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DOCTORAL THESIS ABSTRACT

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RESEARCH ON THE ELECTRICAL PARAMETERS OF SUPERCAPACITORS

DOCTORAL COMMITTEE

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Chapter 1

Introduction

Nowadays, in the field of electronics, great emphasis is placed on the lifespan of electronic devices and, consequently, on the lifespan of the electronic components that make up these devices. Another important point is the search for solutions that meet all the environmental standards imposed at European level, in order to protect both people's lives and the environment. Another requirement in this field is the storage of energy in large quantities and its use in applications when necessary. It has been shown that the supercapacitor is the passive electronic component which incorporated in various electronic devices is capable of meeting all these current market requirements.

1.1. Presentation of the doctoral thesis field

Recently, the problem of powering electronic circuits has become an important issue, especially in mobile devices. The use of mainly classical battery storage systems in industry is not a viable solution, as these devices lose their storage capacity after 2-3 years. On the other hand the materials used to manufacture them are harmful to the environment, even banned in some countries, in accordance with European Union regulations such as RoHS 1 and RoHS 2. Recently a promising solution has become known that is in line with these standards, namely the use of supercapacitors as energy storage devices.

Supercapacitors or electrochemical double-layer capacitors (EDLCs) are components that tend to replace conventional batteries. They do not contain lead or other environmentally harmful materials and can also accumulate large amounts of electrical charge. EDLCs have a very long service life (hundreds of thousands of charge-discharge cycles), the operating temperature range is higher than that of batteries and they have a fairly high power density that allows for current surges when needed in various applications. Supercapacitors are therefore a viable solution for use in an energy storage system. However, since this is a component that is constantly evolving, there is always the question of identifying the best possible operation and performance. This requires numerous tests to be carried out under various operating conditions in order to simulate as closely as possible real settings in which these components could be used. At the same time, the manufacturers of these components do not provide sufficient information on the main electrical parameters of supercapacitors. The only way to determine them is to perform tests on the components and then determine the parameters that are important depending on the application in which these supercapacitors are used.

In terms of construction, supercapacitors are based on three major components, namely: two aluminum foils on which the material for the electrodes is deposited, the electrolyte solution and the separator. Over time, the performance of the supercapacitor has been improved by the use of materials aimed at reducing its shortcomings.

Current research in supercapacitors addresses the problem of using ionic liquids as electrolytes to increase the maximum working voltage of a single cell. In addition, numerous tests are being conducted towards metal organic frameworks (MOFs) to fabricate the electrode material. The major advantage of these metal frameworks is the large active area they provide compared to other carbon-based materials used to fabricate electrodes.

Thus, the supercapacitor is a passive electronic device capable of making an important contribution to the industry in terms of energy recovery given the current and future conditions imposed by international regulations on pollution and energy recovery.

1.2. The purpose of the doctoral thesis

The supercapacitor is a relatively new passive electronic device if we make a comparison with when electronic capacitors were discovered. As it is constantly being developed, it can become a component with great utility in various energy storage applications. Therefore, it is more than necessary to know its behavior by identifying the advantages, as well as the disadvantages of supercapacitors. Consequently, the determination of certain common parameters (equivalent series resistance, self-discharge, leakage current, energy density, power density) of the component is essential because only in this way we can identify, compare and characterize the different components.

This work attempts to contribute to the study of the electrical parameters of supercapacitors by identifying the conduction process of the supercapacitor, by performing investigations on the different materials used in the realization of the device, but also numerous studies to determine the electrical parameters for different supercapacitors available on the market. These experiments are carried out under different test conditions so that the operation of the supercapacitor in real applications can be simulated as well as possible. For this purpose, tests are carried out at different operating temperatures. Moreover, batteries with two and three supercapacitors are created and tested in series and parallel connection, taking into account the absence or presence of a stabilization time.

Thus, as a result of the research conducted, sufficient knowledge was accumulated to realize a supercapacitor. The procedures for realizing and testing the supercapacitor are described in detail in this thesis.

1.3. The content of the doctoral thesis

The present doctoral thesis is divided into 8 chapters, as follows:

- **Chapter 1** of the thesis introduces the topic of the thesis and its purpose.
- **Chapter 2** contains information on concepts from the field of electrochemistry underlying the realization and operation of the supercapacitor, its operating principle, main electrical parameters, and also commercial design variants of supercapacitors.
- **Chapter 3** presents the main materials that can be used in the realization of the electrode, the main electrolyte solutions used and at the same presents the characteristics that a good separator should have. All these are the main components of the supercapacitor.
- **Chapter 4** is an analysis of the main parameters of supercapacitors in accordance with their topology in electrical circuits.

- **Chapter 5** exemplifies two methods for determining the leakage current of supercapacitors. The first method is to directly determine the leakage current, and the second method is to determine the self-discharge in the first phase, and then, according to the mathematical calculations, the value of the leakage current was obtained.
- **Chapter 6** provides information on the application of electrochemical impedance spectroscopy method to various types of commercial supercapacitors.
- In **chapter 7** the process of fabricating a supercapacitor, a pouch type cell is presented in detail. This supercapacitor was tested and the results obtained from the analysis of experimental data are also included in this chapter.
- **Chapter 8** summarizes the results obtained in this thesis and presents the original contributions resulting from the experiments conducted during the research. This chapter also contains the list of papers published during the doctoral stage, but also a series of perspectives for further development, topics that represent a continuity of the research carried out so far.

Chapter 2

Theoretical notions

This chapter contains a brief introduction to electrochemistry, a field that underlines the operation of the supercapacitor, but also provides information about the realization of the electric charge layer from the discovery of the double electric charge layer by Hermann von Helmholtz in 1856 to the definition of this layer by Gouy and Chapman. The latter concluded that there is a multiple charge layer inside the supercapacitor, and not a double layer as initially claimed by Helmholtz. In addition this chapter presents the operating principle of the supercapacitor, commercial design variants of supercapacitors, as well as their electrical parameters.

2.1. Electrolyte solutions

Electrolytes are substances that have the important property of conducting electric current in the molten state or in solution. Since they conduct electricity based on an ionic mechanism, they are called ***second order electrical conductors*** [2].

2.1.1. Degree of electrolytic dissociation

Svante Arrhenius claims that after the electrolytic dissociation process, both undissociated molecules and ions remain in the solution. Therefore, the degree of electrolyte dissociation α is defined as the ratio between the number of molecules dissociated to ions in the electrolyte solution and the total number of molecules in the electrolyte. Thus, after calculating the degree of electrolytic dissociation, we can find out how many parts of the molecules in the electrolyte solution dissociated into ions and how many remained undissociated. In terms of ion dissociation capacity, electrolytes were divided into strong and weak electrolytes. The difference between the two types of electrolytes is the degree of electrolyte dissociation. When both ions and undissociated molecules are present in the solution after the process of electrolytic dissociation, then we speak of weak electrolytes. If only ions are present in the solution after dissociation, we can say that that electrolyte is a strong electrolyte. Thus, the degree of electrolytic dissociation is equal to 1 for strong electrolytes, and for weak electrolytes this value is less than 1.

2.2. Electrode

An electrode is a first order conducting material that is in contact with a second order conducing material. It is in fact an assembly made of two materials: the electronically conductive material on the one hand and the ionic conductive material on the other [3].

2.3. Introduction to the electrochemical charge layer

The concept of the electrochemical double layer of charge appeared in 1853 when Hermann von Helmholtz discovered that a double layer charge is formed at the interface between the electrode and the electrolyte solution, this layer consists of electrically charged charges at the electrode and ions of the opposite sign in the electrolyte solution.

Later, after 1900, Gouy, Chapman, Stern and Grahame conduct extensive research in this field and in some ways contradict Helmholtz's discoveries. They state that this double layer at the electrode-electrolyte interface is in fact a multiple layer consisting of an internal Helmholtz plane (layer), abbreviated PHI, an external Helmholtz plane (layer), abbreviated PHE, and a diffuse layer (see Fig. 2. 3) [2].

