МАТЕМАТИЧЕСКОЕ МОДЕЛИРОВАНИЕ, ЧИСЛЕННЫЕ МЕТОДЫ И КОМПЛЕКСЫ ПРОГРАММ

SUPERCAPACITORS MODELING AND SIMULATION IN MATLAB/SIMULINK: STUDYING THE INFLUENCE OF MODEL ELEMENTS ON THE DURATION OF SELF-DISCHARGE

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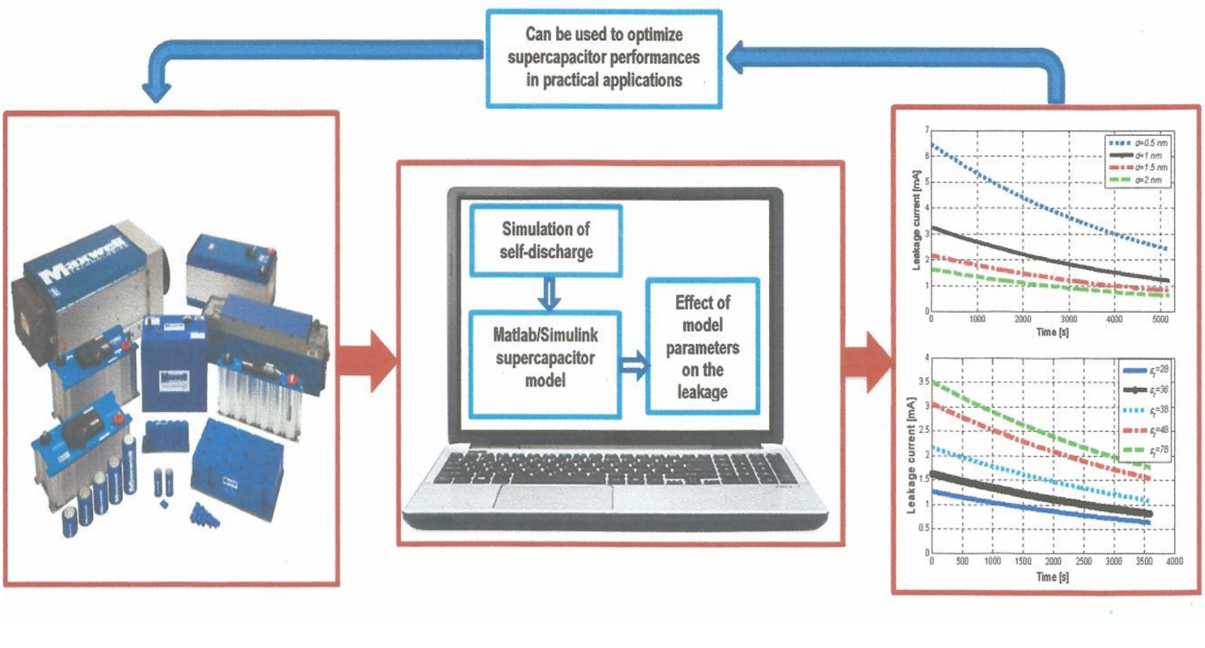
Supercapacitors have appeared as new components intended to help batteries in applications where power consumption peaks is observed including power supply of computer equipment. Unfortunately, supercapacitors have tendency to self-discharge, and this limits their practical use. This paper focuses on the study of the supercapacitors behavior within the self-discharge phenomenon and especially the increasing of its duration by acting on the key parameters involved in modeling: their R_p leakage resistance and electric double layer capacity C_{dl}. This brings us to the implementation of the MATHLAB/Simulink software with elements of the R-C model involved in self-discharge process. To support this study, experiments were performed to validate the computer (simulation) models. Good agreements have been shown between the experimental and simulation results. Our results of simulation show that an increase in supercapacitors duration of self-discharge implies such requirements: high leakage resistance; low permittivity of the electrolyte; small activated surface; relatively thick electrical double layer; charging voltage below the nominal voltage. The results, which have been received by authors, are encouraging and point to a very promising future for supercapacitors in applications during energy storage over long periods requiring power consumption peaks.

Keywords: supercapacitors, modeling, simulation, duration of self-discharge, leakage current, stern capacitor, MATLAB/Simulink, computer technique

Graphical annotation (Графическая аннотация)



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МОДЕЛИРОВАНИЕ И СИМУЛЯЦИЯ СУПЕРКОНДЕНСАТОРОВ В MATLAB/SIMULINK: ИССЛЕДОВАНИЕ ВЛИЯНИЯ ЭЛЕМЕНТОВ МОДЕЛИ НА ПРОДОЛЖИТЕЛЬНОСТЬ САМОРАЗРЯДКИ

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Суперконденсаторы появились как новые компоненты, предназначенные для поддержки работы батарей в тех областях применениях (включая компьютерное оборудование), где наблюдаются пики потребляемой мощности. К сожалению, у суперконденсаторов есть склонность к саморазряду и это ограничивает их практическое применение. В данной статье внимание сфокусировано на исследовании поведения суперконденсаторов во время явления саморазряда и, особенно, увеличения его продолжительности путем воздействия на основные параметры, включенные в модель: сопротивление утечки и емкость электрического двойного слоя. Это привело нас к целесообразности проведения исследования с помощью MATHLAB/Simulink модели типа «R-C», имитирующий процесс саморазряда. Для проверки результатов моделирования были выполнены экспериментальные исследования. При этом было получено хорошее согласие экспериментальных данных и модельных расчетов. Полученные авторами результаты моделирования показывают, что увеличение продолжительности саморазряда суперконденсаторов подразумевает соблюдение таких требований: высокое сопротивление утечки; низкая проницаемость электролита; малая площадь активированной поверхности; относительно толстый двойной электрический слой; напряжение заряда ниже номинального напряжения. Результаты, которые были получены авторами, воодушевляют и указывают на очень перспективное будущее для суперконденсаторов в приложениях, требующих аккумулирования энергии на длительный период времени и поддержки работы батарей во время пиков потребления мощности.

Ключевые слова: суперконденсаторы, моделирование, симуляция, саморазряд, MATLAB, Simulink, ток утечки, конденсатор Стерна, MATLAB/Simulink, вычислительная техника

The emission of greenhouse gases and pollutants, that cause global warming and the search for a better quality of life, have led authorities worldwide to turn gradually to the usage of clean and sustainable energy, including renewable energy [17, 19, 25, 27]. But the major drawback of some renewable energy (particularly wind and solar) is their discontinuity in time [17, 18, 21]. One solution to this problem is to use batteries as key features of electrical energy storages [18].

Indeed, the charge storage process in batteries is based on Faradic processes and is carried out by oxidation-reduction reactions, involving the reactants present in batteries in particular at the electrodes [9]. The process occurs by the consumption or deposition of materials on the electrodes and its transportation in the electrolyte, which may also be involved in the reaction. However, the reaction leading to the structural modification of these components should ideally be reversible – which is not the case in practice. Consequently, batteries have a high energy density (Wh.kg-1) and a limited life span of 5 to 10 years with moderate specific power [5, 8]. This means that they cannot be considered for applications requiring peak or electrical power control over a short time period, as they have in this case too slow dynamics [18].

To overcome the inherent shortcomings of batteries (reduced power demands, reduction in size and increase in life) to meet transient power needs [1, 26], it is important to make a hybrid source, which separates the power and energy functions while combining multiple storage technologies, some (energy batteries) being dimensioned in terms of autonomy and others (power batteries, capacitors) in terms of instantaneous power required over a more or less long period. For periods longer than one second (1s), the use of supercapacitors proves quite adequate. This component (also commonly called supercapacitor, or ultracapacitor, electric double layer or electrochemical capacitor) is ideal for systems requiring to store and release energy for short periods [23].

Unlike batteries, supercapacitors are manufactured with less polluting materials (electrodes made of porous carbon and separated by the electrolyte, which acts as the dielectric) [1, 20] and require a rather light maintenance. The principle of supercapacitor energy storage relies entirely on the accumulation of charges at the surface of electrodes (electrostatic storage) without any chemical or electrochemical transformation [28]. This storage mode coupled with a technology minimizing internal resistance provides supercapacitors with a high power density [7] and a long life cycle, that exceeds 10^6 charge/discharge cycles [5, 8, 25, 28]; a time response about tens of seconds [18]; a yield close to unity. So they are needed in applications, where the requirements are often unmet by traditional energy storage solutions: in public transport to recover braking energy of trains and subways or trams – to develop them without catenary; in industry – to start generators, to provide the call of instantaneous power; in computer engineering – to replace UPS batteries and reduce maintenance costs of battery banks, optimizing the design of electrical distribution systems, improved energy efficiency of embedded systems and reducing the replacement rate of battery banks. It is probably these strengths that differentiate supercapacitors can make them components of the future [2, 25].

Unfortunately, studies have shown that redox faradic reactions occur at the electrode/electrolyte interface, and are the seat of leakage current in supercapacitors [7, 25]. Thus, despite their high power density, they suffer from self-discharge. This circumstance limits their practical use, because it prevents them from keeping energy, stored over a long period.

