National University of Science and Technology Politehnica Bucharest

Doctoral School of Electronics, Telecommunications and Information Technology

CONTRIBUTIONS ON THE CONSTRUCTIVE EFFECT OF SUPERCAPACITOR STRUCTURES ON THEIR ELECTRICAL CHARACTERISTICS

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Chapter 1

Introduction

The evolution in the field of energy storage devices has attracted the attention of many researchers due to their applications, from portable electronic devices to electric vehicles.

The supercapacitor sector, also known as Electrochemical Double Layer Capacitor (EDLC), is an ever-evolving field of research and development with promising prospects in many technological fields. [1]

Through their innovative operating principle and unique features, supercapacitors have become essential components in a variety of applications, from electric vehicles and portable devices to military and space technologies.

This PhD thesis aims to explore this field of supercapacitors, with a focus on developing innovative solutions to improve their performance, as well as developing accurate and efficient measurement methodologies relevant to the industry. In the following, the evolution, operating principles and applications of supercapacitors will be presented in detail, as well as the contribution of this thesis to the development of this ever-expanding field.

1.1. Presentation of the field of the doctoral thesis

Supercapacitors are electronic devices that store and release electricity very quickly and efficiently. They are based on energy storage in the form of charge storage at the interface between a solid electrode and a liquid electrolyte.

An advantage of supercapacitors is that they can store a significant amount of electricity in a small volume, this is due to the electrode envelope, which has a large area in a small volume.

Supercapacitors can discharge and charge very quickly, in seconds or even less, thanks to the charge/discharge process that relies on the migration of ions into the electrode layers. This makes them ideal for applications that require a rapid release of energy, such as accelerating electric vehicles or storing energy in braking energy recovery systems.

1.2. Purpose of the doctoral thesis

An essential part of this research lies in the development and application of original methods for determining capacitance, equivalent resistance and leakage current in supercapacitors. This precise analysis is very important for understanding and optimizing the behavior of these electronic components under various operating conditions, such as extreme temperatures or partial charges/discharges.

Also, the thesis focuses on the manufacture of supercapacitors with improved parameters, developing new recipes for the manufacture of electrodes with increased areas or increased flexibility using unconventional materials for the separator and having parameters that allow a high ionic conductivity inside the component.

1.3. Content of the doctoral thesis

This doctoral thesis is structured in 8 chapters as follows:

• Chapter 1 of the thesis presents the field of the doctoral thesis and its purpose.
• Chapter 2 of the doctoral thesis presents information on the constructive structure of supercapacitors, the electrochemical phenomena underlying the charge-discharge process of these devices, the classification of supercapacitors and the main electrical parameters are explained, as well as a series of physicochemical parameters.
• Chapter 3 performs a comparative analysis of the parameters of three commercial supercapacitors, highlighting the changes in electrical parameters depending on the charge/discharge current, charge/discharge time and operating temperature. These determinations using our own innovative measurement method.
• Chapter 4 focuses on the characterization of the electrical parameters of polydimethylsiloxane polymer-based nanocomposites (PDMS), used as conductive materials with increased flexibility for supercapacitor electrodes.
• Chapter 5 details the development and manufacturing process of supercapacitors that use materials that are non-toxic to the environment and humans, but are at the same time cost-effective, and the characterization of the main electrical parameters of the developed devices.
• Chapter 6 describes in detail the electrode manufacturing process and assembly methods of supercapacitors with working voltages above 3V.
• Chapter 7 provides an exhaustive analysis of the method for developing a supercapacitor with flexible and piezoelectric properties, with a focus on the development of a flexible polyvinylidene fluoride (PVDF) supercapacitor with piezoelectric properties.
• Chapter 8 summarizes the results obtained in the thesis, presents the original contributions resulting from the research and experiments developed during the thesis. Also, in this last chapter is presented the list of works published during the doctoral internship, but also a series of perspectives for further development, topics that represent opportunities for continuity of research until the present moment.

Chapter 2

Supercapacitors. What are they?

2.1. Introduction

Supercapacitors (or ultracapacitors) can store 10–100 times more energy than electrolytic capacitors, and are preferred over batteries due to their fast charging and efficient discharge. They provide rapid power deliveries, allowing high currents at peak power demands and capturing excess energy that would otherwise be lost[9].

2.2. Definition

The structure of a supercapacitor, illustrated in Figure 2.1, shows electrodes with a much larger surface area than that of capacitors, separated by a separator that works in a different way than a conventional dielectric. [11]

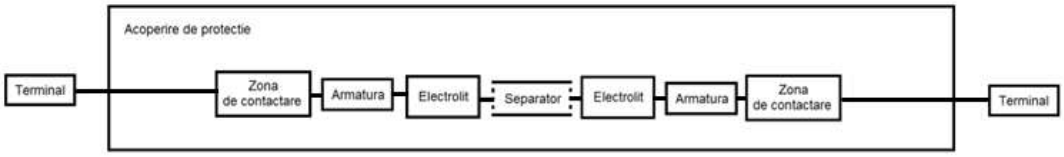

Fig. 2. 1 The constructive structure of a supercapacitor presented by 6 specific zones: 2 terminals, 2 contact zones, 2 armatures, electrolyte, separator and protective coating *[12]*