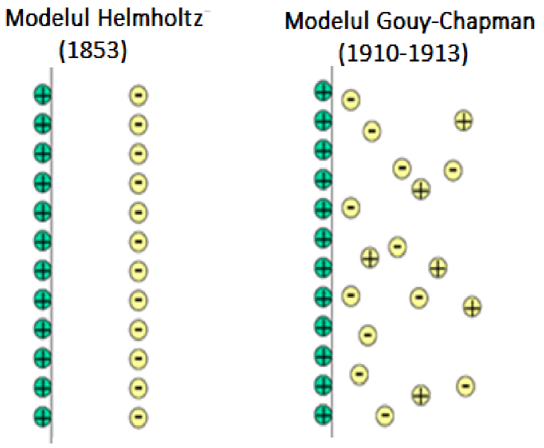


Fig. 2. 3 *The Helmholtz model and the Gouy-Chapman model [2].*

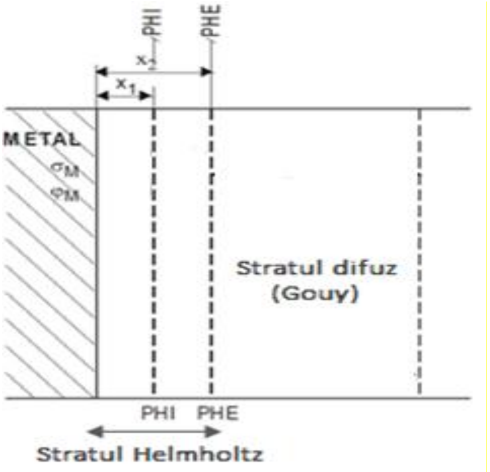


Fig. 2. 4 *The internal structure of the Gouy-Chapman model [4].*

2.4. The constructive structure of the supercapacitor and its principle of operation

As described in the thesis, the supercapacitor consists of three main components: the two aluminum foils on which the material for making the electrodes is deposited, the electrolyte solution (electrolyte) and the separator. A constructive form of the cylindrical supercapacitor is shown in Fig. 2. 8.

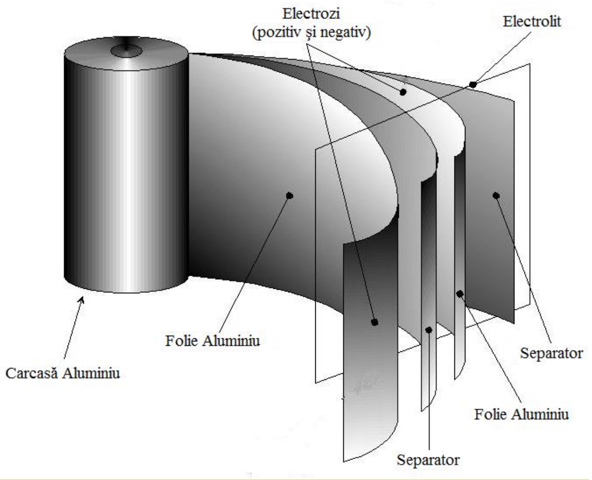


Fig. 2. 8 *The main components of a supercapacitor.*

The principle of operation of the supercapacitor is based on the realization of two multiple layers of electric charge at the interface between the electrode and the electrolyte. In the two charge layers, the ions are adsorbed by the charges of opposite sign at the electrode. The charge layer forms when a voltage is applied to the terminals of the supercapacitor that is less than or equal to the maximum operating voltage specified by the manufacturer in the component data sheet. When no electrical voltage is applied to the electrodes of the supercapacitor, there is no electrical charge on their surface and the ions in the electrolyte solution have a random distribution in the mass of the solution. This process is illustrated at the macroscopic level in Fig. 2. 9 [10].

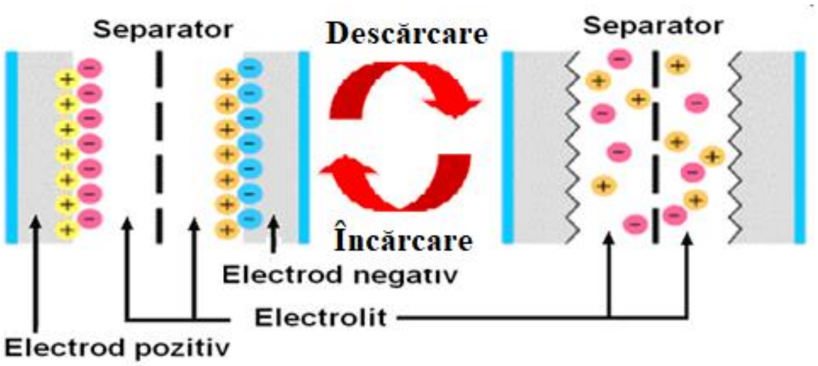


Fig. 2. 9 *The charging / discharging process of a supercapacitor.*

Chapter 3

Materials used in the construction of supercapacitors

This chapter contains information on the materials used in the development of a supercapacitor. Thus, it presents the main properties that the materials used to make the electrodes of a supercapacitor should have, comparisons between the different materials currently used, and information about new materials that have outstanding performance in terms of specific active area. The main material that has been the basis for the realization of supercapacitors since their inception is carbon in various forms. It remains a viable alternative today, although technology has evolved and a number of new materials are helping to improve the performance of these components.

The following table summarizes the main properties of the three types of carbon used as electrodes in the manufacture of supercapacitors.

Tab. 3.1 *The main characteristics of carbon-based materials*

Parameter	**Activated carbon (AC)**	**Graphene**	**Carbon nanotubes**
Energy density (Wh/kg)	4-5	~100	~ 10
Power density (kW/kg)	1-2	~50	~ 20
Specific capacitance (F/g)	< 100	~550	180
Surface area (m^2/g)	> 1000	> 2600	500
Electrical conductivity (S/m)	Much smaller than graphene	200	1000

3.2. Electrolytes

The types of electrolytes used in the development of supercapacitors are also presented, as well as the differences between the three electrolyte solutions (aqueous, organic and ionic liquid) in terms of maximum allowable working voltage, but also in terms of ionic conductivity.

The following table summarizes the characteristics of the electrolyte solutions most commonly used in the manufacture of supercapacitors.

Tab. 3.2 *The main characteristics of the electrolytes most frequently used in the manufacture of supercapacitors*

Solvent	**Electrolyte**	**Operating temperature (˚C)**	**Ionic conductivity (mS/cm)**	**Maximum working voltage (V)**
Aqueous electrolyte				
Water	KOH, 4M	25	540	1,2
	H_2SO_4, 2M	25	750	1,2
	KCl, 2M	25	210	1,2
	Na_2SO_4, 1M	25	91,1	1,2
Organic electrolyte				
Propylene carbonate	Et4NBF4, 1M	25	14,5	2,7
Acetonitrile	Et4NBF4, 1M	25	59,9	2,7
Ionic liquid				
Ionic liquid	[EtMeIm]+[BF4]–	25	8	4
	[EtMeIm]+[BF4]–	100	14	3,25

3.3. Separator

Although the separator is usually not given enough importance in the literature, it plays an extremely important role in the functionality of a supercapacitor, and its selection must take into account a number of characteristics that it should have. For example, a good separator should provide good insulation, have high ionic conductivity, be thin but at the same time have high mechanical strength and not have corrosion problems when in contact with the electrolyte. The most commonly used separators in the production of supercapacitors are polyolefins.

Chapter 4

Analysis of the main parameters of supercapacitors in accordance with their topology in electrical circuits

Chapter 4 contains two important parts regarding the study of the main parameters of supercapacitors, given their behavior in different circuits. Through this investigation, I have tried to simulate certain situations that may occur in practice. It is important to know how these parameters change and what impact they have on the circuits in which the particular supercapacitors are embedded. I have tried to observe the behavior of certain parameters in a situation where the supercapacitor is not used to its full extent according to the requirements of international standards and certain limits are violated because these considerations cannot be fully observed in practice.

In this chapter I have presented the experiments which have been carried out and described the results obtained in various situations as follows:

1. Analysis of the series and parallel connections of two supercapacitors of 22 F/ 2.5 V and 200 F/2.7 V as a function of temperature, or three supercapacitors of 22 F/ 2.5 V taking into account the calculation of the theoretical and experimental capacitance, and even the influence of the stabilization time on the value of the capacitance after loading.
2. The influence of charge/discharge current on various parameters of supercapacitors, such as capacitance, equivalent series resistance (ESR), power dissipation and time required to charge or discharge the supercapacitor.

4.1. Analysis of the series and parallel connections of the supercapacitor and the influence of the stabilization time

4.1.1. Introduction to the issue of series and parallel connections of supercapacitors

In this subchapter I have presented a number of introductory considerations regarding the realization of series and parallel circuits of supercapacitors taking into account the distribution of the maximum working voltage among the individual supercapacitor. In addition, within this subchapter two solutions used in the literature that can achieve a good balance of voltages to avoid destroying a component or the whole interconnection structure by exceeding the maximum voltage specified in the technical datasheet are presented.

4.1.2. Procedure description

One of the objectives of this research is to compare the capacitance values for the individually tested supercapacitors by theoretically calculating the capacitance value for the series and parallel circuits with the values obtained experimentally for series and parallel circuits of the same supercapacitors, also taking into account the influence of temperature. Using mathematical formulas, the above facts be translated according to the following equations:

- Parallel connection:

$$C_{1\text{măs}} + C_{2\text{măs}} =/\neq (C_1 + C_2)_{\text{măs}} \tag{4. 1}$$

- Series connection:

$$\frac{C_{1\text{măs}}C_{2\text{măs}}}{C_{1\text{măs}} + C_{2\text{măs}}} =/\neq \left(\frac{C_1C_2}{C_1 + C_2}\right)_{\text{măs}} \tag{4. 2}$$

The block diagram of the measurement system is shown in Fig. 4. 3. The system includes equipment such as: laboratory power supply, scanner, digital multimeter, data logger and a PC interface (GPIB / USB).

