Equation (34) it is verified that:

$$\begin{aligned} t = t_{(iPD)} - \frac{R_2\left(R_{Co} + R_A + R_1\right)}{R_2 + R_{Co} + R_A + R_1}\Bigg[C\ln\left[\frac{\left(R_{Co} + R_A + R_1\right)i_1(t)}{\left(R_{Co} + R_A + R_1\right)i_1\left(t_{(iPD)}\right)}\right] \\ + k\left(R_{Co} + R_A + R_1\right)\left(i_1\left(t_{(iPD)}\right) - i_1(t)\right)\Bigg]. \end{aligned} \tag{37}$$

with Equation (37), it is possible to calculate the theoretical values of t as a function of the experimental values of $i_1(t)$ obtained in the process of discharging a supercapacitor evaluated by the discharge through resistors, considering that the supercapacitor can be represented by the $2R(C + kU_C(t))$ circuit initially charged by a source of constant potential ε and discharged through resistors R_{Co} and R_A.

The equation to calculate the initial value of R_1 can be found in Equation (1), which is repeated and deduced as follows:

$$-\varepsilon + \left(R_{Co} + R_A + R_1\right)i_1(t) + U_C(t) = 0,$$

$$R_1 = \frac{\varepsilon - U_C\left(t_{(iPC)}\right)}{i_1\left(t_{(iPC)}\right)} - \left(R_{Co} + R_A\right). \tag{38}$$

In Equation (38), $U_C(t_{(iPC)})$ is the electric potential between the terminals of the fixed capacitance capacitor C in the electrical circuit $2R(C + kU_C(t))$ at the beginning of the charging process.

Given the fact that it is not possible to measure $U_C(t_{(iPC)})$ in a supercapacitor, it is necessary that the charging process starts with it fully discharged, which implies that $U(t_{(iPC)})$, which is the electrical potential existing between the terminals of the supercapacitor at the beginning of the charging process, must be equal to zero, thus imposing that $U_C(t_{(iPC)})$ is also equal to zero. Thus, Equation (38) can be rewritten as follows:

$$R_1 = \frac{\varepsilon}{i_1\left(t_{(iPC)}\right)} - \left(R_{Co} + R_A\right), \Rightarrow \tag{39}$$

$$ESR = \frac{\varepsilon}{i_1\left(t_{(iPC)}\right)} - \left(R_{Co} + R_A\right). \tag{40}$$

By using Equation (40), it is possible to calculate the ESR a symmetric electrochemical supercapacitor for the case in which it is charged by a source of constant potential in time ε, that is, as long as it is fully discharged at the beginning of the charging process. The ESR can also be obtained in the shortest time interval in which there is a change from the charging process to the discharging process of the supercapacitor. Considering that the electric potential $U_C(t)$ at the end of the charging process and at the beginning of the discharging process of the capacitor C in the electrical circuit $2R(C + kU_C(t))$ are equal, it can be seen that:

$$U_C\left(t_{(fPC)}\right) = U_C\left(t_{(iPD)}\right). \tag{41}$$

In Equation (41), $U_C(t_{(fPC)})$ is the electrical potential between the terminals of the fixed capacitance capacitor C in the electrical circuit $2R(C + kU_C(t))$ at the end of the process of charge. $U_C(t_{(iPD)})$ is the electric potential existing between the terminals of that capacitor at the beginning of the discharge process.

Considering that:

$$-\varepsilon + \left(R_{Co} + R_A + R_1\right) i_1(t) + U_C(t) = 0,$$

in the case in which t is equal to $t_{(fPC)}$ and $U_C(t)$ is equal to $U_C(t_{(fPC)})$:

$$U_C\left(t_{(fPC)}\right) = \varepsilon - \left(R_{Co} + R_A + R_1\right) i_1\left(t_{(fPC)}\right). \tag{42}$$

so that:

$$\left(R_{Co} + R_A + R_1\right) i_1(t) + U_C(t) = 0,$$

for t equal to $t_{(iPD)}$ it is verified that $U_C(t)$ is equal to $U_C(t_{(iPD)})$, which leads to:

$$U_C\left(t_{(iPD)}\right) = -\left(R_{Co} + R_A + R_1\right) i_1\left(t_{(iPD)}\right). \tag{43}$$