A supercapacitor has two different metallic conductive surfaces (contact area). They are made of metal which is then coated with an electrically conductive, porous substance such as activated carbon, which effectively gives them a larger area for much greater storage of charges, thus forming the electrode. [1] [13]

2.2.1 Definition and principle of operation

EDLCs (electrochemical double-layer capacitors) use two carbon electrodes, an electrolyte, and a separator. The energy is stored electrostatically, without chemical reactions, by forming a double layer at the electrode-electrolyte interface. The ions gather on the surface of the electrodes, being retained by adsorption, without crossing the electrodes. This non-pharadic storage allows for high reversibility and excellent stability in cycles. Due to their large surface area and small electrode spacing, EDLCs achieve higher energy densities than conventional ones.

2.2.2 The Helmholt model

The Helmholtz layer, named after the German physicist Hermann von Helmholtz, describes the structure of the electric double layer (EDL) at the interface between a conductive electrode and an electrolyte. This layer is what causes supercapacitors, which rely on EDL, to have a high capacitance.

Inner Helmholtz Plane (IHP): This layer is made up of solvent molecules and specifically adsorbed ions that are in direct contact with the surface of the electrode.[3] [4] [21]

Outer Helmholtz Plane (OHP): This layer contains solvated ions that are attracted to the electrode but remain in the electrolyte, separated from the electrode by IHP.[3] [4] [21]

The capacitance arises from the separation of charges in the Helmholtz layer that creates a capacitance similar to that of a conventional capacitor, but with a much smaller separation distance (on the order of nanometers), which leads to a larger capacitance. [3] [4] [21]

2.3. Apps

EDLCs are energy storage devices that are rapidly gaining popularity in the automotive industry. For example, in Tesla vehicles, supercapacitors are used to improve the performance of suspension systems and replace 12V batteries. [23]

In the case of BMW and Toyota, supercapacitors are integrated into braking energy regeneration modules, contributing to the energy efficiency of vehicles. Lamborghini Sián uses supercapacitors to provide a quick boost of power needed when starting and accelerating the vehicle. This innovative hybrid system combines a V12 engine with a supercapacitor, ensuring exceptional performance and high energy efficiency. [24] [10] [25]

2.4. Classification

2.4.1 Electrochemical Double Layer Capacitors (EDLCs)

There are two main types of supercapacitors: electrochemical double-layer capacitors (EDLCs) and pseudocapacitors.

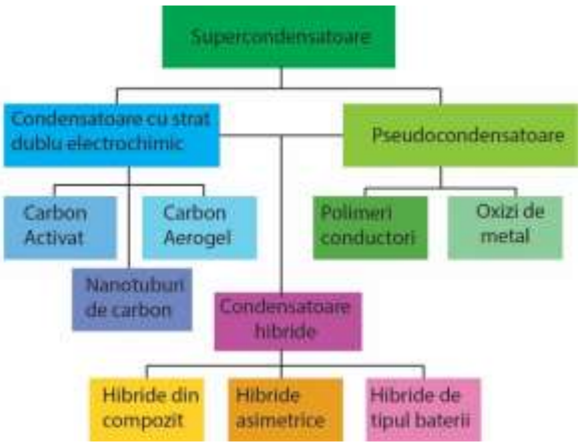

Fig. 2. 2 Classification of Supercapacitors

EDLCs store energy by accumulating ions on the surface of the electrodes. In contrast to EDLCs, which store the electrostatic charge, pseudocapacitors store the pharadic charge by transferring the charge between the electrode and the electrolyte.

2.4.2 Hybrid capacitors

Hybrid capacitors store energy through pharadic processes, achieving higher capacities and energy densities than EDLCs. The electrode materials used include conductive polymers and metal oxides such as RuO_2, MnO_2, nanocomposites with copper or manganese oxides, as well as PVDF and graphene-PTFE composites. These capacitors are classified into three types, depending on the electrode configuration: composite, asymmetrical, and battery type.

2.4.3 Hybrid capacitors

Asymmetric hybrid capacitors combine an EDLC electrode with a pseudocapacitive electrode (e.g. activated carbon and conductive polymer), combining pharadic and non-pharadic processes. Thus, the limits of pseudocapacitive electrodes in terms of stability and voltage are compensated, obtaining higher energy and power densities than in the case of EDLCs. [6] [34]

2.5. Structure of supercapacitors

2.5.1 Electrodes

Carbon electrode materials generally have a larger surface area, lower costs, and more established manufacturing techniques than other materials such as conductive polymers and metal oxides. Different forms of carbon materials that can be used for charge storage in EDLC electrodes are activated carbon, carbon aerogels, and carbon nanotubes. [35] [36]

2.5.2 Electrolyte

Electrolytes, substances with mobile ions, can be liquid or solid and allow electric current to be conducted between electrodes. The performance of EDLCs depends on the type of electrolyte used. Aqueous electrolytes provide low ESR and require smaller pores, but have a limited working voltage due to water electrolysis. In contrast, organic electrolytes (e.g. acetonitrile) allow for higher voltages but impose other design requirements.