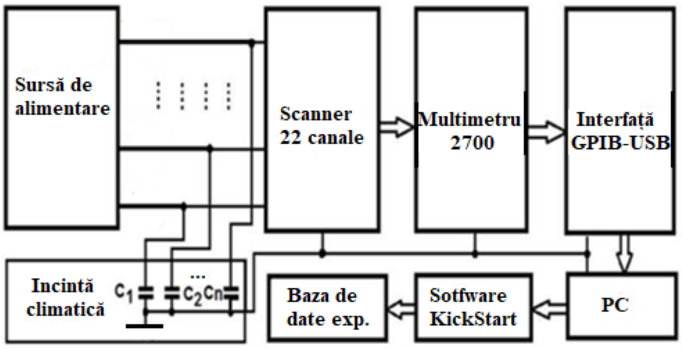


Fig. 4. 3 *Block diagram of the measurement system.*

The measurement system and the tested supercapacitors are shown in the Fig. 4. 4.

Fig. 4. 4*Measurement system with the supercapacitors subjected to testing.*

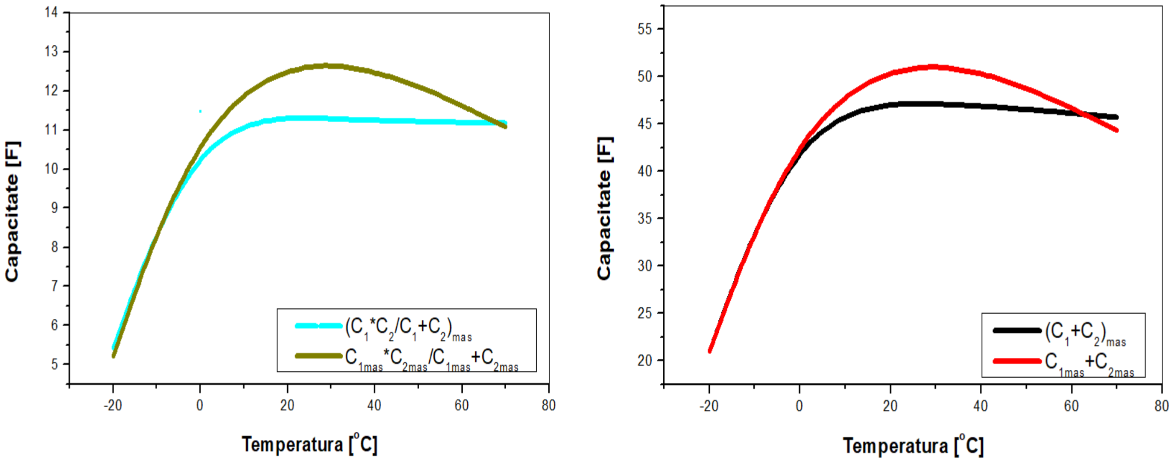
4.1.3. Results

In the experiment conducted in this investigation, two types of supercapacitors were tested, one of 22 F with a maximum working voltage of 2.5 V and one of 200 F with a maximum working voltage of 2.7 V, both individually and in series and parallel connection.
The following table shows the values of the capacitance calculated at different temperature values as previously indicated.

Tab. 4. 1 *Capacitance values depending on the temperature for the 22 F supercapacitor in each individual case.*

Supercapacitors 22 F				
Temperature [˚C]	$\frac{C_{1mas} \times C_{2mas}}{C_{1mas} + C_{2mas}}$ [F]	$(\frac{C_1 \times C_2}{C_1 + C_2})_{mas}$ [F]	$C_{1mas} + C_{2mas}$ [F]	$(C_1 + C_2)_{mas}$ [F]
-25˚C	5,207	5,435	21,050	20,990
0 ˚C	11,633	11,472	46,599	46,960
~30˚C	13,265	11,251	53,713	47,445
70˚C	11,078	11,167	44,321	45,681

In the case of the 22 F supercapacitor, a value of 11 F should ideally have been obtained for connecting two 22 F supercapacitors in series, and a capacitance value of 44 F for connecting the same two supercapacitors in parallel. At the negative temperature at which first the single supercapacitor was tested and then the the series and parallel circuits, an unfavourable behavior of the 22 F supercapacitor is observed. In this case quite low values were obtained in all the situations tested, an indication that operation at negative temperatures is not particularly suitable for this type of supercapacitor.



a). b).

Fig. 4. 7 *Supercapacitors capacitance graph of 22 F/2.5 V in series connection (a), respectively parallel (b) at temperatures of -25ºC, 0ºC, ~30ºC and 70ºC.*

The experimental data given below indicate the effect of the 30 minutes stabilization time on the capacitance and equivalent series resistance when three 22 F supercapacitors are connected in parallel.

Tab. 4. 2 *Influence of stabilization time when three 22 F supercapacitors are connected in parallel.*

	Parameter	**3 EDLC 22 F – parallel - 30 min stabilization**	**3 EDLC 22 F – parallel - 0 min stabilization**
Cycle 1	**C [F]**	71.6	63.1
	ESR [mΩ]	52.7	77.5
Cycle 2	**C [F]**	70.6	62.9
	ESR m[Ω]	53.3	77.5

Fig. 4. 8 shows a clear picture of the influence of the stabilization time on the values of the experimentally determined parameters in the case of the parallel connection of the three 22F supercapacitors.

After the second measurement cycle, the differences in capacitance and ESR remain.

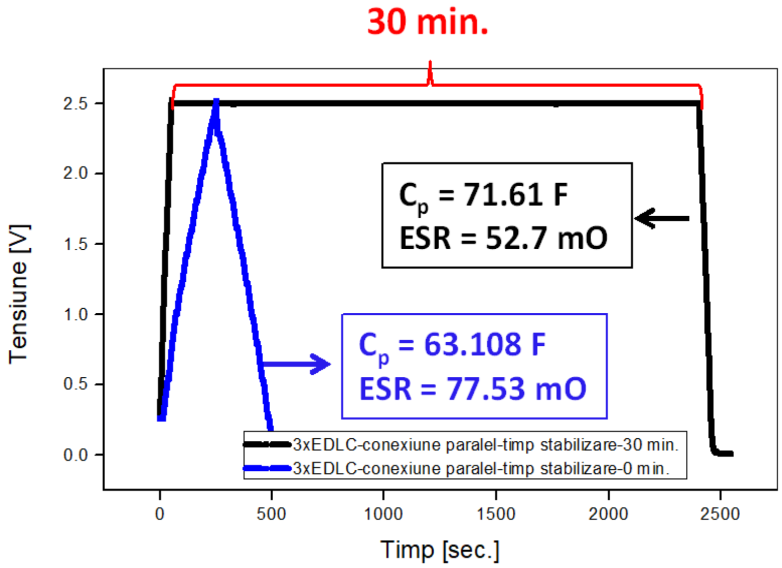


Fig. 4. 8 *Influence of stabilization time when three 22F supercapacitors are connected in parallel.*

4.2. Influence of the charging/discharging current on the different parameters of supercapacitors

Another experiment in this thesis focused on determining the effect of charge/discharge current on the important parameters of the supercapacitor such as: capacitance, equivalent series resistance (ESR), dissipated power and charge/discharge time. The charge/ discharge current leads to important changes in the above parameters. Therefore, it is important to know how the value of the equivalent series resistance changes when we increase or decrease the value of the charge/discharge current and to understand what is actually happening inside the supercapacitor in order to control the various phenomena that occur in practice [22].

An existing measurement system from the National Institute of Research and Development for Cryogenics and Isotopic Technologies – ICSI, Rm. Valcea was used. The equipment used is shown in the figure below:

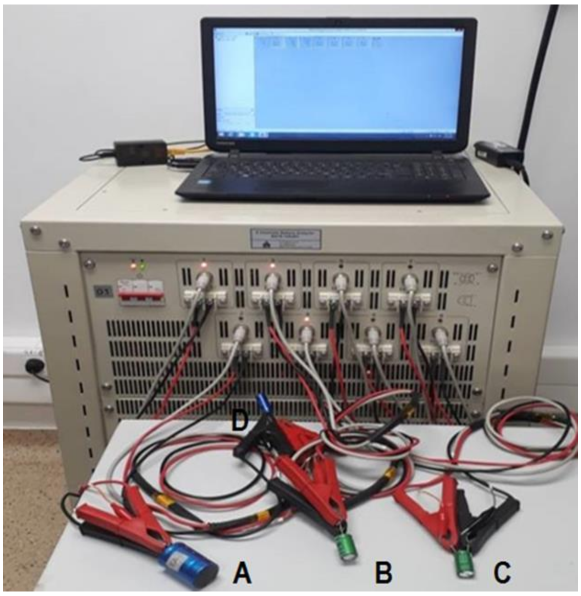


Fig. 4. 10 *The battery analyzer of ICSI Râmnicu Vâlcea together with the tested supercapacitors [21].*

4.2.1. Experimental results

Tab. 4. 10 summarizes the results obtained in the case of the 200 F supercapacitor for the capacitance, equivalent series resistance, dissipated power and charge/discharge time. It is noticeable that the capacitance value does not follow a certain law according to which it varies as a function of he value of the charge/discharge current, but in the case of the ESR, the dissipated power and the charge/discharge time, things are clear: as the value of the charge/ discharge current increases, the values obtained in the case of the ESR and the dissipated power increase and the charge/discharge time decrease [43].