The simplest and most commonly used way to characterize the self-discharge of a supercapacitor is to draw its discharge curve in open circuit, while the first charging component is close to its rated voltage. The self-discharge curves thus obtained have a higher initial slope in absolute value. This implies the existence of a leakage resistance $R_p$which varies in a decreasing manner with tension [3]. Thus, the evaluation of leakage current in supercapacitors is to add a leakage resistor R_p in parallel with the capacity of the electrical double layer C_{dl}. Underthis circumstances, the time constant $\tau = R_p C_{dl}$ determines the time of self-discharge of the supercapacitors [22].

This article focuses on the study of the behavior of supercapacitors and especially on the increase of components self-discharge time by changing the main parameters, involved in modeling leakage resistance R_p and the capacitance of the electric double layer capacitor C_{dl}. In this context, after presenting the structure and surveying the principles of operation of ultracapacitors, we begin by studying the modeling of supercapacitors. Then, interpreting the results of modeling with usage of the MATLAB/Simulink software will be tackled. In the end of this article – the presentation of the analysis and discussion of the simulation results of the influence of model parameters of R_p and C_{dl} on the duration of self-discharge.

Structure and operating principles of supercapacitors. Supercapacitors consist of two electrodes (anode and cathode) in activated carbon [28] (porous carbon) impregnated with electrolyte for the movement of ions between the electrodes. The presence of a separator makes it possible to electrically insulate the two electrodes. The two current collectors often made of aluminum, which provide an interface between the electrodes and connections [5]. Figure 1 shows the structure of a supercapacitor.

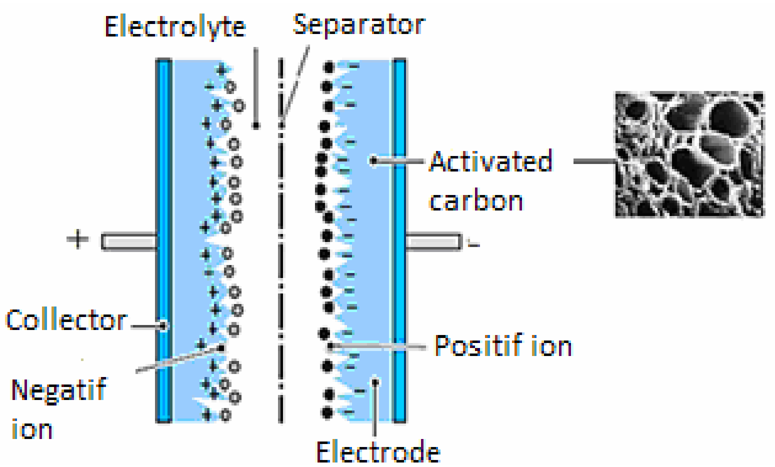

Figure 1 – Schematic simplified structure of supercapacitors

The operating principle of supercapacitors relies on the formation of an electric double layer at the electrode/electrolyte interface [6, 20]. Indeed, when there has been application of a potential difference at the terminals of the whole device, there is migration of ions from the electrolyte that are adsorbed at electrodes of opposite signs. Therefore, at each electrode/electrolyte interface, a layer referred to as a double electric layer or electrochemical is formed [15].

Modeling of supercapacitors. There are a multitude of supercapacitor models presented in the literature according to with varying degrees of accuracy and complexity. We distinguish among others the R-C model builder, offered by manufacturers; the model with two R-C branches of the Canadians Bonert and Zubieta [18, 29]; model Belhachemi [3] etc. It is up to the user to define his own model based on the desired application. This study is limited to the manufacturer of the R-C model (Fig. 2) due to its ease of handling during studies using simulation software. Rs (Equivalent Series Resistance) are the ohmic losses, caused due to self-heating during the process of charging and discharging, as well as limiting the flow of current in the supercapacitor. Rp (leakage resistance or parallel resistance) allows to describe the behavior of supercapacitors during self-discharge.Cdl represents the capacitor of the electric double layer, formed at the electrode/electrolyte interface.

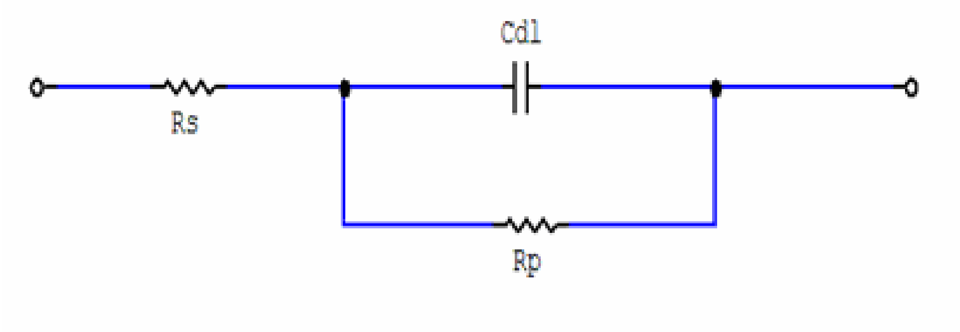

Figure 2 – Model R-C manufacturer supercapacitors

Circuit of supercapacitor self-discharge. During self-discharge, the R_s effect is negligible compared to that of R_p. Therefore, the previous model (Fig. 2) is reduced to that, shown in Figure 3, where U_o and if (which are respectively the self-discharge voltage and the leakage current) responsible for the self-discharge of the supercapacitors. We will focus on modeling leakage resistance, the capacity of the electrical double layer, voltage, self-discharge and leakage current in the following section.

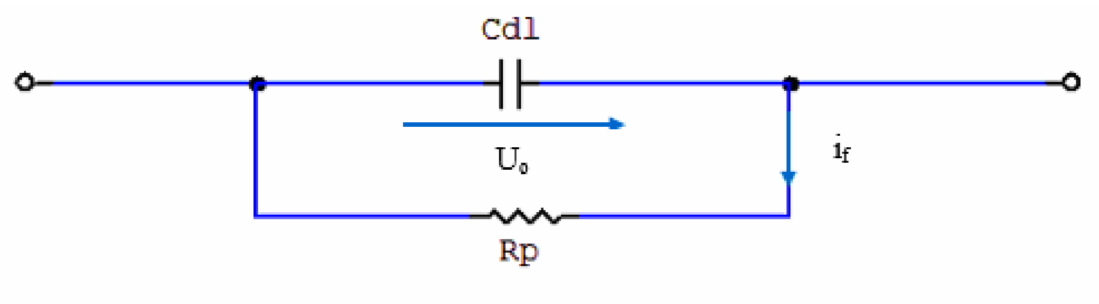

Figure 3 – Equivalent electrical circuit of supercapacitors self-discharge

Modeling of the electric double layer capacity. Three authors are responsible for modeling the capacitance of supercapacitors. It was first studied by Helmholtz [13, 14], and his work has been taken over by Gouy-Chapman [4, 10, 11, 12, 24] and then by Stern [7, 24]. For this study, we retain the Stern model, that looks like a combination of two capacitors in series [16, 24] – the first from the Helmholtz model and the second from the Gouy-Chapman model. The capacitance of the electrical double layer capacitor thus obtained is expressed by the relation (1).

$$1/C_{dl} = 1/C_h + 1/C_{gc}. \tag{1}$$

With: the Helmholtz and the Gouy-Chapman capacitors given respectively by equations (2) and (3).

$$C_h = m\varepsilon_0\varepsilon_r(S/d), \tag{2}$$

$$C_{gc} = mS(2z^2e^2\varepsilon_0\varepsilon_r N_O/kT)^{1/2}\cosh(zeU_{sc}/2kT), \tag{3}$$

with:

$$N_O = 0.86/8N_A r^3, \tag{4}$$

where: N_O is the total ion concentration in mol/m^3; N_A is the Avogadro number in mol^{-1}and r the molecular radius in nm; m is the mass of the activated element, used as electrode material in g; S is the activated surface area in m^2/g; d is the Helmholtz length or thickness of the electrical double layer; ε_0 is the absolute permittivity of vacuum in F/m^2; ε_r is the relative permittivity of the electrolyte; z is the valence of the ionic species of the electrolyte; e is the elementary charge of the ions in the electrolyte C; k is the Boltzmann constant in J/K; T is the absolute temperature in °K; U_{sc} is the supercapacitor voltage in V.