2.5.3 Separator

The separator material has the role of preventing short circuit, retaining electrolyte and allowing ion migration during charging and discharging. For optimal performance, the separator must be porous, ensuring efficient electrolyte absorption and ion mobility. Polyolefins, such as polypropylene (PP) and polyethylene (PE), are the most widely used materials. The final performance of the device depends on the properties of the separator, as well as the chosen combination of electrodes and electrolyte. [52]

2.6. Supercapacitor parameters

The most important parameters of a supercapacitor include capacitance (C), equivalent series resistance (ESR), and equivalent parallel resistance (EPR, also called leakage resistance). C is the parameter that decides the capacity of electricity that can be stored in a supercapacitor.

2.6.1 Capacity (C)

Capacity is the ability of a component or circuit to collect and store electrical energy in the form of an electrical charge. The supercapacitor differs from a regular capacitor in that it has a very high capacitance. [27] [54]

2.6.2 Equivalent series resistance (ESR)

ESR, or series equivalent resistance, in a supercapacitor is determined by its chemical composition as well as the constructive structure of the cell. To achieve the lowest ESR, it is necessary to use well-designed chemistry and solid connections at the terminals. Charge-discharge cycles, exposure to high temperatures and low voltages are factors that contribute to the increase in ESR. . [27] [55]

2.6.3 Warburg impedance

Also called the Warburg diffusion element, it is an equivalent electrical circuit component that models the diffusion process in dielectric spectroscopy. This element is named after the German physicist Emil Warburg. In equivalent circuits it is denoted by the following symbol —W— .

Equation (2.9) for the semi-infinite linear diffusion impedance is relatively simple: [56]

$$Z_w = \mathcal{J}\omega^{-1/2} - j\mathcal{J}\omega^{-1/2} \qquad (2.9)$$

Where: Z_w [Ω] is the Warburg impedance, [$\Omega s\mathcal{J}^{-1/2}$] is the Warburg coefficient, ω[s^{-1}] is the radial frequency.

Chapter 3

Innovative Methods for Testing Supercapacitors for the Automotive Industry

3.1. Introduction

Supercapacitors are becoming increasingly popular in modern applications, such as the automotive sector, due to the many advantages they offer. They are often compared to traditional batteries due to their ability to h ACCUMULATO rge/discharge currents, short charging time, and large number of charge/discharge cycles, as shown in Figure 3.1.

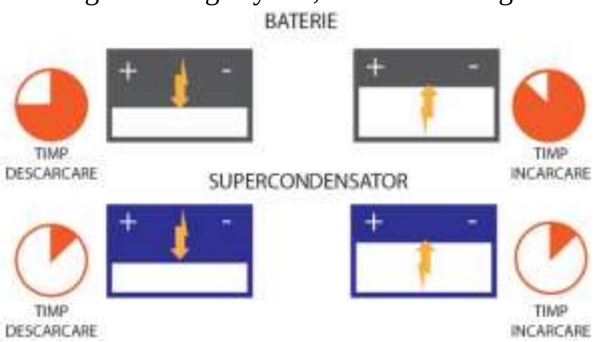

Fig. 3. 1 Comparison of the increased charge/discharge time of a battery compared to the low time for charging/discharging a supercapacitor *[58]*

In contrast to batteries, the disadvantages of EDLC supercapacitors lie in the relatively high values of series equivalent resistance (ESR) and leakage current caused by the self-discharge of supercapacitors.

3.2. Batteries vs. supercapacitors

The main objective of this research was to investigate the electrical performance of three commercial supercapacitors from three different manufacturers in relation to temperature and charge/discharge current, with the aim of advancing the efficiency and reliability of energy storage solutions for the automotive industry.

3.2.1 Difference between batteries and supercapacitors

Supercapacitors have attracted significant attention in the automotive industry due to their ability to store and deliver energy quickly, making them a promising alternative to traditional battery packs. They can provide high power density and long life, making them suitable for applications such as regenerative braking, start-stop systems, and engine starting.

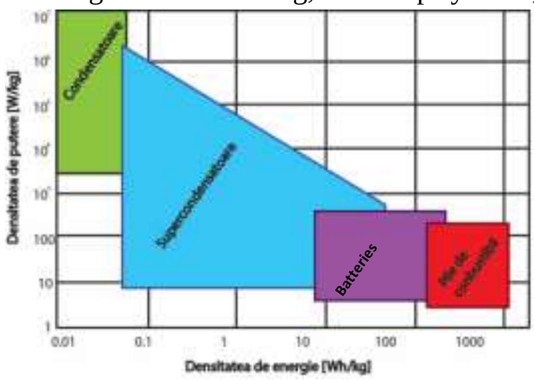

Fig. 3. 2 Classification of energy storage devices according to power density and energy density *[64]*