Tab. 4. 3 *Influence of the charge/discharge current on the parameters of the 200 F supercapacitor.*

EDLC 200F	**I = 0.5 A**	**I = 1 A**	**I = 1.5 A**
C [F]	183.918	182.311	183.881
ESR [Ω]	14.8	16.8	17.4
$P_{dissipated}$ [W]	0.0037	0.0168	0.0391
Time [min]	15.88	7.78	5.23

The charge/discharge curves of the maximum voltage across the terminals of the 200 F supercapacitors as a function of time at different values of charge/discharge current are shown in Fig. 4. 11.

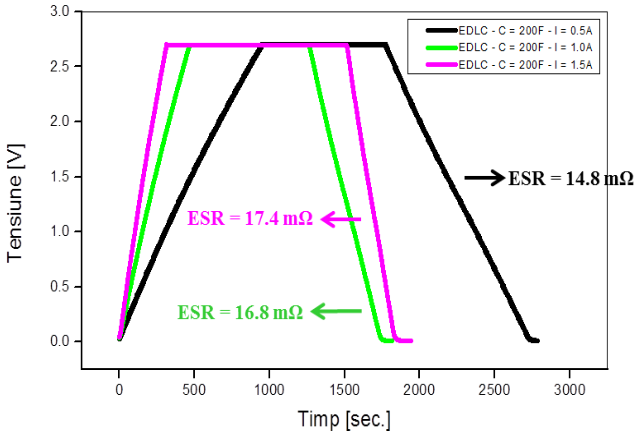


Fig. 4. 11 *Influence of the charge/discharge current on the parameters of the 200 F supercapacitor.*

Chapter 5

Methods for determining the leakage current of supercapacitors

Leakage current is one of the key factors of supercapacitors. More precisely, its influence on the main parameters of the supercapacitor and can have a great negative impact on the component. In fact the occurrence of this leakage current is determined by the presence of two types of current, namely:

- leakage current (I_{lc}) caused by various undesirable processes, such as the presence of loss resistance, the uneven distribution of charge on the surface of the electrode pores, the short-circuiting of the anode and cathode if proper sealing was not achieved during the development of the supercapacitor, or the occurrence of thermal energy when working at higher temperatures.
- Faradic leakage current (I_{lcF}) occurs when the electrode potential exceeds the electrochemical decomposition limits of the electrolyte. This leads to faradic reactions, resulting in the transfer of charge within the EDLC [23].

It is very important to determine the value of the leakage current and to understand the operation of the EDLC because in this way we can reduce its drawbacks. Therefore, two methods will be used to determine the leakage current:

1. Applying a continuous voltage to the terminals of the supercapacitor and monitoring the current required to keep the value of this voltage constant. This current represents the value of the leakage current.
2. Charging a supercapacitor with a given continuous voltage and then monitoring it in an open circuit for a long period (72 hours are specified). The self-discharge is given by the difference between the maximum voltage value before leaving the supercapacitor in open circuit and the voltage value after the monitoring time [ΔV] [5].

5.1. Determining the leakage current (first method)

The steps for performing the test for measuring the leakage current are as follows:

a. Charging the supercapacitor with a constant current (1 A – the value used in my experiments for the charge-discharge current) to a maximum voltage of 2.5 V in the case of the 22 F supercapacitor, respectively 2.7 V in the case of the 200 F supercapacitor.

b. The procedure performed basically is essentially to keep the supercapacitors at the maximum voltage for a long period of time (for the performed tests, they are monitored for 12 hours) until the current value decreases significantly and then remains constant. This value at which the current stabilizes is the leakage current value [22].

c. Discharging the supercapacitors at the same current value at which they were charged (1A).

All tests were carried out at different temperatures, and a climatic chamber (enclosure) was used for this purpose.

5.2. Determining the self-discharge (second method)

The steps for performing the test to measure self-discharge are as follows:

a. Charging with a constant current (1 A – the value used in my experiments for the charge/discharge current) up to the maximum voltage of 2.5 V in the case of the 22 F supercapacitor and 2.7 V in the case of the 200 F supercapacitor.

b. Maintaining supercapacitors at maximum voltage for 30 minutes to achieve stabilization.

c. Monitoring the supercapacitors in open circuit for a maximum of 72 hours.

d. Discharging supercapacitors at the same current value at which they were charged (1A).

Again, all tests were performed at different temperatures, which also required a climatic chamber.

5.3. Experimental results

For this work, two types of supercapacitors were tested using the two methods described above. The two types of supercapacitors have a capacitance of 22 F and 200 F respectively, and a rated voltage of 2.5 V and 2.7 V, respectively. In the case of the 22 F supercapacitor we tested two components, one new (unused) and the other used in several previous experiments, to determine the losses in both situations and to observe what happens to a supercapacitor over time, after it has been subjected to several tests.

5.3.1. Results obtained through the first method- leakage current

Using this method, it was possible to determine the value of the leakage current for the three supercapacitors tested of 200 F, the used 22 F, and the new 22 F. The supercapacitors were kept at the maximum voltage of 2.7 V or 2.5 V respectively for a period of about 12 hours until the current value remained constant, this value being the value of the leakage current.

Tab. 5. 1 *Leakage current values obtained through the first method at different temperature values.*

Leakage current [mA]	**Temperature [ºC]**	**EDLC – 200 F**	**EDLC – 22 F - used**	**EDLC – 22 F - new**
I_{lc}	-20	1.041	0.058	0.345
	0	1.225	0.065	0.050
	25	3.879	1.015	0.548
	50	8.459	1.371	1.286

5.3.2. Results obtained through the second method – self-discharge

The second method made it possible to determine the self-discharge of the tested supercapacitors over a long period of time (max. 47 hours). Some difficulties were encountered when testing the components at -20 ºC, as the data storage system had some errors and the monitoring could only be performed for 24 hours.

Tab. 5. 2 *Self-discharge voltage values obtained through the second method for the 200 F / 2.7 V supercapacitor.*

Temperature [ºC]	**Time of self-discharge [ore]**		**Self-discharge of the 200 F – ΔV supercapacitor [V]**	
-20	24	-	0.163	-
25	24	43	0.625	0.728
50	24	47	0.681	0.854

Chapter 6

Investigations on electrochemical impedance spectroscopy on different types of supercapacitors

In Chapter 6 research on three supercapacitors of 5 F, 10 F and 22 F respectively is presented. This is a rarely published study since most EIS determinations are in the range of up to 1 F and I believe that EIS determinations for higher capacitances should be known to the community. To verify the accuracy of the experimental data obtained by the electrochemical impedance spectroscopy method, I used another direct method (DM), electronic, with high-performance devices and obtained experimental data that was processed to determine the parameters of the supercapacitors. From a theoretical point of view the data was verified by means of Kramers-Kronig relations.

6.1. Electrochemical impedance spectroscopy method (EIS) and direct method (DM)

Electrochemical impedance spectroscopy (EIS) is a method of investigation used in electrochemical systems. It is usually implemented in a potentiostat and involves superimposing a small amplitude (5-10 mV) sinusoidal signal over a continuous voltage and monitoring the magnitude and phase angle of the resulting alternating current. The resulting impedance is usually represented as a complex quantity, as in equation (6. 1):

$$Z(\omega) = Z'(\omega) + jZ''(\omega) \tag{6. 1}$$

EIS data can be represented in the complex plane as so-called Nyquist diagrams. The real part Z' and the negative imaginary part of the impedance -Z" are plotted in the complex plane, where Z' is on the OX axis and -Z" is on the OY axis, and the result is a graph with frequency as a parameter.

Using the method of electrochemical impedance spectroscopy, the results of three investigations are presented in this chapter:

a) The dependence of the capacitance on the voltage applied to the terminals of the supercapacitors.
b) The influence of temperature on the real part Z’, respectively the imaginary part Z’’ of the impedance for three types of supercapacitors.
c) The application of the mathematical relations of Kramers-Kronig to the experimental data obtained in earlier investigations.