In this way, it appears that:

$$-\left(R_{Co} + R_A + R_1\right) i_1\left(t_{(iPD)}\right) = \varepsilon - \left(R_{Co} + R_A + R_1\right) i_1\left(t_{(fPC)}\right), \tag{44}$$

$$R_1 = \frac{\varepsilon + \left(R_{Co} + R_A\right)\left(i_1\left(t_{(iPD)}\right) - i_1\left(t_{(fPC)}\right)\right)}{i_1\left(t_{(fPC)}\right) - i_1\left(t_{(iPD)}\right)}, \tag{45}$$

$$ESR = \frac{\varepsilon + \left(R_{Co} + R_A\right)\left(i_1\left(t_{(iPD)}\right) - i_1\left(t_{(fPC)}\right)\right)}{i_1\left(t_{(fPC)}\right) - i_1\left(t_{(iPD)}\right)}. \tag{46}$$

By means of Equation (46), it is possible to calculate the *ESR* based on the values of the electric current $i_1(t)$ at the end of the charging process and at the beginning of the discharging process of a supercapacitor evaluated by means of charge in constant potential and of discharge through resistors.

3. Experimental

The experimental values of the electric current $i_1(t)$ and the respective experimental values of t presented in this study were obtained by the analysis of a commercial symmetrical electrochemical activated carbon supercapacitor with 1 F of nominal capacitance using discharge by resistors after charge at a constant potential. Mostly used electrolytes in these supercapacitors with carbon material electrodes are tetraethylammonium tetrafluoroborate salt (NEt4BF4) in acetonitrile (ACN) or propylene carbonate (PC), for the good conductivity [2]. Care was taken for not exceeding the full scale of the ammeter with the experimental electric current $i_1(t)$ and the supercapacitor maximum nominal potential (5.5 *V*). The charging process of the supercapacitor was terminated as soon as the electric current intensity $i_1(t)$ reached 5% of the value verified at the beginning of the charging process. As soon as the charging process was completed, the discharging process began. It was found that the intensity of the electric current at the beginning of the discharging process was slightly lower than that verified at the end of the charging process. The discharge process ended as soon as the intensity of the electric current $i_1(t)$ reached a value equal to 5% of the value verified at the beginning of the charging process. The interruption of the charging process of the carbon-based supercapacitor based on the value of 5% of the electric current at the beginning of the charging process was determined by providing experimental values of $i_1(t)$ and t suitable for the purposes of generating the theoretical curves. It was verified by testing that experimental curves generated with very long discharge times for the supercapacitor (12 hours) presented great similarity to those obtained with one-hour duration (considering their non-asymptotic region). Cyclic voltammetry and galvanostatic cycling were used as a comparison of real-time experimental setup using a Versastat 4 potentiostat.

4. Results and Discussion

Table 1 shows the values of t and $i_1(t)$ collected during the charging and discharging processes of the commercial activated carbon supercapacitor with the nominal capacitance of 1 F which was charged to a constant potential of 5.5 V from a source ε with an internal resistance R_A of 6.84 Ω in series with resistance R_{Co} of

Table 1. Values of t and $i_1(t)$ collected during the charging and discharging processes of a commercial symmetric electrochemical supercapacitor with nominal capacitance of 1 F.

Charging Process				*Discharging Process*			
t (s)	$i_1(t)$ (A)	t (s)	$i_1(t)$ (A)	t (s)	$i_1(t)$ (A)	t (s)	$i_1(t)$ (A)
0	0.00712	900	0.00228	3619	−0.00679	4519	−0.00239
60	0.00629	1200	0.0017	3679	−0.0061	4819	−0.00161
120	0.00574	1500	0.0013	3739	−0.00572	5119	−0.00108
180	0.00527	1800	0.00101	3799	−0.00537	5419	−0.00071
240	0.00485	2100	0.00081	3859	−0.00505	5719	−0.00047
300	0.00448	2400	0.00065	3919	−0.00475	6019	−0.00031
360	0.00415	2700	0.00054	3979	−0.00446	6319	−0.00021
420	0.00385	3000	0.00046	4039	−0.00417	6619	−0.00014
480	0.00359	3300	0.00039	4099	−0.00391	7219	−0.00007
540	0.00335	3600	0.00034	4159	−0.00366		
600	0.00316	3619	0.00033	4219	−0.00342		

750 Ω (the ammeter was set to the microampere reading scale). Figure 3 shows the curve of $i_1(t)$ as a function of t for the charging and discharging processes of the supercapacitor evaluated with discharge by resistors. Using Equation (40) and considering that $\varepsilon = 5.5$ V, $i_1(t_{(iPC)}) = 0.00712$ A (see Table 1), $R_{Co} = 750$ Ω and $R_A = 6.84$ Ω, R_1 was calculated as being 15.6 Ω. Identical value (15.6 Ω) was obtained using Equation (46), using $\varepsilon = 5.5$ V, $i_1(t_{(iPC)}) = 0.00033$ A (see Table 1), $i_1(t_{(iPD)}) = -0.00679$ A (see Table 1), $R_{Co} = 750$ Ω and $R_A = 6.84$ Ω.