3.2.2 Advantages and disadvantages of supercapacitors

In recent years, supercapacitors have emerged as promising solutions for energy storage, offering advantages such as high power density, long life, numerous charge/discharge cycles, operation over a wide temperature range, and low maintenance [60]. However, they also have disadvantages: low energy density, voltage drop, high costs and limitations of the working voltage. [60]

3.3. Experimental methods

3.3.1 Test method according to DIN EN 62391-1:2012

To test the supercapacitors, two different test methods were used. For the first method, the supercapacitors were charged using the method of the DIN EN 62391-1:2012 standard of charge-discharge, where they were fully charged and then discharged using the same current. The supercapacitors were maintained at maximum voltage and direct current for 30 minutes after full charge. The second test method is presented in section 3.3.2 .[67]

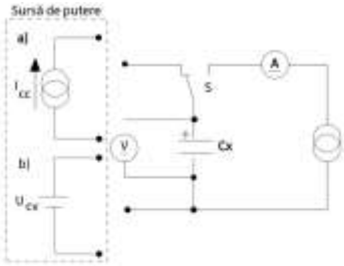

Fig. 3. 3 Diagram for testing supercapacitors according to DIN EN62391-1 standardWhere: Icc – constant current source; Ucv – constant voltage source, V – voltmeter, A – ammeter, DC power supply with adjustable load, Cx – the supercapacitor to be measured [67]

For the calculation of the Series Equivalent Resistance (ESR), the formula mentioned in the standard (3.1) was used: [67] $R_{ESR} = \frac{V_{max} - V_{dis}}{I}$ (3.1)

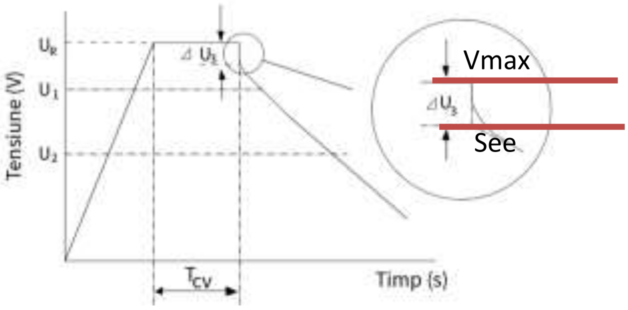

Fig. 3. 4 The characteristic on the basis of which the parameters of a supercapacitor are calculated according to the DIN EN 62391-1 standard, where Vmax is the maximum charging voltage, Vdis is the voltage at the beginning of the discharge process and Tcv is the charging time *[67]*

3.3.2 Test method developed to simulate the automotive environment

An original test method has been developed, adapted to the real conditions of use in a vehicle. The supercapacitors were charged for 5 minutes at 2.7 V DC, using currents of 0.5 A, 0.1 A, and at 60°C — 0.08 A, to determine the capacitance. After charging, they were discharged through a variable load DC source. The test scenario simulates descending a slope with braking for 5 minutes, followed by the transfer of the accumulated energy to the battery. The ESR was determined using formula (3.2), different from the classical standards:[68] [69] [70] $R_{ESR} = \frac{V_{max} - V_{dis}}{2I}$ (3.2)

Where: Vmax is the maximum rated voltage according to Fig.3.4 , Vdis is the value of the voltage after the immediate decrease according to Fig.3.4, I is the charging current.

3.3.3 Experimental setup

To ensure accurate results, an oscilloscope was used to monitor and record the data. The Diligent Analog Discovery 2 digital oscilloscope was used. A direct voltage source was also used for charging and a direct current source with adjustable load for discharging. To set the temperature conditions, a climatic chamber was used. The experimental setup is shown in Figure 3.5.

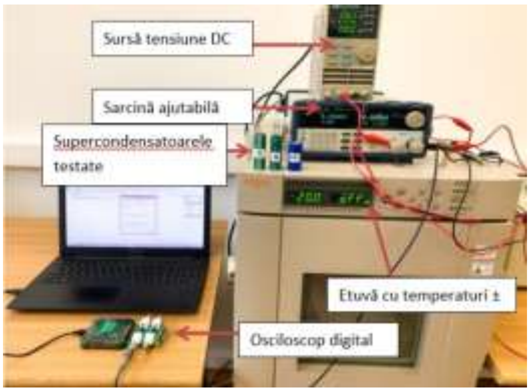

Fig. 3. 5 Configuration of the apparatus for carrying out experiments

3.3.4 Equipment used

DC power supply (IT6720 – Programmable Power Supply).

Direct current source with adjustable load for discharge: "Bk Precision 8600 DC electronic load", through which they could discharge at a constant current.

A "Spec oven" was used. (-20ºC to 60ºC).

nalog Discovery 2 from Digilent. Only the function of Oscilloscope connected via USB was used (a data recording frequency of 2kHz was chosen).

3.3.5 Experimental procedure

For testing, three commercial supercapacitors from three different manufacturers were selected, each with a capacitance of 100 F and a nominal working voltage of 2.7V. The selected supercapacitors were denoted with codes: from A1, E2 and code 3 respectively. The experiments aimed to monitor ESR (equivalent series resistance) and supercapacitor capacitance under three different temperature conditions: ambient temperature (21°C), 60°C and -20°C.