6.1.1. The dependence of capacitance on the voltage applied to the supercapacitors terminals using the electrochemical impedance spectroscopy method

Method of measurement

As mentioned before, data obtained by the electrochemical impedance spectroscopy (EIS) method were compared with another experimental data set obtained by an electronic method, locally referred to as the direct method (DM).

Experimental results

The results are based on measurements performed on two types of supercapacitors: 22 F and 5 F which have a maximum voltage of 2.5 V and 5.4 V respectively. The measurements using the direct method were performed in accordance with IEC standard 62391 [9].

The capacitance values obtained at different voltages for the 22 F supercapacitor through the direct method (DM) and through the electrochemical impedance spectroscopy (EIS) method, respectively, are shown in Tab. 6. 1.

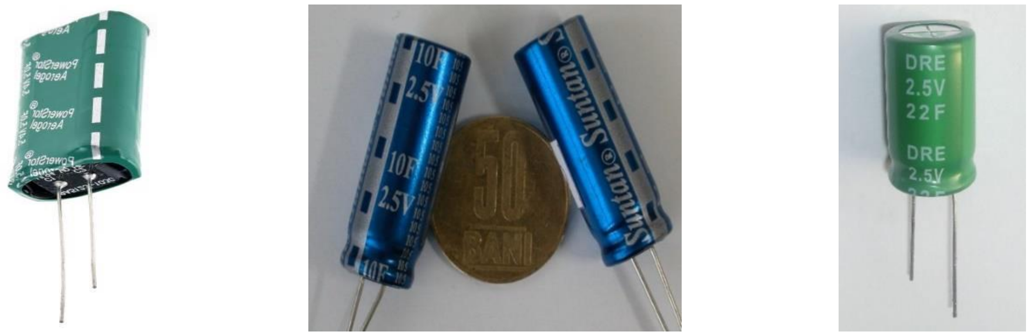
In order to obtain the capacitance values as a function of the voltage applied to the terminals through the electrochemical impedance spectroscopy method, I fitted the experimental data using the simple Randles equivalent circuit in conjunction with the Helmholtz model presented in the thesis.

Tab. 6. 1 *Capacitance values as a function of working voltage for the 22 F supercapacitor.*

EDLC-22 F	**EIS**	**DM**
V_{max} [V]	**C [F]**	**C[F]**
2.5	24.9	25.42
2	22.3	23.14
1.6	21.4	22.01
1.2	20	20.48
0.8	18.7	19.49
0.4	17.8	17.89

6.1.2. The influence of temperature to the real part Z’, respectively the imaginary part Z’’ of the impedance for three types of supercapacitors

For this research I investigated the behavior of 3 types of supercapacitors with different capacitance values: 5 F, 10 F [48] and 22 F (see Fig. 6. 1) at different temperature values. The aim of this study was to observe the behavior of these components at different temperatures with the help of EIS. The supercapacitors were kept at the maximum voltage for 30 minutes. This is the optimum time recommended in the international standards for stabilization, after reaching the threshold of maximum working voltage specific to each component. The equipment used to take the measurements was a potentiostat. All data were monitored and tabulated using the dedicated Nova software.



(a) (b) (c)

Fig. 6. 1 *Tested supercapacitors : (a) 5 F / 5.4 V, (b) 10 F / 2.5 V, (c) 22 F / 2.5 V.*

The variation of the negative imaginary part of the impedance as a function of time at different temperature values (~ 24 °C - ambient temperature, 80 °C and 100 °C) for the tested supercapacitors is shown in Fig. 6. 2. Surprisingly temperature change has no influence on the capacitance values of the three supercapacitors.

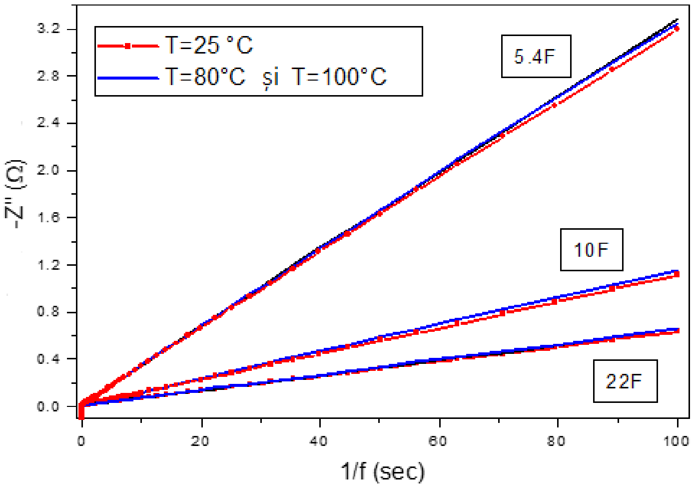


Fig. 6. 2 *The negative of the imaginary part of impedance as a function of time graph.*

To calculate the capacitance value, I used equation **Eroare! Fără sursă de referință.**) resented in the thesis and I considered the points in the graph corresponding to the time of 20 seconds and 100 seconds, respectively, and calculated the slope of the line in the case of the graph obtained. The results can be found in Tab. 6. 2.

Tab. 6. 2 *Calculated values (C_{calc}) and fitted (C_{fit}) of the capacitance obtained for the tested supercapacitors.*

Temperature [°C]	**EDLC-5F-5.4 V**		**EDLC-10F-2.5 V**		**EDLC-22F-2.5 V**	
	C_{calc} [F]	C_{fit} [F]	$C_{calc.}$ [F]	C_{fit} [F]	$C_{calc.}$ [F]	C_{fit} [F]
~ 24	5.04	5.18	14.34	15.01	25.35	27.83
80	4.96	5.18	13.96	14.31	24.43	26.22
100	4.88	5.12	14.07	14.33	24.32	25.89

To fit the experimental data obtained by electrochemical impedance spectroscopy I developed a circuit based on Randles simplified equivalent circuit. This circuit is shown in the figure below:

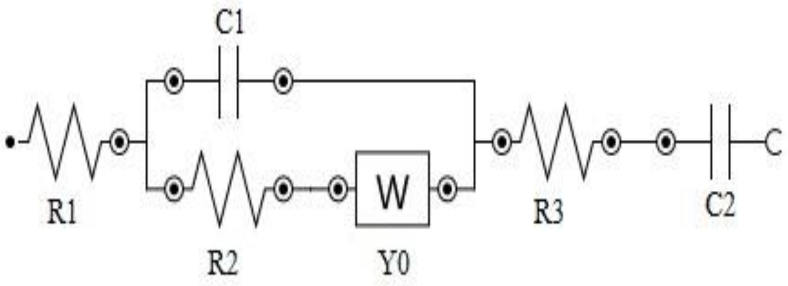


Fig. 6. 3 *The equivalent circuit used for the fitting of EIS measurements.*

The variation of the real part of the impedance as a function of the different frequency values for the 22 F supercapacitor is shown in Fig. 6. 4. It can be seen that the values of the real part of the impedance are different at the three tested temperatures.

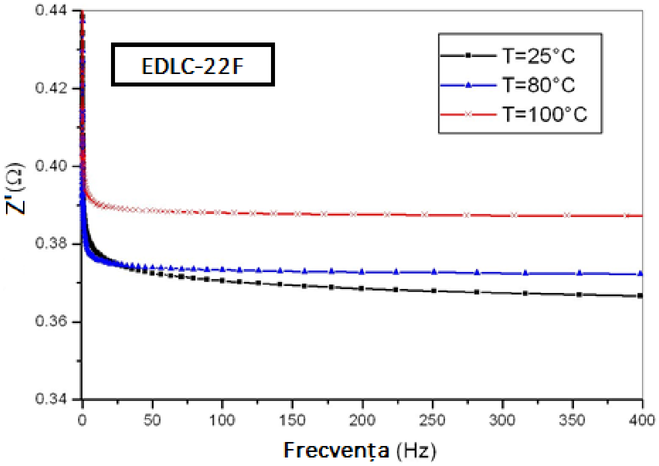


***Fig. 6. 4** The real part of impedance as a function of the frequency at different temperature values.*

6.1.3. Implementing the Kramers-Kronig mathematical equations on experimental data obtained in previous research

Using the experimental data obtained by electrochemical impedance spectroscopy, and presented in subchapter 6.1.1 of the thesis, I used the two Kramers-Kronig mathematical equations to verify the accuracy of the measured data. The two equations are presented below:

$$Z_{re}(\omega) - Z_{re}(0) = \frac{2\omega}{\pi}\int_0^\infty \frac{\frac{\omega}{x}Z_{im}(x) - Z_{im}(\omega)}{x^2 - \omega^2}dx \qquad (6.\,2)$$

$$Z_{im}(\omega) = \frac{2\omega}{\pi}\int_0^\infty \frac{Z_{re}(x)-Z_{re}(\omega)}{x^2-\omega^2}dx \qquad (6.\,3)$$

Where ω is the angular frequency and x is the integration variable.