Study of self-discharge in supercapacitors: modeling of leakage resistance, voltage, self-discharge and leakage current. In open circuit, there is circulation of leakage current which causes discharge of the supercapacitor, characterized by a gradual decrease in voltage across it. The origin of this leakage can be attributed to several phenomena – such as the redistribution of loads in porous electrodes and chemical phenomena of redox type. In fact, in addition to primary chemical reactions, charge redistribution causes other additional chemical reactions, which in turn cause leakage currents. In short, faradic reactions are largely responsible for self-discharge in supercapacitors. In this study, we focus on the simple parallel connection of a leakage resistance with the supercapacitor capacitance to model self-discharge (Fig. 3). The change in the voltage across the supercapacitor during the phenomenon of self-discharge is given by equation (5), in which leakage resistance and faradic current or leakage current are given by the equation (6).

$$U_o(t) = R_p i_f(t)\,, \quad (5)$$

$$i_f(t) = -C_{dl}(d/dt(U_o(t)))\,, \quad (6)$$

where: C_{dl} is the capacity of the double layer, formed at the electrode/electrolysis interface and $U_o(t)$ is the voltage of self-discharge. The negative sign comes from the direction, taken by the loads through the electrode/electrolyte interface during self-discharge. Relations (5) and (6) are used to write the integral defined by equation (7).

$$\int dt = -R_p C_{dl} \int (d(U_o(t))/U_o(t)\,. \quad (7)$$

To determine the value of the resistance R_p, it is necessary to know the initial conditions in order to easily integrate the relation (8). In this case, these conditions are presented as follows: at initial time $(t = t_0)$, the supercapacitor is charged up to a maximum voltage $U_{sc\max}$ before being disconnected at source (start self-discharge) at time $(t = t_q)$; a voltage self-discharge $U_{sc\min}$ is observed across the supercapacitor (end of the self-discharge). In these conditions equation (7) becomes equation (8).

$$\int_{t=t_0}^{t=t_q} dt = -R_p C_{dl} \int_{U_o=U_{sc\max}}^{U_o=U_{sc\min}} d(U_o(t))/U_o(t)\,. \quad (8)$$

According to (8), the expression for leakage resistance is given by equation (9).

$$R_p = -(t_q - t_0)/(C_{dl} \ln(U_{sc\min}/U_{sc\max}))\,. \quad (9)$$

Knowing the value of R_p and the value of C_{dl}, self-discharge voltage can be calculated according to relation (10).

$$U_o(t) = U_o \exp(-t/R_p C_{dl})\,, \quad (10)$$

where: U_o – the initial voltage across the supercapacitor before it is put in open circuit and *t* – the duration of self-discharge.

Modeling Results. This section presents the implementation of different models such as the capacitor of Stern, the leakage resistance, voltage self-discharge and the leakage current of a supercapacitor, using MATLAB/Simulink.

Implementation of the Stern capacitor. The evolution of the electrical double layer capacitor, proposed by Stern, depending on the voltage across the supercapacitor implemented using MATLAB/Simulink with analytical formula (1), is represented in Figure 7. This model depends on the capacitor of Helmholtz and of Gouy-Chapman. Relations (2) and (3) make it possible to respectively implement the capacitor of Helmholtz and of Gouy-Chapman, whose Simulink functional schemes are respectively shown in Figures 4 and 6. The encapsulated block diagram of the specific capacitance of the capacitor of the Helmholtz model (Fig. 4) is presented in Figure 5. The input parameters of the model of Figure 4 are for example ε_r *(E_r), S, d* and *m*. On fig. 4C (F/g) is the specific capacitance of Helmholtz expressed in F/g. The output Ch (Ch (F)) is the capacitor of Helmholtz in Farad.

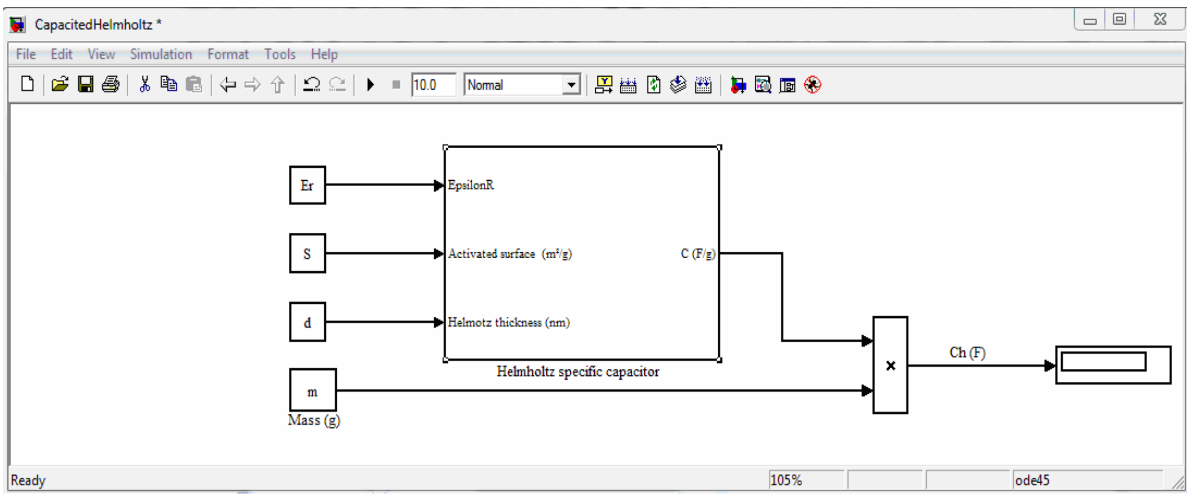

Figure 4 – Simulink model of the capacitor of Helmholtz

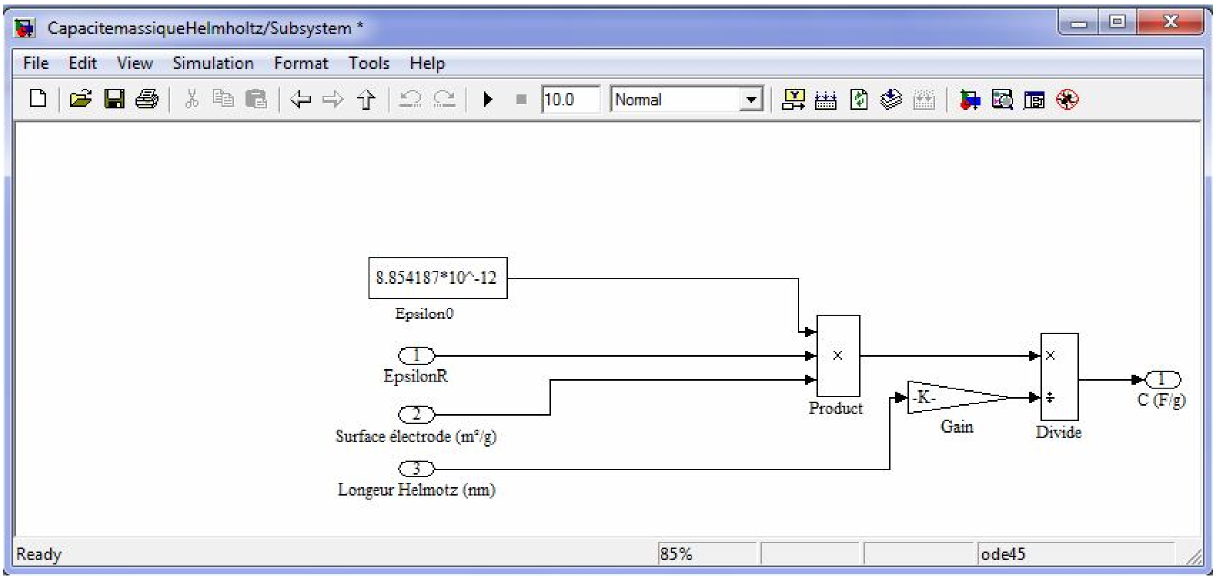

Figure 5 – Simulink block diagram of Helmholtz specific Capacitor

Input parameters for the Gouy-Chapman capacitor (GC-C) are *z*, ε_r (E_r), *T*, U_{sc}, *r*, *m* and *S*. The model output is Cgc (GC-C (F)).