Fig. 3. 6 The 3 commercial supercapacitors from 3 different manufacturers available of 100F and 2.7V: A1, E2, code 3.

For the determination of ESR and verification with the value in the catalog sheet, each supercapacitor was charged up to 2.7V with a constant current of 2A at a temperature of 21°C. [67]

ESR was calculated from the voltage drop, as can be seen in Figure 3.10, using equation 3.1, where I is the charge/discharge current

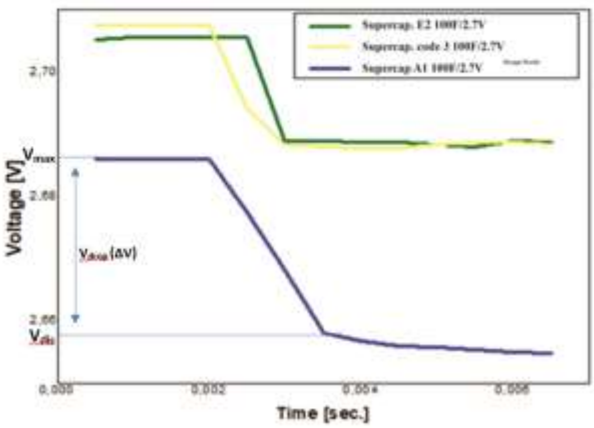

Fig. 3. 7 The discharge characteristics of the three 100F 2.7V supercapacitors. Vmax is the maximum charging voltage, Vdis is the voltage drop at the beginning of EDLC discharge, and Vdrop(ΔV) is the difference between the two.

An original test method was used to mimic the real-world scenario of sudden charging on a running machine.

For the temperature of 60°C it was observed that there was too sudden a voltage drop, which made it impossible to calculate the capacity for a current of 0.5A. Thus, the measurements were redone maintaining a current of 0.1A and 0.08A.

The currents of 0.5A, 0.1A and 0.08A respectively were chosen to make it easier to calculate the 2 parameters, ESR and capacitance.

3.3.6 Presentation of the processing algorithms of the collected data

For data processing, a script was developed using the R programming language and the Rstudio software.

3.4 Results

For the determination of the parameters and their correlation with the catalog sheet, the standardized determination method was used, according to the DIN EN 62391-1:2012 standard. Equation 3.1 was used to determine the ESR. [67]

Manufacturer	Maximum charging voltage V_{max} [V]	Voltage Drop at Discharge V_{Diss} [V]	Current I [A]	ESR=(V_{max} - V_{dis})/I [Ω]	ESR [mΩ]
Code 3	2,708	2,688	2	0,0098	9,8
E2	2,705	2,689	2	0,008	8,2
A1	2,686	2,658	2	0,014	14,0

Table 3. 1 ESR values calculated for the 3 supercapacitors at 21°C

Using the experimental method described in section 3.3.2 simulating the automotive environment, different results were obtained from those in the catalogue sheet.

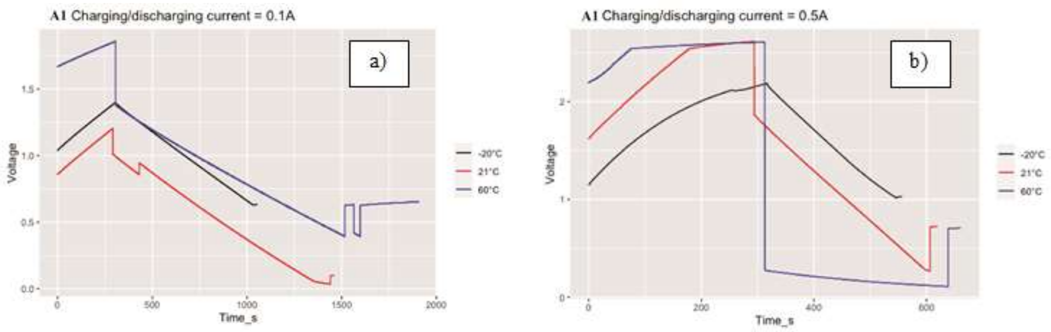

Fig. 3. 8 Characteristics of the A1 commercial supercapacitor in relation to temperature: black -20°C, red 21°C and blue 60°C, at different charge/discharge currents: a) 0.1A and b) 0.5A.

3.4.1 ESR behaviour in relation to temperature changes and the intensity of the charge/discharge current.

The charging current significantly influences the ESR and capacitance of the A1 supercapacitor. As the current increases, the ESR increases and the capacity decreases, according to the values in Table 3. High temperatures accentuate the voltage drop, which leads to an increase in ESR, an effect that is especially noticeable at -20 °C, where the lowest voltage drop is recorded for the currents of 0.1 A and 0.5 A.