These two equations establish the relationship between the real and imaginary parts of the complex impedance of the supercapacitor under test. They are used to prove the accuracy of the experimental data obtained using EIS because there are situations where we obtain negative values or values of the order of teraohm for resistances using this method or in the case of the Nyquist diagram we obtain distorted circles. The applicability of these equations is to determine the real part of the impedance when the imaginary part of the measured data is known, or vice versa.

After applying the mathematical equations of Kramers-Kronig, in a finite range of operating frequencies, it can be observed from the graph obtained in the case of the tested supercapacitor of 22 F, presented below, that these equations can be used as a computational method to verify the accuracy of data obtained experimentally with electrochemical impedance spectroscopy.

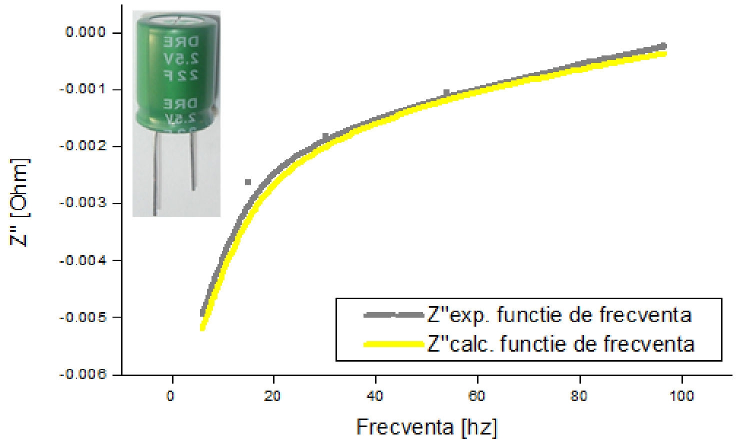


***Fig. 6. 5** Z" (ω) - measured and calculated values at T = 100 °C as a function of frequency for the 22 F supercapacitor.*

Chapter 7

Technology for developing a pouch-type cell (supercapacitor) and testing it

In this chapter the technology used to develop a pouch-type supercapacitor is presented. This cell was developed together with a team from the National Institute of Research and Development for Cryogenic and Isotopic Technologies (ICSI), Râmnicu Vâlcea.

7.1. Constructive types of supercapacitors within ICSI, Râmnicu Vâlcea

In the Institute of Cryogenics and Isotropic Technologies of Râmnicu Vâlcea it is possible, from a constructive point of view, to develop two types of supercapacitors, namely:

- Cylindrical type supercapacitors 18650
- Pouch-type cell (supercapacitor)

7.2. Method for developing the pouch-type cell (supercapacitor)

7.2.1. Supercapacitor vs. Battery

Supercapacitors and batteries are devices designed to store the energy required in various applications. Therefore, the use of such devices has become essential over time. Depending on the application, you can opt for a system that is based on a supercapacitor, on batteries or for a hybrid battery-supercapacitor system. In order to properly determine the need of the storage system for the specific application we need to know very well the operation, but also the advantages and disadvantages of each device.

In order to realize the supercapacitor, the pilot line within the ICSI – ROM-EST laboratory was used for the production of Lithium-Ion batteries since these two components have similarities from the design point of view. The main components are the same, the difference is in the materials from which they are made and in their operating process, which is completely different. They also differ in a number of characteristic parameters. For example, the equivalent series resistance in the case of the supercapacitor has a lower value, and the number of charge/discharge cycles is significantly higher, but we should not forget that the maximum working voltage of a single cell is higher in the Lithium-Ion battery. Moreover, the phenomenon of self-discharge is less pronounced in the case of the battery and the energy density is slightly higher compared to the supercapacitor.

7.2.2. Technical characteristics of the pouch-type cell

In this subchapter the dimensions of the electrode are presented as well as information about the amount of material deposited on the aluminum foil used to make the electrodes. Additionally the dimensions of the casing are given, which have been determined in accordance with the dimensions of the electrodes.

7.2.3. Materials used in developing the pouch-type cell supercapacitor

Electrode composition: - Mixture: CB - Carbon black (95 %), PVdF - Polyvinylidene fluoride (5 wt.%), NMP - N -Methyl-2-pyrrolidone.
Separator: - Celgard 2325 (three layers, PP (polipropilena)-PE (polietilena)-PP (polipropliena), 25 µm).
Electrolyte: - BMI.BF4 - 1-Butyl-3-methylimidazolium tetrafluoroborate ≥97.0% (HPLC) (Sigma-Aldrich) [38].

7.2.4. The process of developing the pouch-type cell

This subchapter details the steps of the process of developing the pouch cell (supercapacitor). It details how the material for depositing the electrodes was obtained, how the electrodes were cut and folded together with the separator, how the capsule was sealed, and also how the electrolyte was filled into the capsule. Ten electrodes were used to make the pouch-type cell (supercapacitor), eight with double-sided deposition and two with deposition only on the front side. The supercapacitor obtained is shown in the figure below:

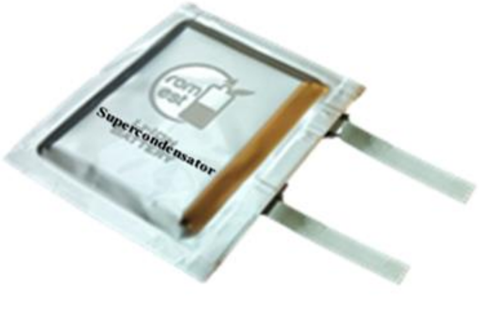


Fig. 7. 1 *Pouch-type cell developed in ROM-EST laboratory, ICSI, Râmnicu Vâlcea.*

7.3. Test method for the pouch-type cell (supercapacitor) and its experimental test results

The research aims to obtain as much information as possible about the supercapacitor created. More precisely, by obtaining the values from the calculations of the main parameters (self-discharge voltage, equivalent series resistance, capacitance, power and energy density) and also their graphical representation we will establish whether the choice of using such an electrolyte was a good choice or not.

7.3.1. Test procedure for the developed cell

The testing of the developed pouch-type cell (supercapacitor) consisted in charging of with different charging currents, gradually increasing the value of the maximum working voltage. I decided to subject the pouch-type cell to these tests charging it successively starting with 20 mV voltage value and charging current of 10 μA and gradually increasing these values. I resorted to this procedure in order not to exceed the maximum voltage threshold and to see what would happen to the freshly developed cell during the tests.

7.3.2. **Experimental results**

Determining the main parameters of the Pouch-type cell

- *Monitoring the self-discharge in different scenarios*

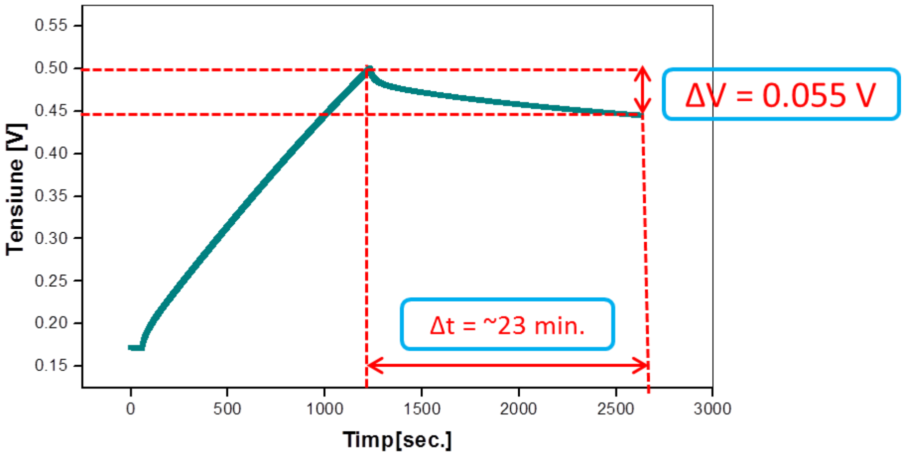


Fig. 7. 2 *Monitoring the charge and self-discharge of the Pouch-type cell at 500 mV, 100 μA.*

Fig. 7. 2 shows an example of charging with a current of 100 μA up to the maximum voltage of 500 mV, which is reached in about 20 minutes. After open circuit monitoring of the cell at its terminals for 23 minutes, a self-discharge of 55 mV is observed. This value corresponds to about 10% of the total value of the maximum voltage of 500 mV applied to the terminals of our supercapacitor. From the calculations performed, it appears that most of the self-discharge occurs in the first 5 minutes, namely 30 mV.