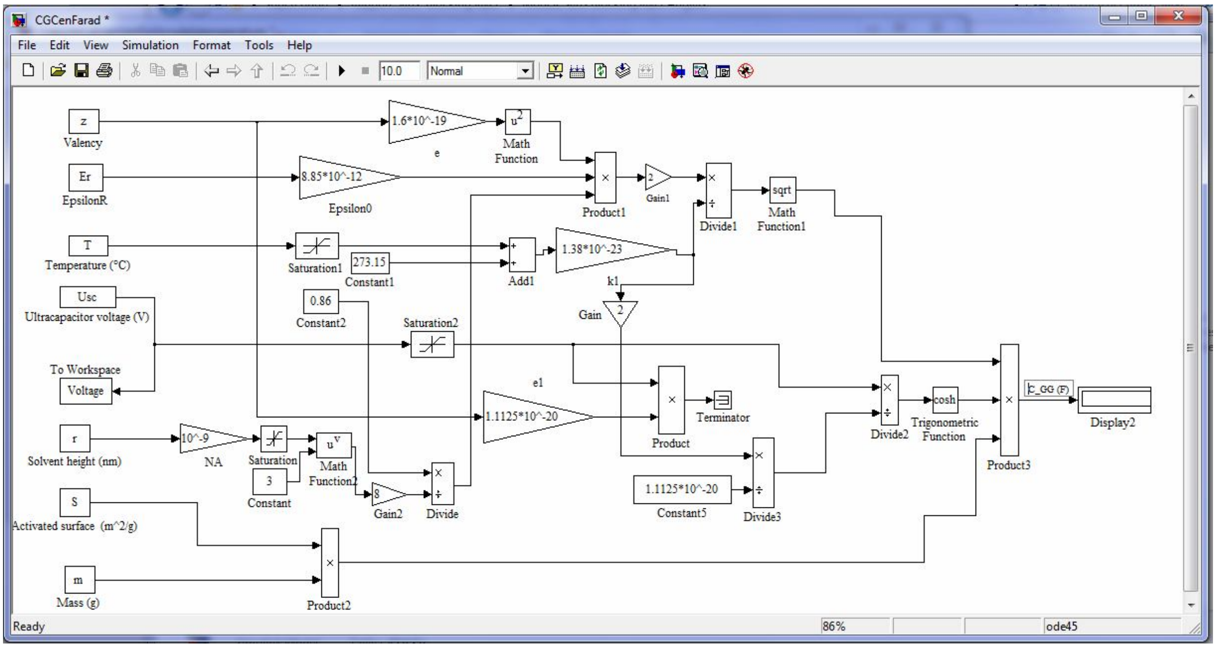

Figure 6 – Simulink block diagram of Gouy-Chapman capacitor

Implementation of leakage resistance, self-discharge voltage and leakage current. Indeed, the resistor R_p is dependent on the duration of self-discharge; the initial voltage across the supercapacitor before it is placed in open circuit, the final open-circuit voltage and the capacitor of the double layer formed at the electrode/electrolyte interface, see equation (9). The implementation of this relation in Simulink gives the block diagram for leakage resistance shown in Figure 8. The encapsulated Simulink block diagrams models (BLOCK A and BLOCK B) are respectively represented by Figures 9 and 10. As for the encapsulated model called capacitor of Stern, it depends on the capacitor of Helmholtz and the capacitor of Gouy-Chapman whose block diagrams were presented in the previous sections.

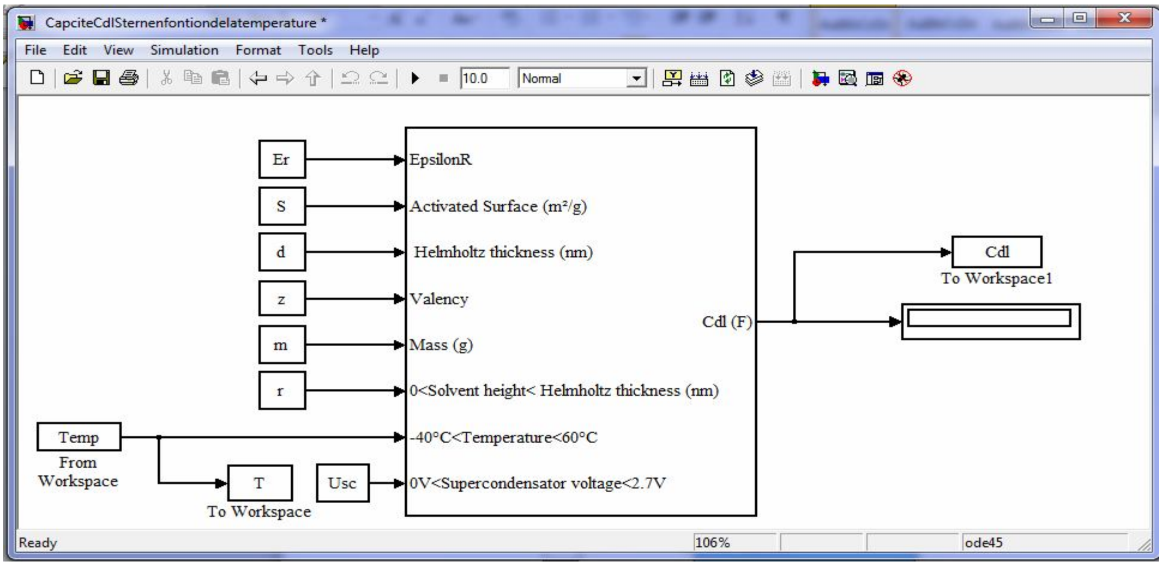

Figure 7 – Simulink model to simulate Stern capacitance versus voltage

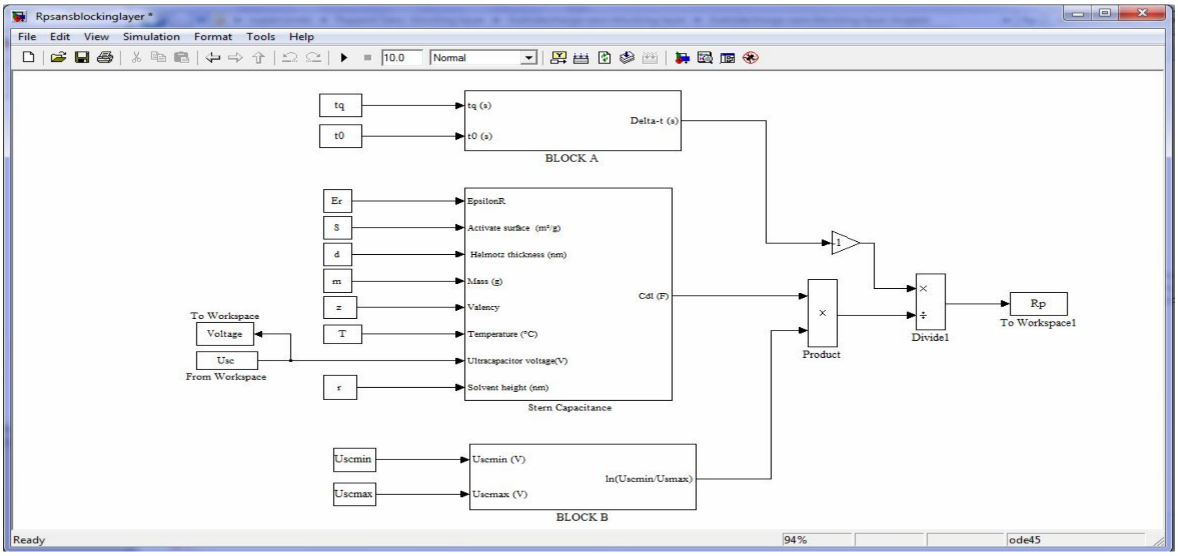

Figure 8 – Simulink model of the leakage resistor

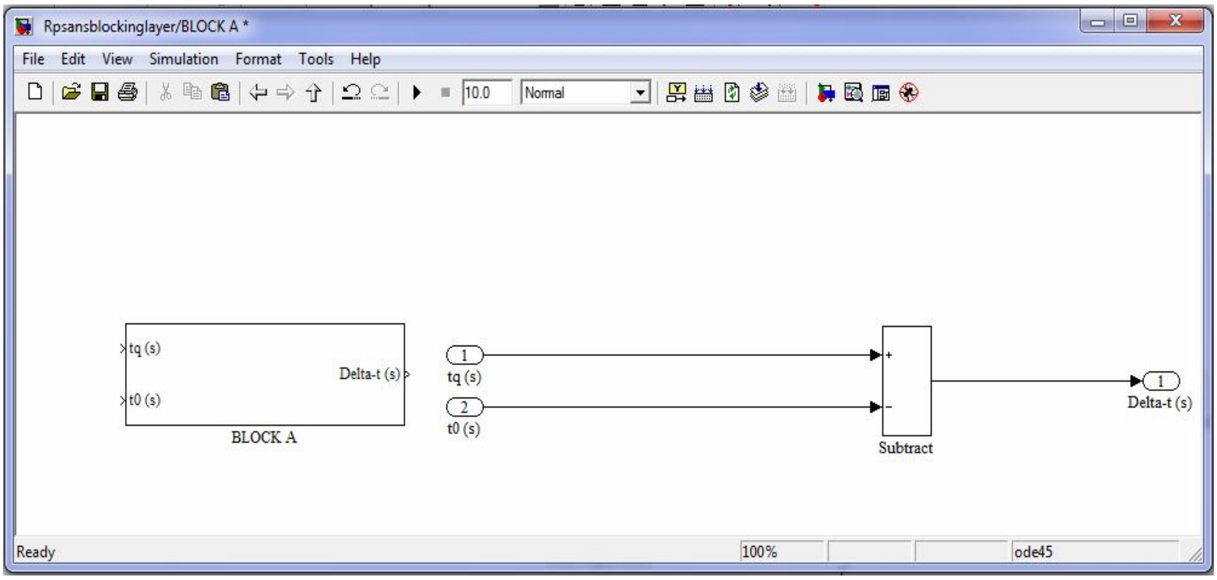

Figure 9 – BLOCK A (left), with the Simulink block diagram (right)