Current	0.5 A		
Temperature	-20°C	21°C	60°C
A1	10.5 mΩ	0.48 Ω	2.35 Ω
E2	11 mΩ	0.84 Ω	2.2 Ω
Code 3	12 mΩ	0.87 Ω	2.3 Ω

Table 3. 2a. Variation of the ESR of 3 commercial supercapacitors in relation to the variation of temperature at a current of 0.5A

Current	0.1 A			0.08 A
Temperature	-20°C	21°C	60°C	
A1	17.5 mΩ	0.95 Ω	3.25 Ω	3 Ω
E2	2.3 mΩ	1.05 Ω	3 Ω	3.62 Ω
Code 3	15 mΩ	0.97 Ω	5.5 Ω	3.12 Ω

Table 3. 3b. Variation of the ESR of 3 commercial supercapacitors in relation to the temperature variation at a current of 0.1A/0.08A

As the current decreased, the ESR increased for all three supercapacitors. An increase in ESR was also observed with the increase in temperature.

3.4.2 Capacity Behavior in relation to temperature changes and the intensity of the charge/discharge current.

In conclusion, for supercapacitors A1 and E2, an increase in temperature leads to an increase in capacitance. In contrast, for the code 3 supercapacitor, an increase in temperature leads to a decrease in capacitance.

In addition, with the decrease in charge/discharge current, the capacitance decreased for both E2 and code 3 supercapacitors. On the other hand, for the A1 supercapacitor, with the decrease in the charging current, the capacity increased.

The self-discharge current was determined using the method indicated by Kemet Electronics. The supercapacitor was charged at 2.7V and 1A until the maximum voltage was reached and was maintained at this voltage for 30 minutes. It was then disconnected from the source and the supercapacitor was left in open circuit for 18 hours. After this time, the drop in blood pressure was measured. The self-discharge current was calculated using equation 3.17 :[68][76]

$$I_{sd} = \frac{C[F]*\Delta V[V]}{Timp[s]}[A] \quad (3.17)$$

Where: C represents the supercapacitor capacitance, ΔV represents the difference between the maximum charge voltage and the voltage after 18 hours, Time represents the time of 18h in seconds (64 800s).

The lowest values were obtained at a temperature of -20ºC, and the highest at a temperature of 60ºC. This is also directly correlated with the variation in ESR that was discussed in the previous section, ESR that tends to increase with increasing temperature.

This suggests that the parameters of supercapacitors can vary considerably depending on the working conditions.

3.4.4 Comparative analysis of supercapacitor performance

As observed for the commercial code3 supercapacitor, the capacitance increased with temperature, while the ESR values increased with the increase in temperature. In terms of current, a lower current resulted in a lower capacity.

Similar to the commercial supercapacitor A1, the commercial supercapacitor E2 also exhibits the same phenomenon where an increase in temperature leads to an increase in voltage drop, and the charge/discharge current has a significant impact on it. This leads to an increase in ESR values with increasing temperature and current, and a decrease in capacity

According to performance, the code3 supercapacitor had the lowest self-discharge current, but the E2 supercapacitor had low values very close to those of code3.

In terms of capacitance value, supercapacitor A1 has the highest capacitance at a current of 0.1A, while supercapacitor E2 has the highest capacitance at a current of 0.5A.

Considering the above, we can conclude that the best performing supercapacitor was the E2, with a high capacitance and a low discharge current.

3.5 Conclusions

In conclusion, the experiments carried out demonstrate that the temperature of the environment has a significant impact on the parameters of supercapacitors. The results indicate that with increasing temperature, ESR increases. For the three commercial supercapacitors tested, A1, E2 and code 3, it was observed that both the series equivalent resistance (ESR) and the leakage current increase with temperature

In addition, the capacity of supercapacitors varies with temperature, but the direction of variation depends on the brand. For supercapacitors A1 and E2, the increase in temperature leads to an increase in capacitance, while for the code 3 supercapacitor, the capacitance decreases with the increase in temperature.

The direct impact of charge/discharge current on supercapacitor parameters was also discovered. For supercapacitor A1, a decrease in charge/discharge current leads to an increase in capacitance, while for supercapacitors E2 and code 3, a decrease in charge/discharge current leads to a decrease in capacitance. Also, as the charge/discharge current decreases, the ESR of all three supercapacitors increases. [78, 1]

Chapter 4

Characterization of PDMS-based nanocomposites and conductive nanomaterials for supercapacitors

4.1. Getting Started. Overview.

This chapter aims to explore the development and detailed study of polydimethylsiloxane-based materials (PDMS) and conductive active nanomaterials for supercapacitor electrodes (Figure 4.1).

Fig. 4. 1 PDMS-MWCNTs nanocomposite samples made with different amounts of MWCNTs (4% wt, 7% wt and 10% wt) and Carbon black (5% wt, 7% wt, 10% wt and 10.7% wt).

4.2. Purpose of the research

The objective of this research is to make a positive contribution in improving the electrical conductivity of flexible electrode structures by developing PDMS-based nanocomposite samples using multi-walled carbon nanotubes (MWCNT) and Carbon Black CB as active materials. This study aims to investigate the influence of different concentrations of MWCNT and CB on the electrical properties of nanocomposites.