- ***Charging the supercapacitor at different working voltage values***

Fig. 7. 3 shows an example of charging the supercapacitor at different voltage values, namely 500 mV, 750 mV, 2 V, 3 V. As it can be seen, the shape of the graph V(t) takes the form of charging an ideal supercapacitor only at a voltage value of 3 V. This aspect explains the ability of the electrolyte used, which is an ionic liquid, to allow charging at a voltage greater than or equal to 3 V.

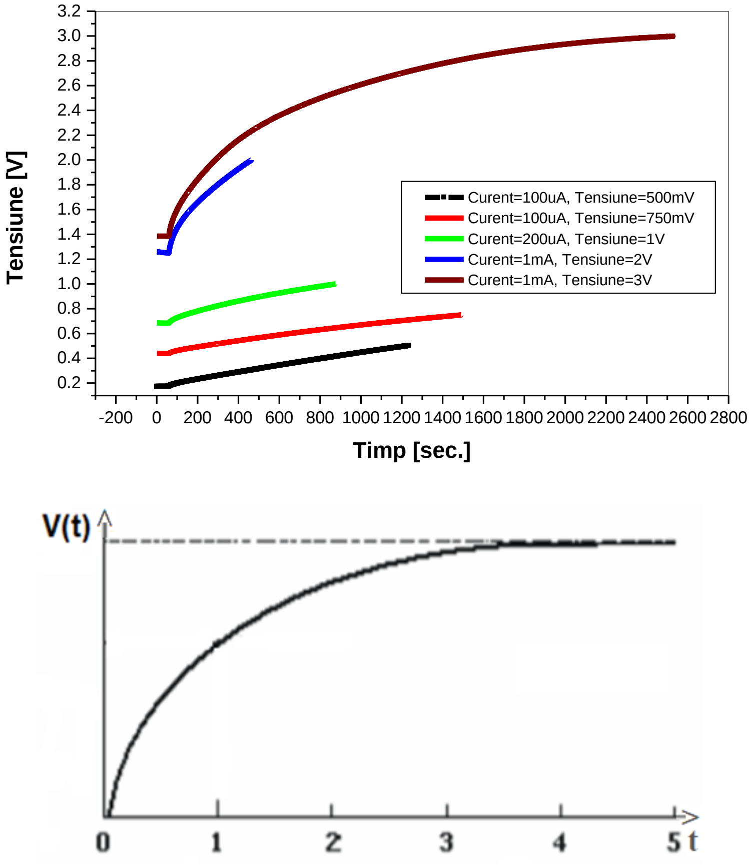


***Fig. 7. 3** Charging of the developed supercapacitor at different voltage values vs. the V(t) graph of ideal charging of a capacitor [40].*

The capacitance value of the supercapacitor determined from the calculations was 95.76 mF, and the equivalent series resistance determined from experimental data using the Nyquist diagram has a value of 581.28 mΩ.

Chapter 8

Conclusions

8.1. Obtained results

Chapter 2: Research on the electrochemical processes that take place inside the supercapacitor and the realization of the electric charge layer.

Chapter 3: Research on the different materials for electrodes, electrolytes and separators used in the development of the supercapacitor.

Chapter 4: Identification of experimental results on two types of supercapacitors with capacitances of 22 F and 200 F respectively, as follows:

- highlighting the differences between the value of experimentally obtained capacitance for series and parallel connections of two or three supercapacitors and the value of the capacitance for the same series or parallel circuits determined by theoretical calculations. The experiments were performed at different temperatures (-25ºC, 0ºC, ~30ºC and 70ºC)
- highlighting the influences of the stabilization time of 0 minutes or 30 minutes on the capacitance and the equivalent series resistance for series and parallel circuits of three 22 F supercapacitors.
- obtaining the capacitances, equivalent series resistance and power values for different values of charge/discharge current.

Chapter 5: Determining the leakage current at different temperatures for two types of supercapacitors with capacitances of 22 F and 200 F respectively.

Determining the self-discharge at different temperatures for two types of supercapacitors with capacitances of 22 F and 200 F respectively.

Chapter 6: Identification of the capacitance dependence on the working voltage for two types of supercapacitors (5 F/5.4 V and 22 F/2.5 V) by two methods, an electronic method and another using electrochemical impedance spectroscopy.

Identification of temperature influence on the real part Z', respectively the imaginary part Z" of the impedance for three types of supercapacitors (5 F/5.4 V, 10 F/2,5 V, 22 F/2.5 V).

Chapter 7: Detailed description of the process of developing the pouch-type cell. Testing the pouch-type cell supercapacitor, under laboratory conditions up to a maximum voltage of 3 V.

8.2. Original contributions

- Determining the main parameters such as capacitance, equivalent series resistance, dissipated power for supercapacitors of 22 F and 200 F considering variations in charge/discharge current. The methods of determination and the results obtained are presented in Chapter 4 and published in [14].
- Determining both the theoretical and experimental capacitances of series and parallel connections of two supercapacitors of 22 F and 200 F respectively. The tests were carried out at different temperature values and the obtained results are presented in detail in Chapter 4 and published in [8].
- The effect of stabilization time of 0 minutes and 30 minutes on the capacitance and equivalent series resistance for series and parallel connections of three 22 F supercapacitors. The results obtained are presented in detail in Chapter 4 of the thesis and published in [14].
- Detailed presentation in chapter 5 of the thesis of two methods for determining the leakage current. The methods were published in [12].
- Performing measurements to determine the leakage current and self-discharge on two 22 F supercapacitors, one of which is new and the other has been used before, in order to show any differences in the values that occur over time for the above mentioned parameters. These experiments are detailed in Chapter 5 of the thesis and have been published in [12].

- Design and construction of a specialized circuit (active load), under laboratory conditions for discharging supercapacitors to a voltage of 0 V. The results are published in [1].
- Identifying the capacitance variation as a function of maximum working voltage using two methods, an electronic method and the electrochemical impedance spectroscopy method for two supercapacitors of 22 F/2.5 V and 5 F/5.4 V. Comparing the results obtained by using the two methods. The research is presented in Chapter 6 of the thesis and published in [11].
- Development of an equivalent circuit for the supercapacitor starting from the simplified Randles circuit. This developed equivalent circuit was used to fit the experimental data obtained using electrochemical impedance spectroscopy in the case of three supercapacitors. This circuit is presented in chapter 6 and published in [7].
- Comparative analysis of three types of supercapacitors (5 F/5.4 V, 10 F/2.5 V and 22 F /2.5 V) in terms of capacitance values obtained by calculation using the formula for the slope of the line and the capacitance values obtained by fitting the experimental data using the developed equivalent circuit. The research and the obtained results are presented in Chapter 6 and published in [7].
- The application of the mathematical equations of Kramers-Kronig to experimental data obtained by electrochemical impedance spectroscopy. The method for applying the Kramers-Kronig equations is presented in Chapter 6 and published in [8].
- Presentation of some comparisons between the values calculated using the mathematical equations of Kramers-Kronig and the experimentally obtained data at different temperature values, both negative and positive, for two supercapacitors of 5 F/5.4 V and 22 F /2.5 V respectively. The comparative analysis is presented in Chapter 6 and published in [8].
- The development of a pouch-type cell supercapacitor, using an existing equipment in Romania. The electrolyte used for the development of the supercapacitor is an ionic liquid. The whole process of developing the supercapacitor is presented in chapter 7 of the thesis and published in [17].
- Conducting tests on the pouch-type cell supercapacitor, by gradually increasing the maximum working voltage and charging current up to a maximum voltage of 3 V and a charging current value of 1 mA, respectively. The test procedure for the supercapacitor is presented in Chapter 7 of the thesis and published in [17].

8.3. List of original papers

1. Ionescu, C., Vasile, A., Negroiu, R., *Accurate modeling of supercapacitors for DC operation regime*, **2015 IEEE 21st International Symposium for in Design and Technology in Electronic Packaging (SIITME)**, pp. 303-306, Conference Location: Brașov, Romania, 22-25 Oct. 2015, **DOI:** 10.1109/SIITME.2015.7342344, **WOS:** 000377765500056, ISBN:978-1-5090-0332-7, ISSN: 2641-287X, Publisher: IEEE.
2. Alexandru Vasile, Rodica Negroiu, Niculina Badalan, *Research and development of a system for measuring electrical parameters of EDLC*, **2015 IEEE 21th International Symposium for Design and Technology in Electronic Packaging (SIITME),** Brasov 2015, pp. 353-356, **DOI:** 10.1109/SIITME.2015.7342352, **WOS:**000377765500064, ISBN 978-1-5090-0332-7, Publisher: IEEE.
3. R Negroiu, N Bădălan, Al Vasile, C Marghescu; *A research of the characteristics of materials used in the construction of EDLCs***, 2015 IEEE 21th International Symposium for Design and Technology in Electronic Packaging (SIITME),** Brasov 2015; Date of

Conference:22-25 Oct. 2015; Page(s):95-98; Location :Brasov, Romania, **DOI:** 10.1109/SIITME.2015.7342302, **WOS:**000377765500014, ISBN 978-1-5090-0332-7, Publisher: IEEE.