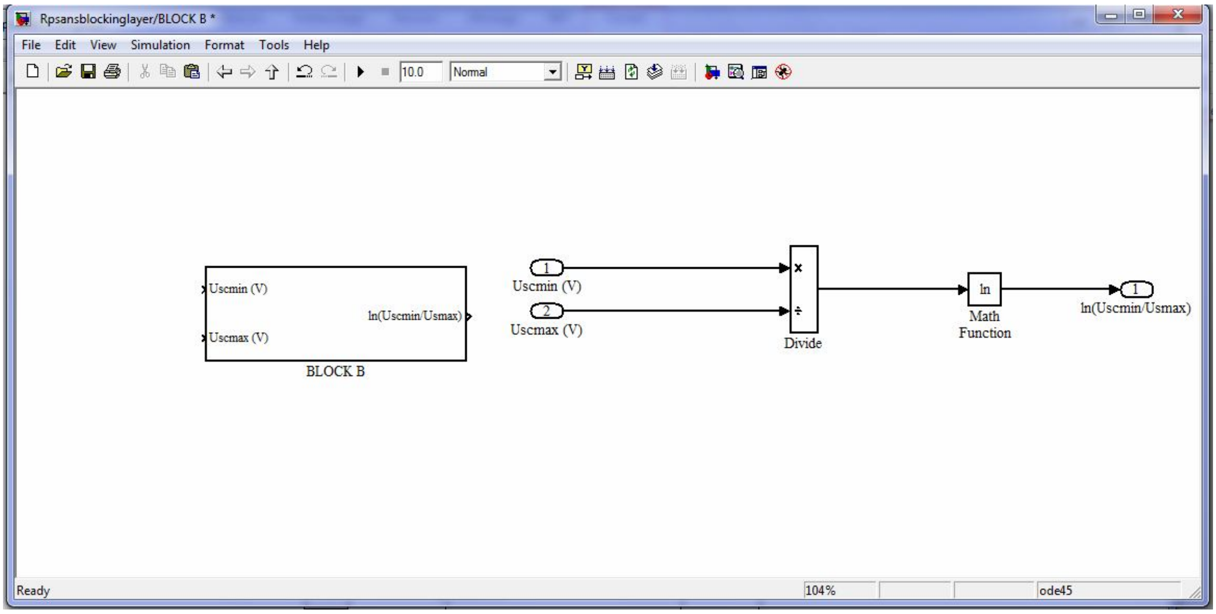

Figure 10 – BLOCK B (left), with the Simulink block diagram (right)

Figures 11 and 12 show respectively the implementation of leakage current and self-discharge voltage of the supercapacitor respectively see relations (6) and (10). These models depend on the R_p leakage resistance and the capacitor C_{dl} whose Simulink block diagrams were previously presented.

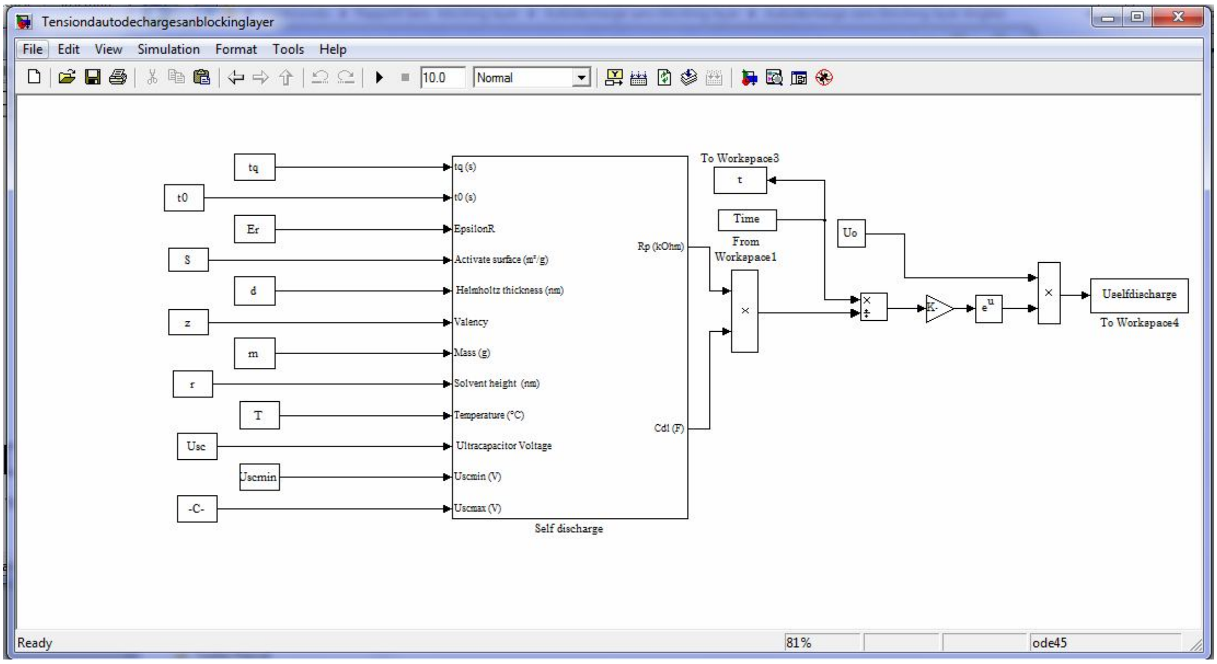

Figure 11 – Simulink model of self-discharge voltage

Validation of the capacitor of Stern. An example of C_{dl} versus U_{sc} simulation for different values of input parameters of the model (table 1) compared to results, obtained by experiment for a 2600 F supercapacitor with a nominal voltage of 2.7 V at a temperature of 25 °C is presented in Figure 13. Acetonitrile is the organic solvent used. The analysis of the curve, obtained by simulation presented in Figure 13, shows that the electric double layer model proposed by Stern, has a capacitance which varies depending on voltage. The capacitance of the double layer is minimum (2129.4 F) for a voltage of 0 V; maximum (3055.6 F) – when the voltage across the supercapacitor is 2.7 V. Hence, the idea that the capacitance of the double layer capacitor varies theoretically non-linearly, is confirmed.

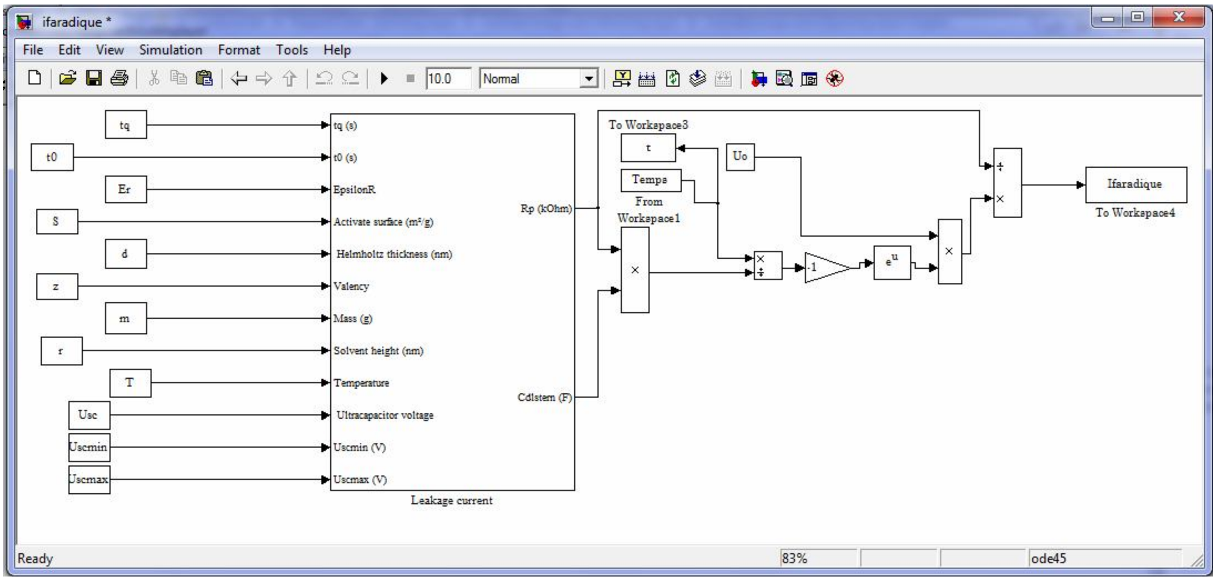

Figure 12 – Simulink model of leakage current

Table 1 – Simulation input parameters for the capacitor proposed by Stern

Designation	Parameters	Values
ε_r	Permittivity	36
S	Activated Surface	1964 m^2/g
d	Helmholtz Lentgh	2 nm
z	Valence	1
m	Mass	10 g
r	Radius of the molecule	1,5475 nm
T	Temperature	25°C
U_{sc}	Supercapacitor voltage	[0 V ; 2,7 V]