4.3. Experimental setup

To perform the testing of the nanocomposite samples, two different test methods and devices were used: the HP 4145B semiconductor parameter analyzer and Keithley's Unit of Measurement and Source (SMU) (Sourcemeter 2612B).

4.4. Test Method

To evaluate the strength of the nanocomposite samples, two points at different distances were chosen for measurement. The first point was about 16 mm away from the second point. A second measurement was made between two points at a distance of 4mm. A device with needles placed at equal distances from each other was used for this purpose (Figure 4.4).[84] [85]

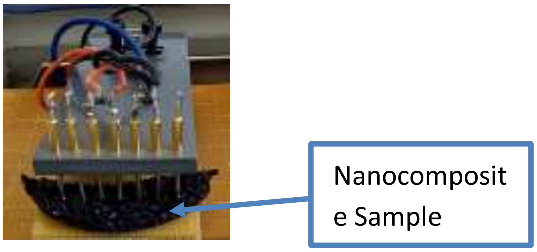

Fig. 4. 2 The measuring device used for measurements.

4.5. Experimental results

Curent / Temperatură	25 °C	50 °C	70 °C	90 °C	110 °C
	Rezistența[Ω]				
0.1mA	280	240	260	460	570
1mA	293	198	269	465	593
10mA	245	206	267	456	555
	ρ [Ω*cm]				
0.1mA	18.110	37.329	38.253	41.865	47.509
1mA	17.725	27.828	36.412	41.853	46.831
10mA	17.657	27.386	35.959	42.600	46.638
	σ [S/cm]				
0.1mA	0.0552	0.0267	0.0261	0.0239	0.0210
1mA	0.0564	0.0359	0.0274	0.0238	0.0213
10mA	0.0566	0.0365	0.0278	0.0235	0.0214

Table 4. 1 Values of Electrical Resistance, Resistivity and Electrical Conductivity for PDMS-Carbon black 10% wt Sample at Different Temperatures

4.6. Conclusions

Based on the analysis of the measured data and the interpretation of the results, it can be concluded that the PDMS sample with CB at 10% by weight showed the most favorable electrical properties among the tested samples. This sample recorded an average resistance of 275 Ω over a distance of 16 mm and an average resistance of 208 Ω over a distance of 4 mm. In addition, the mean values of electrical resistivity and electrical conductivity for this sample were determined to be, respectively, 17.6 Ω*cm2 and 0.056 S/cm2.

In conclusion, the PDMS sample with CB at 10% by weight demonstrated promising electrical properties, while the samples with MWCNTs and CB at 5% by weight did not exhibit the desired conductive behavior. These findings highlight the significant influence of factors such as nanocomposite structure, particle size and surface characteristics of samples on electrical performance. Further research in this direction should focus on optimizing the formulation of the nanocomposite to achieve better conductivity and explore alternative materials to improve the overall performance of nanocomposites in various applications.

Chapter 5

Development of cost-effective and sustainable methods for the manufacture of supercapacitors

5.1. Getting Started.

This chapter aims to investigate the development of new supercapacitors that are not only affordable, but also sustainable. By leveraging advances in materials science, engineering, and manufacturing techniques, this research aims to establish viable pathways to overcome current obstacles and enable the widespread adoption of supercapacitors in various applications.

5.2. Materials used.

5.2.1 Electrolyte

To ensure safety and minimize the risk of injury or contamination associated with organic electrolytes, it was decided to use an aqueous electrolyte. For the preparation of the electrolyte solution, KOH flakes dissolved in water were used. Research has concluded that a concentration of 30% KOH is optimal.

5.2.2 Collector

It was decided to use nickel sheets with a purity of 99.9% as the preferred material for the collector. Despite the slightly higher cost compared to aluminum, the long-term benefits and durability offered by nickel justify its selection. The superior corrosion resistance of nickel in the presence of aggressive salts in the KOH solution ensures the stability and longevity of the collector material.

5.2.3 Electrode

As a binder, a PVA-based adhesive dissolved with water was chosen. Through experimentation, it was determined that a concentration of 15% adhesive would be ideal for fixing activated carbon on the collector surface. For the mixture of activated carbon and PVA, 85% activated carbon was combined with 15% PVA binder. Water was used as a solvent for this mixture.

Fig. 5. 1 The mixture deposited on the Nickel collector.

5.2.4 Separator

Both cellulose and polyethylene are known for their porous nature, which allows for efficient electrical insulation in supercapacitor systems.

The initial material was cut to the size of 4x5 cm to prepare the cellulose separator and the polyethylene separator, providing an additional 1 cm of space compared to the electrode sizes.

5.3. Cell assembly

The electrodes were cut to the size of 3cmx4 cm. Subsequently, the electrodes were weighed, and those with similar weights were grouped in pairs. This led to the formation of two pairs of electrodes: D1 and D2, respectively D3 and D4.

For the first pair, D1 and D2, which exhibited comparable weights, were assembled using three layers of cellulose. The resulting supercapacitor was named M1. As for the second pair, D3 and D4, which also had similar weights, were assembled using four layers of polyethylene. The resulting supercapacitor was named M2.