The value of the capacitance index dependent on the electrical potential k was initially considered null. Using Equations (19) and (37), $R_1 = 15.63$ Ω, $R_2 = 694.00$ kΩ (obtained through the self-discharge technique for a total of 80 hours), $C = 1.12$ F (obtained through the technique of direct current discharge I) and $k = 0$ FV^{-1}, it was possible to produce the theoretical inverted charge and discharge curves in accordance with the theoretical values of t and the respective experimental values of $i_1(t)$. These curves are shown in Figure 3.

Taking Figure 4 as a reference, it can be seen that the theoretical curves obtained by means of Equations (19) and (37) are very different from the experimental curves, indicating that the initial parameters obtained by other techniques need to be adjusted. The value of the sum between the modules of the differences of the theoretical and experimental values of t of the curves presented in Figure 4 was approximately 22,498 s.

Figure 5 shows the comparison between the experimental curves of $i_1(t)$ as a function of t and inverted theoretical curves of t as a function of $i_1(t)$. The inverted theoretical curves were produced by inserting the values $R_1 = 15.63$ Ω, $R_2 = 18$ kΩ, $C = 1$ F and $k = 0$ FV^{-1} in equations (19) and (37). As can be seen, there was a significant improvement in terms of similarity between the theoretical and experimental curves of $i_1(t)$ as a function of t. The value of the sum of the modules

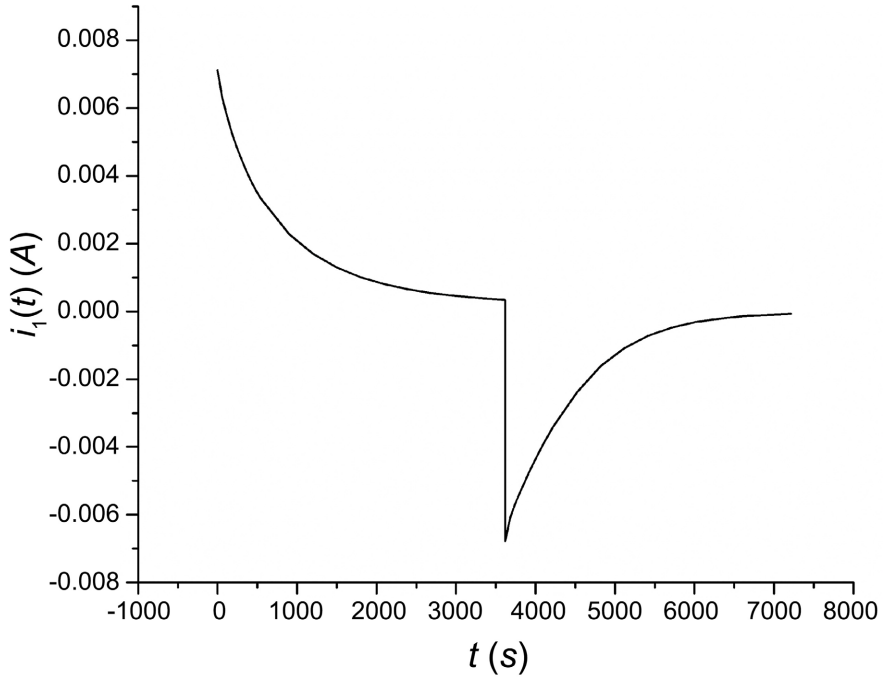

Figure 3. Curve of $i_1(t)$ as a function of t generated during the charging and discharging processes of the commercial supercapacitor with a nominal capacitance of 1 F evaluated by means of the technique of charging at constant electric potential in time and discharging through resistors.