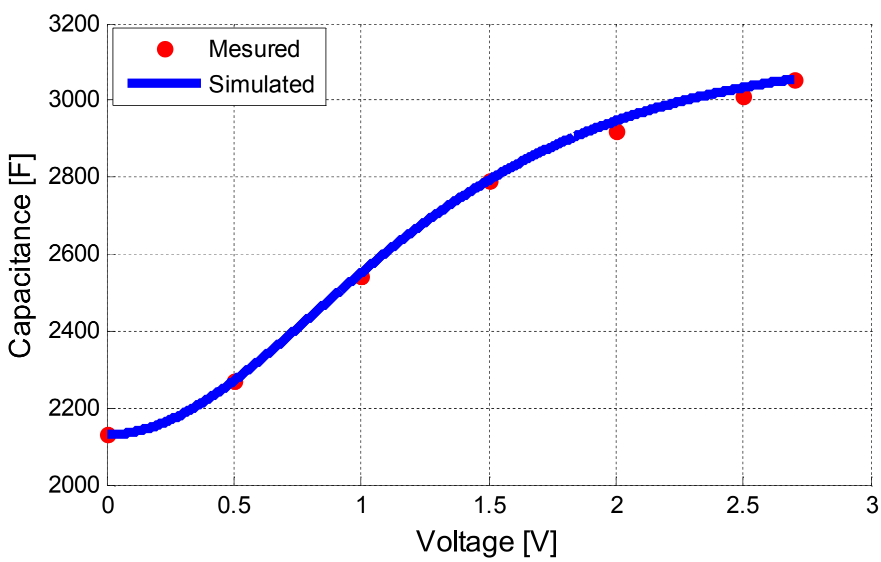

Figure 13 – Capacitance of Stern capacitor versus voltage

The simulation results and those obtained by experiment are compared in Table 3. Calculated relative percent error (relation (11)), confirms the validation of the Stern capacitor model implemented using the MATLAB/Simulink library.

$$E_r(\%) = \left| \frac{mesured - simulated}{mesured} \right| \times 100 \qquad (11)$$

Table 2 – Relative percentage errors for simulation and experimental results

$C_{dlmesured}$ [kF]	***$C_{dlsimulated}$ [kF]***	***E_r (%)***
2,129	2,129	0,003
2,180	2,183	0,142
2,265	2,268	0,154
2,373	2,376	0,151
2,533	2,549	0,622
2,780	2,790	0,387
2,880	2,893	0,464
2,940	2,945	0,190
3,030	3,033	0,099
3,050	3,055	0,182

The capacitance of the Stern capacitor is invariant as a function of temperature for a given voltage range [16]. This reflects the fact, that the accessibility of the electrode surface is not affected by temperature. Such result is confirmed by the simulation of the electric double layer capacitor with a voltage of 2,7 V in the interval [–40 °C; 70 °C], shown in Figure 14. The data used for the simulation are shown in Table 3.

Table 3 – Important parameters to simulate the invariance of the Stern capacitance as function of temperature

Designation	**Parameters**	**Values**
ε_r	Permittivity	36
S	Activated Surface	1964 m^2/g
d	Helmholtz Length	2 nm
z	Valence	1
m	Mass	10 g
r	Radius of Molecule	1,547 nm
T	Temperature	[–40 °C; 70 °C]
U_{sc}	Supercapacitor voltage	2,7 V

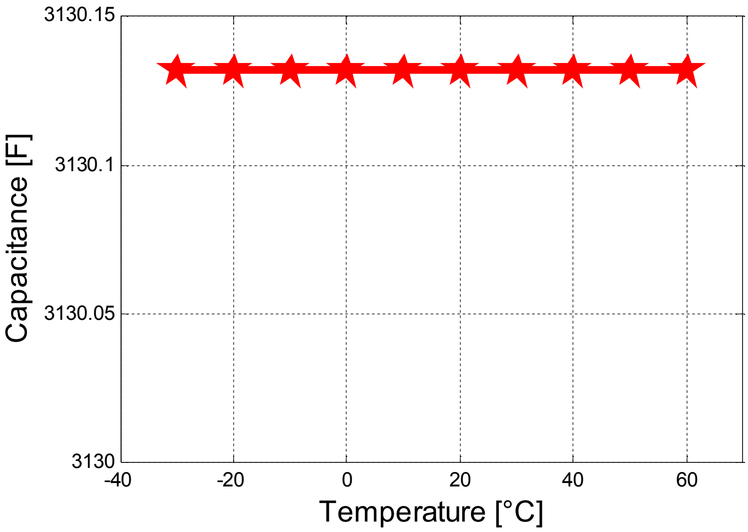

Figure 14 – Capacitance of the electric double layer capacitor versus temperature

<u>**Analysis and discussion of simulation results.**</u> The goal of this section, is to simulate the influence of the capacitance of the electrical double layer capacitor and leakage resistance during self-discharge while changing the main parameters considered in the models, see relations (12) and (13). Moreover, the simulation of self-discharge as function of the initial voltage (see equation (10)) and the impacts, generated by the variations of these parameters on the energy performance of supercapacitors, will be presented.

$$C_{dl} = f(\varepsilon_r, S, d, z, m, r, T, U_{sc}), \quad (12)$$

$$R_p = f(t_q, t_0, C_{dl}, U_{sc\min}, U_{scmax}), \quad (13)$$

where: t_0 – the initial time of self-discharge; t_q – the time at the end of self-discharge; $U_{sc\min}$ – the voltage across the supercapacitor before it is placed in an open circuit; $U_{sc\max}$ – the final voltage circuit; C_{dl} – the capacitance of the electric double layer capacitor formed at the electrode / electrolyte interface, dependent on the parameters, presented by relations (1), (2), (3) and (4).

Effect of initial charge voltage U_o on self-discharge. Figure 15 shows the simulation of the self-discharge of an organic supercapacitor at 25 °C for different values of initial voltages (2,5 V and 2 V; 1,5 V; 1 V and 0,5 V) over a period of 3600 s. The results at the end of simulation are listed in Table 4. A voltage drop is calculated by (14) and is presented in the table 4.

$$U_{au} = U_o - U_o', \tag{14}$$

where: U_o – the initial charge voltage; U_o' – the end of simulation voltage across the supercapacitor.

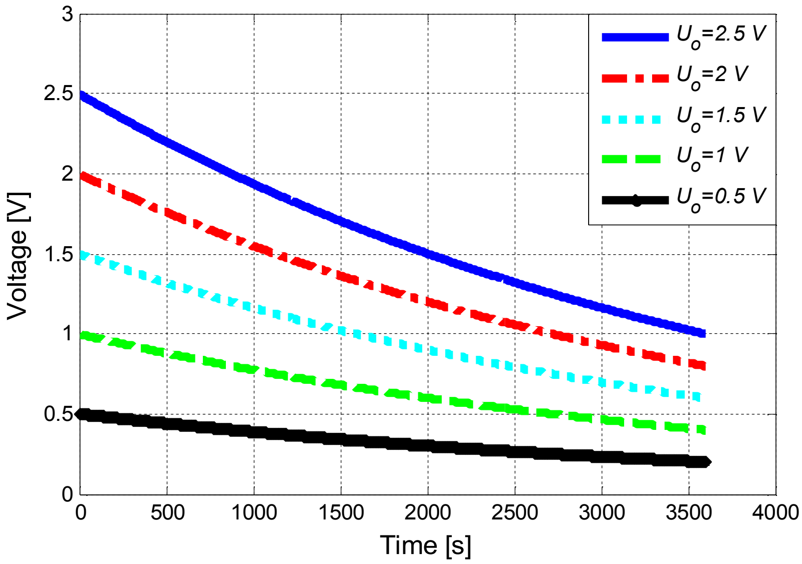

Figure 15 – Simulation of the effect of initial charge voltage U_o on self-discharge

Table 4 – Variation of voltage across the supercapacitor during self-discharge

U_o (V)	U_o' (V)	U_{au} (V)
2,5	0,997	1,502
2,0	0,798	1,202
1,5	0,598	0,901
1,0	0,399	0,601
0,5	0,199	0,300

Analysis of the results in Figure 15 and Table 4 show that self-discharge is fast in the case of strong voltage and slow at weak voltages. Work about the phenomenon of self-discharge of supercapacitors, presented in [25], show that Faradic reactions responsible for the self-discharge of a supercapacitor grows exponentially with the available voltage within the component; and the voltage plays a very important role in the activation of faradic reactions within the supercapacitor. For this reason, it is advisable to charge it to a threshold voltage lower than that of the decomposition of electrolyte – in order not to arouse accelerating irreversible electrochemical reactions within the component, that can sometimes be responsible for its destruction.

Effect of temperature T on self-discharge. Temperature also affects leakage current. This influence is difficult to observe on a curve (Fig. 16) to such an extent that it is more desirable to present the results of simulation in Table 5 for a given temperature range (–35 °C, 0 °C, 35 °C and 45 °C) with initial charge voltage equal to 2,5 V. The simulation is done over a period of 3600 s.

Table 5 – Effect of temperature on leakage current

Time (s)	**Leakage current (mA)**			
	–35 °C	**0 °C**	**35 °C**	**45 °C**
3600	0,842	0,842	0,842	0,841

From the results in Figure 16 and Table 5, temperature has no significant effect on leakage current. Therefore, it has no effect on the time constant of self-discharge. This is due to the invariance of the capacitance of the electric double layer capacitor as a function of temperature for newer supercapacitors.