4. R. Negroiu, P. Svasta, Al. Vasile, C. Ionescu, C. Marghescu, *Comparison between Zubieta Model of Supercapacitors and their Real Behavior*, **2016 IEEE 22nd International Symposium for Design and Technology in Electronic Packaging (SIITME),** 20-23 October, 2016 Băile Felix, Oradea, Romania, **WOS:** 000390557400041, ISBN:978-1-5090-4446-7, Publisher: IEEE.
5. Ciprian Ionescu, Alexandru Vasile, Rodica Negroiu, *Investigations on balancing circuits for supercapacitor modules,* **39th International Spring Seminar on Electronics Technology (ISSE)**, pag. 521-526, May 18-22, 2016, Location: Pilzen Czech Republic, pp. 18-20, ISSN: 1041-1135, **DOI:** 10.1109/ISSE.2016.7563253, **WOS:** 000387089800103.
6. Ciprian Ionescu, Alexandru Vasile, Norocel Codreanu, Rodica Negroiu, *Comparative studies on dimming capabilities of retrofit LED lamps*, **Advanced Topics in Optoelectronics, Microelectronics and Nanotechnologies VIII**, 100102Z (December 14, 2016), **WOS:** 000391359600107, ISBN:978-1-5106-0424-7; 978-1-5106-0425-4.
7. Rodica Negroiu, Paul Svasta, Ciprian Ionescu, Alexandru Vasile, *Investigation of Supercapacitor's Impedance Based on Spectroscopic Measurements*, **1st PCNS Passive Components Networking Symposium**, Page(s): 56-62, 12-15th Sep 2017, Brno, Czech Republic, ISBN: 978-80-905 768-8-9.
8. R Negroiu, C Ionescu, P Svasta, A Vasile, *Influence of temperature on supercapacitors behavior in series/parallel connections,* **2017 IEEE 23rd International Symposium for Design and Technology in Electronic Packaging (SIITME)**, Page(s): 367-370, Location: Constanta, Romania, **WOS:** 000428032300078, **DOI:** 10.1109/SIITME.2017.8259927, ISBN:978-1-5386-1626-0, Publisher: IEEE.
9. IB Brezeanu, PA Paraschivoiu, R Negroiu, LA Chiva, *Applications of Kramers-Kronig relations,* **2017 IEEE 23rd International Symposium for Design and Technology in Electronic Packaging (SIITME)**, Page(s): 82-85, Location: Constanta, Romania, **DOI:** 10.1109/SIITME.2017.8259862, **WOS:** 000428032300013, ISBN:978-1-5386-1626-0, Publisher: IEEE.
10. P Svasta, R Negroiu, Al Vasile, *Supercapacitors — An alternative electrical energy storage device,* **2017 5th International Symposium on Electrical and Electronics Engineering (ISEEE),** Page(s): 1-5, Conference Location: Galati, Romania, **DOI:** 10.1109/ISEEE.2017.8170626, **WOS:** 000428234400002, ISBN: 978-1-5386-2059-5, Publisher: IEEE.
11. R Negroiu, P Svasta, C Pirvu, Al Vasile, C Marghescu, *Electrochemical impedance spectroscopy for different types of supercapacitors*, **2017 40th International Spring Seminar on Electronics Technology (ISSE)**, Page(s): 1-4, May 10-14, 2017, Location: Sofia, Bulgaria, **DOI:** 10.1109/ISSE.2017.8000889, **WOS:** 000426973000012, ISBN:978-1-5386-0582-0, Publisher: IEEE.
12. R Negroiu, P Svasta, Al Vasile, C Ionescu, *Methods for Determining the Leakage Current of Supercapacitors*, **2018 41st International Spring Seminar on Electronics Technology (ISSE)**, Zlatibor, Serbia, 2018, pp. 1-4, May 16-20, 2018, **DOI:** 10.1109/ISSE.2018.8443685, **WOS:** 000449866600059, Electronic ISSN: 2161-2536.
13. A. Vasile, N. Codreanu, M.-O. Dima, C. Ionescu, R. Negroiu, P. Svasta,

M.Pantazica, M.Jurba, *Fast Control System and Algorithms for Stabilizing of Mobile Platforms*, **2018 41st International Spring Seminar on Electronics Technology (ISSE),** Zlatibor, 2018, pp. 1-5, May 16-20, 2018, **DOI:** 10.1109/ISSE.2018.8443669, Electronic ISSN: 2161-2536, **WOS:**000449866600043.

14. Rodica Negroiu, Paul Svasta, Alexandru Vasile, Ciprian Ionescu, Popescu Ileana Iulia, *The Performance of Supercapacitors' Main Parameters According to Topology of the Electrical Circuits in Which They are Used*, **2018 IEEE 24th International Symposium for Design and Technology in Electronic Packaging (SIITME)**, Iași, 2018, pp. 187-190, **DOI:** 10.1109/SIITME.2018.8599214, **WOS:** 000466960400038, ISBN:978-1-7281-7506-5, ISSN: 2641-287X .

15. Irina Bristena Bacis (Vasile); Iulia Ileana Popescu; Rodica Negroiu (Pavel), *Methods of ensuring the quality of intelligent optical fiber telecommunication networks*, **Advanced Topics in Optoelectronics, Microelectronics and Nanotechnologies-ATOM 2018**, Constanța, Vol. SPIE no. 9658, ISBN 9781628413235823, Proc. SPIE 10977, 1097718 (31 December 2018), **DOI:** 10.1117/12.2324874, **WOS**: 000458717900043.

16. MM Chițu, Al Vasile, R Negroiu, *Evaluation of brushless DC motors functionality in automotive electronic systems*, **Advanced Topics in Optoelectronics, Microelectronics and Nanotechnologies-ATOM 2018**, Constanța, Vol. SPIE no. 9658, ISBN 9781628413235823, Proc. SPIE 10977, 1097718 (31 December 2018); **DOI:** 10.1117/12.2325846, **WOS:** 000458717900110.

17. R Negroiu, P Svasta, Al Vasile, C Ionescu, MR Buga, *Realization and Testing of a Supercapacitor, Pouch Type Cell*, **2020 IEEE 26th International Symposium for Design and Technology in Electronic Packaging (SIITME)**, 2020, pp. 71-74, **DOI:** 10.1109/SIITME50350.2020.9292280, **WOS:** 000651085100012, ISBN:978-1-7281-7506-5, ISSN: 2641-287X

18. Alexandru Vasile, Irina Bristena Bacîş, Rodica Cristina Negroiu, *High reliability hybrid power supply systems for PON passive and AON active optical communications networks*, **Advanced Topics in Optoelectronics, Microelectronics and Nanotechnologies X**, 2020, volum 11718, DOI: 10.1117/12.2575685, **WOS:** 000641147900116, ISBN:978-1-5106-4272-0, ISSN: 0277-786X.

19. R. Negroiu, P. Svasta, M. R. Buga, A. Spinu Zaulet, C. Ungureanu, *Realization and Testing of Electrodes for Supercapacitors based on MOFs and Activated Carbon*, **2021 IEEE 27th International Symposium for Design and Technology in Electronic Packaging (SIITME)**, October 27-30, 2021, în curs de indexare.

8.4. Prospects for further development

- Extending the range of the charge/dischharge current to higher values and processing the obtained experimental data to verify that the conclusions of the research carried out in the thesis are respected.
- Tests to measure the stabilization time in the range of 0-30 minutes to determine the time to optimal stabilization.
- Adjustment of the self-discharge of the supercapacitor over time. More specifically, after what period of time from the moment it is left in an open circuit some stabilization occurs (the change in self-discharge over time)

- To investigate the phenomenon of self-discharge in two supercapacitors with aqueous and organic electrolytes and to identify their respective advantages in comparison.
- To investigate Warburg impedance and, related to it, the diffuse layer. How to form it depending on the type of electrolyte used. To find an equivalent circuit as compact and reliable as possible to fit the experimental data obtained by the method of electrochemical impedance spectroscopy.
- To develop a cylindrical supercapacitor whose properties will depend on the materials available at the time.
- Designing supercapacitors with different values of the amount of material deposited on the electrodes and testing them to determine the influence of these amounts on the supercapacitor's performance.
- Producing material for electrodes with varying amounts of black carbon.
- Conducting tests on the pouch-type cell supercapacitor at different temperature values using a climatic chamber.
- Carrying out tests by increasing the values of the maximum charging voltage up to a value of 5 V, provided that the supercapacitor technically supports this.
- Investigations of electrodes made of organic metal frameworks (MOFs) at the Research and Development Institute for Cryogenic and Isotropic Technologies (ICSI) in Râmnicu Vâlcea and the subsequent development of supercapacitors with MOF-based electrodes.

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