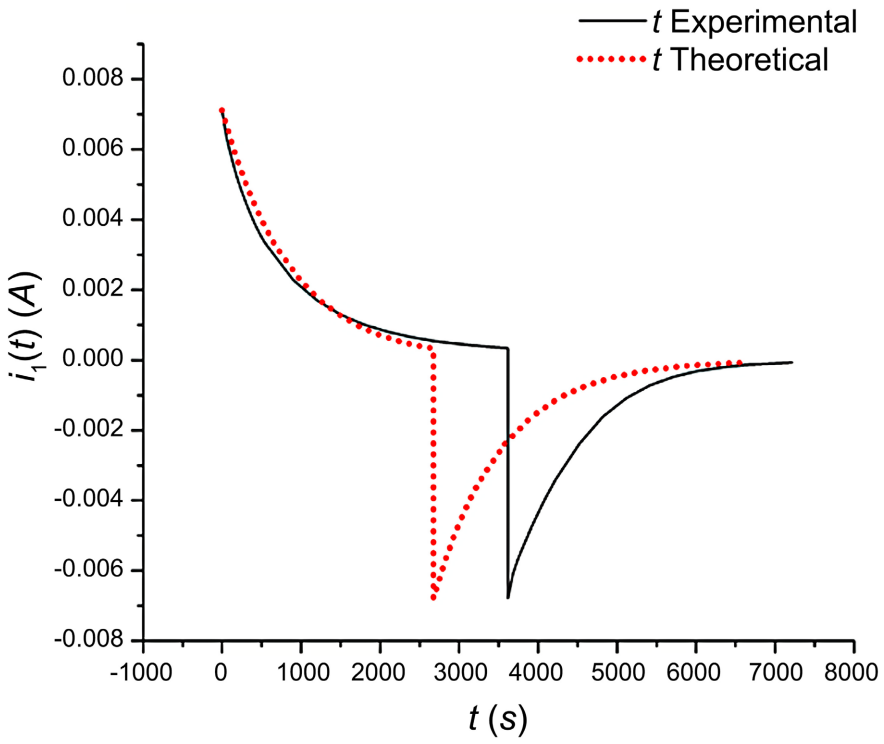

Figure 4. Comparison between theoretical and experimental curves of the electric current $i_1(t)$ as a function of t considering that the theoretical curves were plotted in accordance with $\varepsilon = 5.5$ V, $R_{Co} = 750\ \Omega$, $R_A = 6.84\ \Omega$, $R_1 = 15.63\ \Omega$, $R_2 = 694$ kΩ, $C = 1.12$ F and $k = 0$ FV^{-1}.

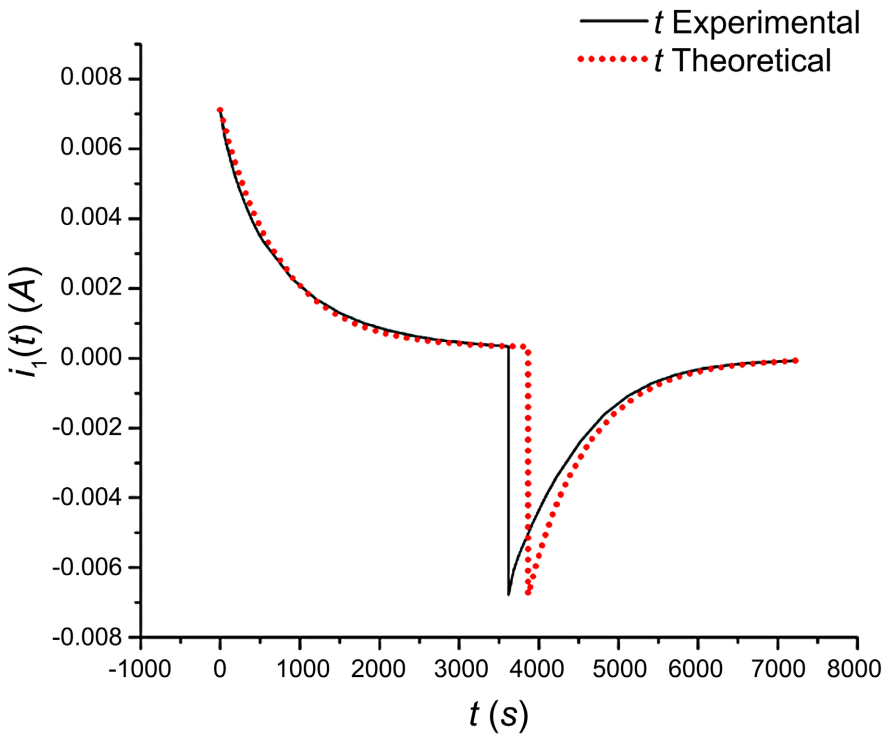

Figure 5. Comparison between theoretical and experimental curves of the current intensity $i_1(t)$ as a function of t considering that the theoretical curves were generated in accordance with $\varepsilon = .5$ V, $R_{Co} = 750\ \Omega$, $R_A = 6.84\ \Omega$, $R_1 = 15.63\ \Omega$, $R_2 = 18$ kΩ, $C = 1$ F and $k = 0$ FV^{-1}.