Effect of molecular radius (r) and valency of ionic species (z) on self-discharge. The molecular radius and valence of the ion species have no influence on the capacitance C_{dl} of supercapacitors; therefore they do not affect self-discharge and the time constant of self-discharge. Indeed, the Stern model is an association in series of the Helmholtz capacitor and Gouy-Chapman capacitor. However, the latter is rather important so that the capacitor of Stern is substantially equivalent to the Helmholtz capacitor. Since the model of Gouy-Chapman is dependent on the molecular radius and the valence of the ionic species, it is obvious that they will have no influence on the capacitor of the electrical double layer and hence the duration of self-discharge since the Stern capacitor will always depend on the model with the lowest capacitance. These results are presented in Figures 17 and 18 for an organic supercapacitor operating under an initial charge voltage (U_o) of 2,5 V and at an operating temperature of 25 °C. The data used to simulate the influence of molecular radius and valence of the ionic species are respectively shown in Tables 6 and 7.

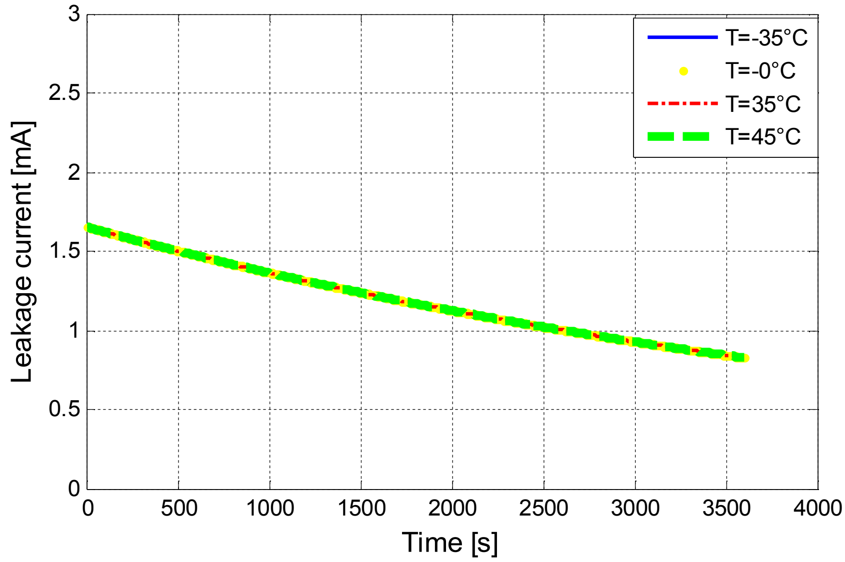

Figure 16 – Simulation of the effect of temperature on leakage current

Table 6 – Values for input parameters, used for simulation the influence of molecular radius on self-discharge

Parameters	Designation	Values
ε_r	Permittivity	36
S	Activated Surface	1964 m^2/g
d	Helmholtz Length	2 nm
z	Valence	1
m	Mass	10 g
T	Temperature	25 °C
U_{sc}	Supercapacitor Voltage	2,7 V
t_0	Initial Time	10 s
t_q	End Time	3610 s
U_{scmax}	Maximal Voltage	2,5 V
U_{scmin}	Minimal Voltage	1,0 V

Table 7 – Input parameter values used for simulation the influence of the ionic species valence on self-discharge

Parameters	designation	Values
ε_r	Permittivity	36
S	Activated Surface	1964 m^2/g
d	Helmholtz Length	2 nm
r	Molecular radius	1,5475 nm
m	Mass	10 g
T	Temperature	25 °C
Usc	Supercapacitor Voltage	2,7 V
t_0	Initial Time	10 s
t_q	End Time	3610 s
Usc_{max}	Maximal Voltage	2,5 V
Usc_{min}	Minimal Voltage	1,0 V

Effect of the Helmholtz length (d) on self-discharge. Figure 19 shows the simulation of the self-discharge of an organic supercapacitor at 25 °C for different values of thickness of the double layer (2 nm, 1,5 nm, 1 nm and 0,5 nm) over a period of 3600 s. The parameters, used in the simulation and the results obtained, are respectively listed in Tables 8 and 9. The variation of leakage current is calculated by (15) and is presented in Table 9.

$$\Delta i_f = i_f(0) - i_f(3500), \tag{15}$$

where: $i_f(0)$ is the leakage current at $t = 0$ s; $i_f(3500)$ is the leakage current at $t = 3500$ s.

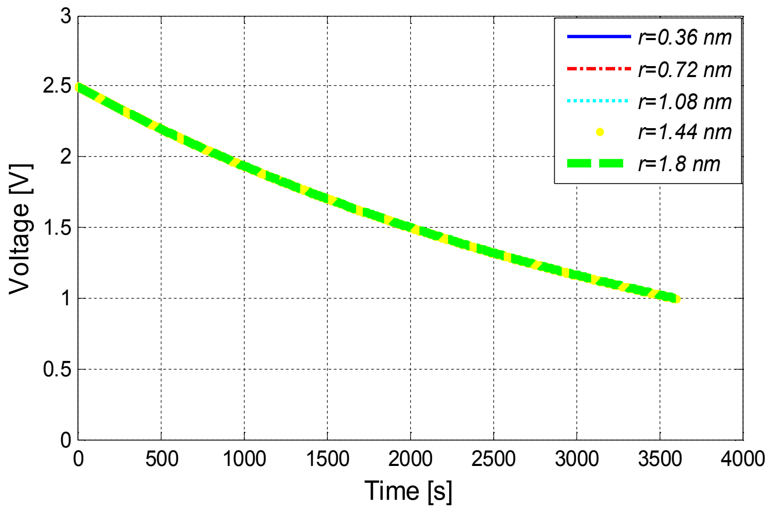

Figure 17 – Simulation of the effect of molecular radius (r) on self-discharge

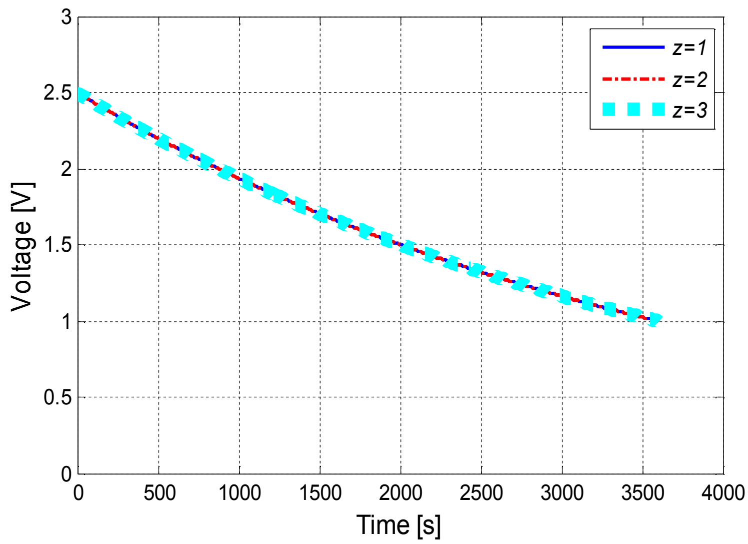

Figure 18 – Simulation of the effect of the valence of the ionic species on self-discharge

Table 8 – The input parameters for the simulation of the influence of Helmholtz length on self-discharge

Parameters	designation	Values
ε_r	Permittivity	36
S	Activated Surface	1964 m^2/g
r	Molecular radius	1,5475 nm
z	Valence	1
m	Mass	10 g
T	Temperature	25°C
Usc	Supercapacitor Voltage	2.7 V
t_0	Initial Time	10 s
t_q	End Time	3610 s
U_{scmax}	Maximal Voltage	2,5 V
U_{scmin}	Minimal Voltage	1,0 V

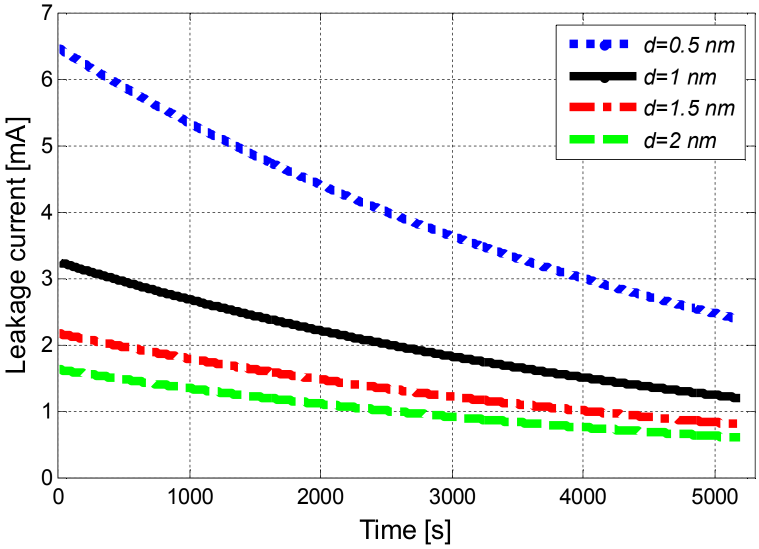

Figure 19 – Simulation of the effect of Helmholtz length on the self-discharge

Table 9 – The self-discharge time constants obtained for different values of thickness of the electric double layer capacitor

d (nm)	C_{dl} *(kF)*	R_p *(kΩ)*	*τ (h)*	i_f *(mA)*		Δi_f *(mA)*
				0 s	*3500 s*	
2,0	3,127	1,7	1,442,8	1,624	0,828	0,796
1,5	4,167	1,2	1,442,3	2,165	1,103	1,061
1,0	6,247	0,9	1,442,7	3,245	1,654	1,591
0,5	12,470	0,4	1,443,1	6,472	3,299	3,173