of the differences between the theoretical and experimental values of t was approximately 5471 s, demonstrating that the values of R_1 and C were more adequate than the previous ones.

Figure 6 shows the theoretical curve using $R_1 = 15.63\ \Omega$, $R_2 = 40$ kΩ, $C = 0.95$ F and $k = 0.10$ FV^{-1} in Equations (19) and (37) and maintaining the values of ε, R_{Co} and R_A. It can be seen that there was a significant increase in similarity between the theoretical and experimental curves. Quantitatively, the value of the sum between the modules of the differences of the theoretical and experimental values of t changed from approximately 5471 s to about 4792 s.

After performing several adjustments, the values of parameters $R_1 = 6\ \Omega$, $R_2 = 30$ kΩ, $C = 0.97$ F and $k = 0.07$ FV^{-1} made the sum of the modules of the differences between the theoretical and experimental values of t to be approximately 2390 s for a total of 42 points taken as a basis. The result of the insertion of such parameters in Equations (19) and (37) is shown in Figure 7. Considering the smallest possible value of the sum of the modules of the differences between the theoretical and experimental values of t, it is possible to state that these are the correct values of the supercapacitor with the nominal capacitance of 1 F.

The sum of the modules of the differences between the theoretical and experimental values of t obtained cannot be null since the present electrical circuit is too simplistic and does not have the conditions to simulate all the effects of ionic

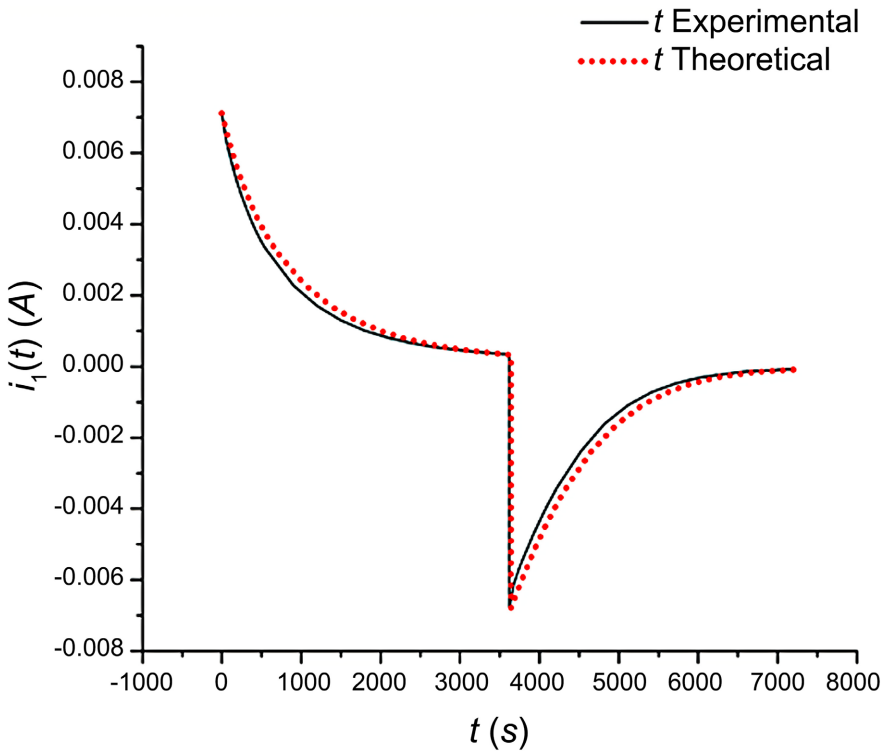

Figure 6. Comparison between theoretical and experimental curves of the current $i_1(t)$ as a function of t, considering that the theoretical curves were plotted in accordance with the parameters $R_1 = 15.63\ \Omega$, $R_2 = 40\ \text{k}\Omega$, $C = 0.95$ F, $k = 0.1\ \text{FV}^{-1}$, $\varepsilon = 5.5$ V, $R_{Co} = 750\ \Omega$ and $R_A = 6.84\ \Omega$.

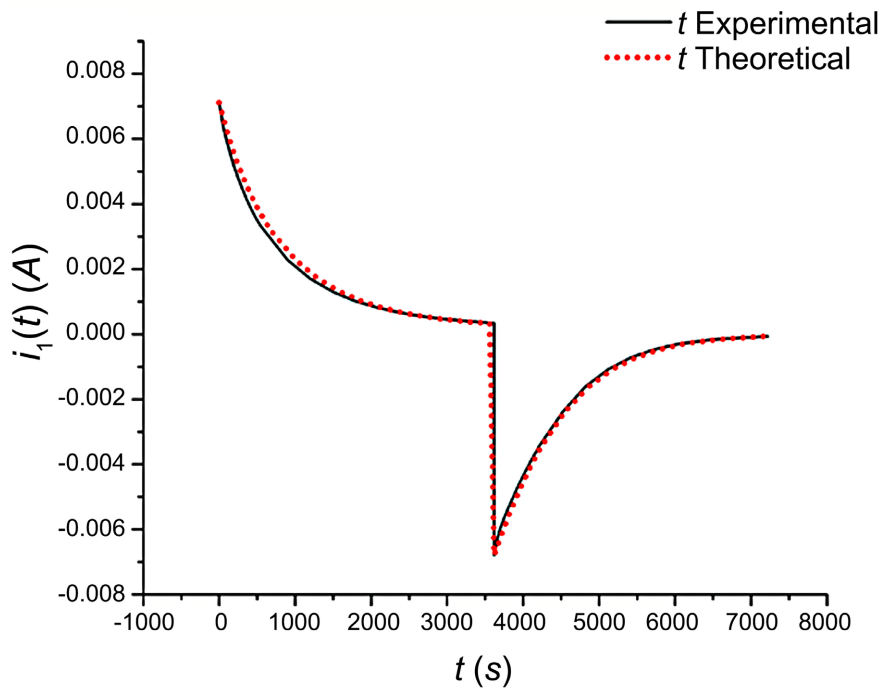

Figure 7. Comparison between theoretical and experimental curves of the current $i_1(t)$ as a function of t considering that the theoretical curves were plotted using $R_1 = 6\ \Omega$, $R_2 = 30\ \text{k}\Omega$, $C = 0.97$ F, $k = 0.07\ \text{FV}^{-1}$, $\varepsilon = 5.5$ V, $R_{Co} = 750\ \Omega$ and $R_A = 6.84\ \Omega$.

diffusion and transport of electric charges that occur in a symmetrical electrochemical supercapacitor. One of the factors considered preponderant for the non-similarity between the values of the aforementioned electrical parameters obtained by means of other conventional techniques and the technique discussed here was the difference between the elapsed time used in carrying them out. This could be the case of obtaining the value of the *EPR* through self-discharge, which can take hundreds of hours to occur, while obtaining the value of this electrical parameter by discharging through resistors took about an hour.

Figure 8 shows the voltammogram curves of the commercial carbon supercapacitor with the nominal capacitance of 1 F using a real time setup potentiostat. A capacitance of 0.82 F was obtained at 75 mVs^{-1} and 1.06 F at 50 mVs^{-1}. The latter was somewhat closer to the 0.97 F obtained using the low-cost experimental setup. Figure 9 shows the galvanostatic curves for this supercapacitor also using a real time setup potentiostat. An *ESR* of 25 Ω was obtained at a discharge current of 5 mA and 32 Ω at 14 mA. A lower value (6 Ω) was obtained using the low-cost setup and this can be attributed to the different power sources' signal and the duration of the charge-discharge cycle time of each method. Galvanostatic cycling uses a direct current source, whereas cyclic voltammetry uses a ramp signal. The present setup uses a source of constant potential in time. Furthermore, the capacitance value determined by the voltammogram area depends on the scan rate whereas in the galvanostatic discharge curve on de current density.