Analysis of the results in Table 9 and Figure 19 shows that a reduction of the thickness of the electric double layer capacitor leads to an increase in the supercapacitor capacitance and a reduction of leakage resistance. This is explained by the fact that the electrical double layer capacitor mobilizes the charges contained in the electrolyte for energy storage. For d = 0,5 nm, the self-discharge time constant is 1,443.1 h with a capacitance of the electrical double layer of value 12,470 kF and a leakage resistance value of 0,4 kΩ. The leakage current decreases from 6,472 and reached 3,299 mA that is a variation of 3,173 mA. While for d = 2 nm, the leakage current is 0,796 mA, a quarter (1/4) of the previous variation and leakage resistance value is 1,661 kW with a capacitance equal to 3,127 kF. Consequently, an increase in the duration of the self-discharge of supercapacitors sometimes involves a large capacitance value to the detriment of leakage resistance. However, excessive minimization of leakage resistance will cause a high leakage current within the component. It would therefore be advantageous to control the leakage resistance when one wanted to improve self-discharge following an increase in capacitance through variation of the thickness of the electric double layer.

Effect of the activated surface (S) on self-discharge. The greater is the specific activated surface, the greater the capacitance of the supercapacitor. Since the time constant of self-discharge depends on capacitance, it is therefore obvious that a high capacitance can increase the duration of self-discharge. It would be interesting to simulate the influence of the activated surface on the capacitor of the electrical double layer especially on leakage current and hence the time constant of self-discharge. Values of the activated surface range from 600 m^2/g to 3000 m^2/g in steps of 600 m^2/g. The parameters have retained their values shown in Tables 6 and 7. The different values of the time constant, obtained by varying the activated surface are shown in Table 8. From the data in Table 10, the self-discharge period decreases as the activated surface increases. This is explained by the increase of the capacitance of the electric double layer capacitor, that considerably decreases leakage resistance according to relation (13).

The results in Table 10 are confirmed by the graphs in Figure 20. From this Figure, it is noted that for a specific activated surface equal to 600 m^2/g, the leakage current decreases from 0,656 mA (t =0 s) to a value of 0,269 mA. Whence a leakage current drop of 0,386 mA for a leakage resistance value of 5,4 kΩ with 1,442.6 h bas duration of self-discharge. While for a specific activated surface equal to 3000 m^2/g, the leakage current drops by 1,935 mA with a leakage resistance equal to 1,1 kΩ and 4,776 kF as capacitance. The duration of self-discharge in this case is 1,442.01 h. These results allow us to say that an increase in activated surface accelerates self-discharge of supercapacitors. In other words the reactions are more important for a specific activated surface that is too high. Indeed, it would be interesting to have a very high leakage resistance to limit the self-discharge of supercapacitors. Moreover this is what is often most recommended. It is only possible by having a small activated surface area, but it should be noted that a reduction in the latter causes a decrease in storage capacity, and therefore, a reduction in the energy performance of supercapacitors.

Table 10 – Self-discharge time constants obtained for different values of activated surface

S (m^2/g)	C_{dl} *(kF)*	R_p *(kΩ)*	*τ (h)*	i_f *(mA)*		Δi_f *(mA)*
				0 s	*3500 s*	
600	0.955	5,4	1,442.6	0,656	0,269	0,386
1200	1,910	2,7	1,442.5	1,312	0,538	0,773
1800	2,866	1,8	1,442.5	1,969	0,807	1,161
2400	3,821	1,4	1,442.4	2,625	1,077	1,548
3000	4,776	1,1	1,442.1	3,281	1,346	1,935

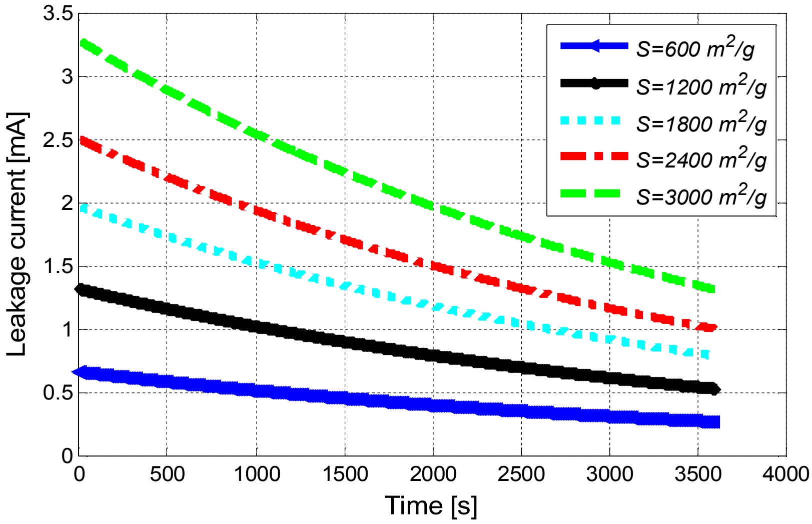

Figure 20 – Simulation of the effect of the activated surface on self-discharge

Effect of relative permittivity (ε_r) of electrolyte on self-discharge. The capacitance of the electric double layer capacitor reaches extremely high values for electrolytes having a high dielectric constant. Figure 21 shows the profile of the leakage current for various types of electrolytes. The parameters used in simulation are from Tables 6 and 7 and the simulation results are presented in Table 11. The analysis of this table shows that capacitance may reach extremely high values for electrolytes having a high dielectric constant with low leakage resistance. It is possible that the duration of self-discharge is great in this case; but given that leakage resistance dropped significantly, this cannot fill the high value of leakage current (Fig. 21).

Table 11 – Self-discharge time constants obtained for different values of dielectric constant

ε_r	C_{dl} *(kF)*	R_p *(kΩ)*	*τ (h)*	i_f *(mA)*		Δi_f *(mA)*
				0 s	*3500 s*	
28	3.096	1.7	1,443.1	1.264	0.644	0.619
36	3.980	1.3	1,442.8	1,625	0,828	0,796
38	5,306	1,0	1,442.8	2,167	1,105	1,060
48	7,575	0,7	1,442.7	3,069	1,564	1,505
78	8,619	0,6	1,442.7	3,520	1,794	1,726

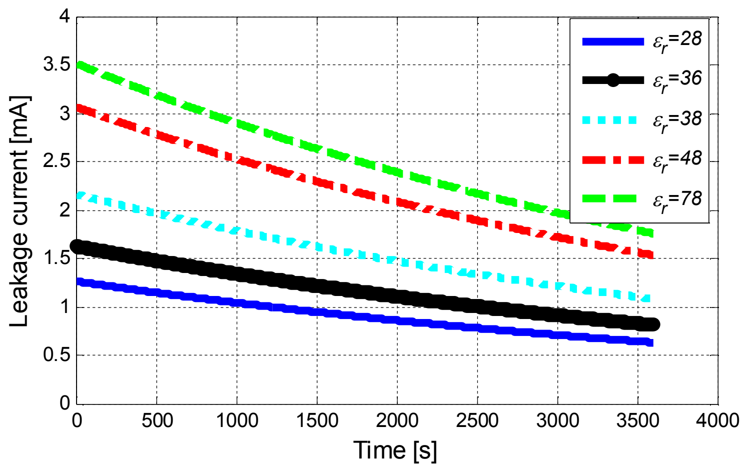

Figure 21 – Simulation of the effect of relative permittivity (ε_r) on self-discharge

Conclusion. In this paper, models of a supercapacitor and leakage resistor were implemented and validated. The procedure for increasing the duration of self-discharge has been explained. Indeed, an increase in this time involves changing the main parameters constituting leakage resistance and capacitance of the electrical double layer capacitor. This study allowed us to say that a high capacitance sometimes allows to have a long duration of self-discharge (in other words, it is difficult to conclude on the value of capacitance). However leakage current is very important because leakage resistance is very low. It is therefore better to have high leakage resistance; low permittivity of the electrolyte; small activated surface; relatively thick electrical double layer; charging voltage below the nominal voltage. Other parameters (such as valence, temperature) had no significant influence on leakage current and therefore the time constant of self-discharge.

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