The obtained values of the electrical parameters fixed capacitance *C* and *ESR* by the cyclic voltammetry differ slightly from the values presented by the resistor technique not only because the source signal is different but also because of the

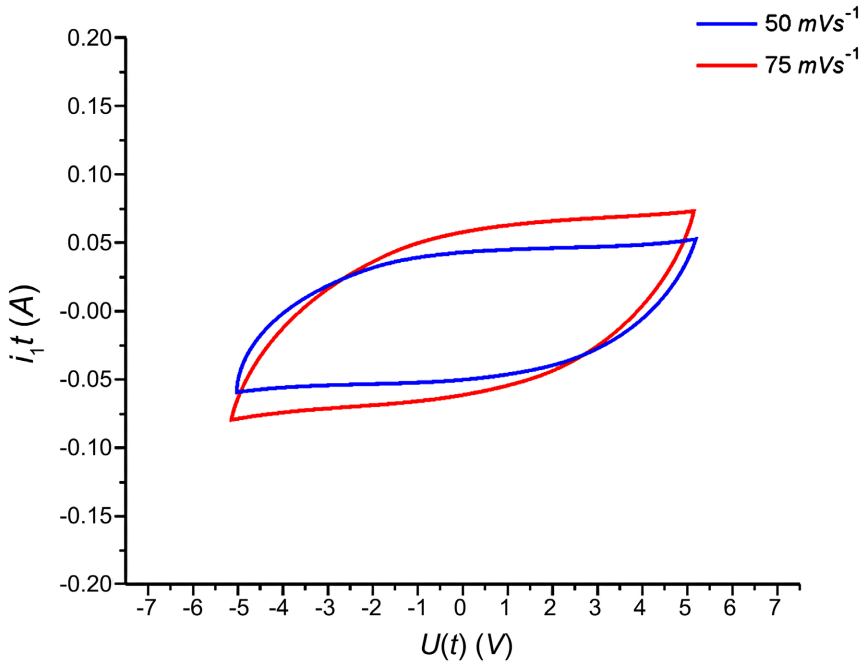

Figure 8. Voltammogram curves for the commercial supercapacitor with nominal capacitance of 1 F using a real-time setup potentiostat.

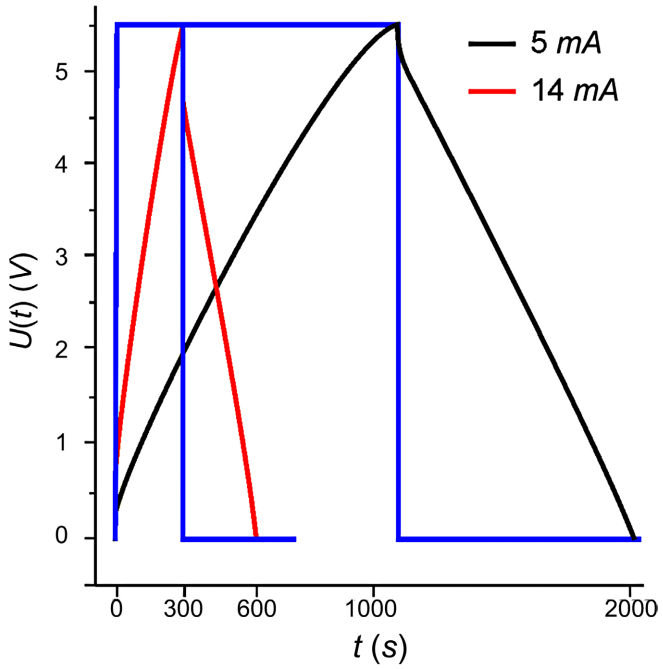

Figure 9. Galvanostatic curves for the commercial supercapacitor with nominal capacitance of 1 *F* using a real-time setup potentiostat.

duration of each cycle of loading and unloading for each of the methods presented. In the galvanostatic cycle a direct current source is used and in the cyclic voltammetry the source generates a ramp signal (at each instant, the potential is increased or reduced in the potentiostat source). In this work, the source is of constant electric potential in time. Test time is preponderant in the case of the *EPR* parameter, which, when evaluated by means of self-discharge, can take tens, perhaps hundreds of hours to be obtained, while in the method presented in this article, it is obtained in a few hours. In the present technique the supercapacitor must be fully discharged to be tested.

The technique presented here can be used together with conventional techniques in order to provide a comparison of values, as well as for cases in which a potentiostat/ galvanostat is unavailable. It can also be used to provide a comparison between supercapacitors produced in series based on a reference charge and discharge curve. In this case, it should be borne in mind that the technique is valid only for symmetrical electrochemical supercapacitors.

Although this study does not address the main theorem to be studied, it has as an innovation the presentation of equations through which it is possible to simulate charge and discharge curves of electrochemical supercapacitors that are obtained in sophisticated and expensive equipment, as is the case of a potentiostat/galvanostat typically used in the analysis of the electrical parameters equivalent series resistance (*ESR*), equivalent parallel resistance (*EPR*) and capacitance *C* of electrochemical supercapacitors by means of an apparatus of simple assembly and of low cost constituted basically of a potentiometer, a voltmeter and an ammeter. The method, and therefore the equations presented here, also has the

advantage of providing values of the capacitance parameter dependent on the electric potential $kU_C(t)$, which cannot be obtained by means of cyclic voltammetry and galvanostatic cycle analysis techniques.

Given the present theoretical results, future studies are being carried out using the $2R(C + kU_C(t))$ circuit fed by a triangular potential source in order to generate equations in the frequency domain and create a method of analysis of symmetrical supercapacitor electrical parameters considering the potential capacitance dependence in the frequency domain.

5. Conclusion

The majority of publications on electrochemical supercapacitors circuit analysis are in the frequency domain and this paper is in the time domain. The electrical potential capacitance dependence in the time domain is a complicating factor for obtaining the analytical expressions. Despite that, the mathematical equations that aim to simulate the curves of the electric current intensity in the terminals of an activated carbon symmetrical electrochemical supercapacitor with organic electrolyte were successfully deduced in the time domain. Evaluation has been carried out by the charging technique in constant electric potential and discharge by resistors. The activated carbon material supercapacitor was represented by an equivalent modeled electrical circuit $2R(C + kU_C(t))$. These equations managed to simulate with good similarity the experimental curves of a commercial carbon-based supercapacitor and after performing several adjustments, the optimum parameters were: $R_1 = 6\ \Omega$, $R_2 = 30\ \text{k}\Omega$, $C = 0.97$ F and $k = 0.07\ \text{FV}^{-1}$. The sum of the modulus of the differences between the theoretical and experimental values of t approximated 2390 s, for a total of 42 points taken as a basis. Time domain mathematical expressions allowed simulation of the experimental curves of an electrically modeled electrochemical supercapacitor composed of activated carbon material electrodes. Discharge curves of the standard galvanostatic cycling technique allowed obtaining only two electrical parameters (C and ESR), whereas with time domain expressions presented in this manuscript, it is possible to obtain four fundamental parameters (ESR, C, k and EPR).

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Conflicts of Interest

The authors declare that there is no conflict of interest.

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Symbol List

C fixed capacitance of a symmetrical electrochemical supercapacitor; unit: farad (F);

$i_1(t)$ intensity of the electric current present in the terminals of a symmetrical electrochemical supercapacitor; unit: ampere (A);

$i_1(t_{(iPC)})$ intensity of the electric current present in the terminals of a symmetrical electrochemical supercapacitor at the beginning of the charging process; unit: ampere (A);

$i_1(t_{(iPD)})$ intensity of the electric current present in the terminals of a symmetrical electrochemical supercapacitor at the beginning of the discharge process; unit: ampere (A);

k electrical potential-dependent capacitance index of a symmetrical electrochemical supercapacitor; unit: farad per volt (FV^{-1});

R_A internal resistance of the ammeter; unit: ohm (Ω);

R_{Co} control resistance; unit: ohm (Ω);

R_1 equivalent series resistance (ESR) of a symmetrical electrochemical supercapacitor; unit: ohm (Ω);

R_2 equivalent parallel resistance (EPR) of a symmetrical electrochemical supercapacitor; unit: ohm (Ω);

t elapsed time in the discharge process of a symmetrical electrochemical supercapacitor; unit: second (s);

$t_{(iPC)}$ at which the charging process of a symmetrical electrochemical supercapacitor begins; unit: second (s);

$t_{(iPD)}$ time at which the discharge process of a symmetrical electrochemical supercapacitor begins; unit: second (s);

$U_C(t)$ electric potential existing between the terminals of the fixed capacitance capacitor C contained in the electric circuit $2R(C + kU_C(t))$;

$U_C(t_{(fPC)})$ electric potential existing between the terminals of the fixed capacitance capacitor C contained in the electric circuit $2R(C + kU_C(t))$ at the end of the charging process; and,

$U_C(t_{(iPD)})$ electrical potential existing between the terminals of the fixed capacitance capacitor C contained in the electrical circuit $2R(C + kU_C(t))$ at the beginning of the charging process.