In both cases, a KOH solution with a concentration of 30% as an electrolyte was used.

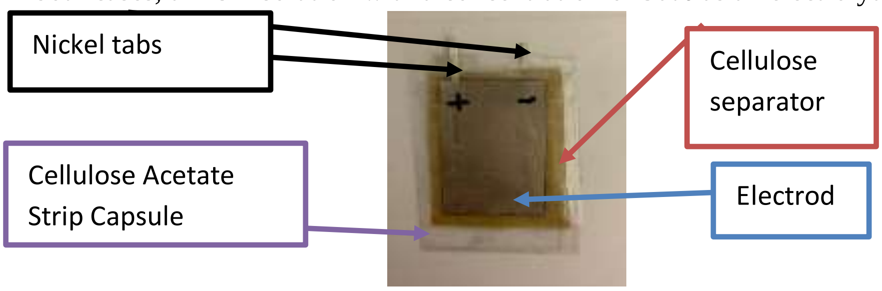

Fig. 5. 2 The M1 supercapacitor assembled in a pouch cell.

5.4. Testing methodology

To evaluate the charge-discharge characteristics of supercapacitors, the charge-discharge method specified in the DIN EN 62391-1:2012 standard was used.[67]

5.5. Experimental results

ESR	Supercapacitor	
	M1	M2
	70 Ω	7 Ω

Table 5. 1 Series equivalent strength calculated for M1 and M2

Ability	Supercapacitor	
	M1	M2
	61.78 F	20.26 F

Table 5. 2 Calculated capacity for M1 and M2

The self-discharge current was determined to be 2,487mA for M2 and 6,178mA for M1.

5.6. Conclusions

Through rigorous testing and data analysis, the performance characteristics of the supercapacitors were determined. For M1, it was found that the ESR is 70Ω, most likely the separator having a great influence on this parameter. However, the M1 showed an impressive capacitance of 61.78F, taking into account the small area of the electrodes, specifically 12cm2.

On the other hand, M2 demonstrated a lower ESR with a value of 7Ω, indicating better performance and stability over time. However, the capacity was significantly lower, at 20.26F, possibly due to the uneven distribution of the carbon pulp.

The capacity obtained per area is 0.35F/cm2 for M1 and 0.377F/cm2 for M2

The self-discharge test revealed that both M1 and M2 exhibit a certain level of self-discharge over a period of 2 hours. M2 demonstrated a self-discharge current of less than 2,487mA compared to M1, which had a self-discharge current of 6,178mA. This indicates that the M2 has better long-term stability, maintaining the charge for a longer period. [92]

The experimental results indicate that the materials, assembly techniques and test procedures chosen have led to promising results.

Chapter 6

Development of supercapacitors with working voltages above 3V

6.1. Introduction

This chapter will focus on the manufacture of supercapacitors with a high working voltage of 3V or higher, and aims to explore innovative materials, electrode types, and manufacturing techniques that allow such components to be realized. By overcoming the conventional voltage limits of commercial supercapacitors, it aims to overcome the limitations associated with energy storage systems and pave the way for compact, high-voltage supercapacitors with improved performance characteristics.

6.2. Materials used

1. Activated Carbon: Activated carbon powder from Sigma Aldrich was used. This activated carbon has a particle size of 100 mesh.
2. Graphene Oxide (GO)
3. Custom Cells Aluminum Foil
4. Fiberglass Separator
5. Electrolyte: In the experiments presented in this chapter, the following were used as electrolytes: 1-ethyl-3-methylimidazolium dicyanamide (from Sigma Aldrich) and LP30 - solution of lithium hexafluorophosphate in ethylene carbonate and dimethyl carbonate, with a concentration of 1.0 M LPF in EC/DMC in a ratio of 50/50.
6. Binder: Poly-vinylidene difluoride (PVDF) [100]

6.3. Manufacture. Assembly

6.3.1 Manufacturing

A solution of 5% PVDF (Polyvinylidene Fluoride) in NMP (N-methyl-2-pyrrolidone) has been prepared. This solution served as a binder for the electrode materials.

For the first variant, a mixture consisting of 70% GO (graphene oxide), 25% AC (activated carbon) and 5% PVDF (by weight) was prepared in the 5% PVDF solution (Fig.6.1.). For the second variant, a mixture consisting of 90% AC and 10% PVDF was prepared.

Using the mixture from the second variant, the electrodes were deposited on custom-cut aluminum foil substrates using a Doctor Blade system. Wet layers with thicknesses of 30 μm and 50 μm were obtained.

6.3.2 Assembly

The assembly of the supercapacitor cells was carried out in a glove-box, with low humidity and low oxygen levels, to prevent oxidation, corrosion and electrolyte-related accidents. An organic electrolyte was used for the assembly process. During assembly, a CR2023 metal cassette was used.

Fig. 6. 1 The Glove-Box inside which the cells were safely assembled

6.4. Experimental results

6.4.1 Impedance Testing

The first test performed was impedance testing, performed using the Solatron analytical test system. For this test, the Nyquist diagram was used, which allowed us to analyze the impedance behavior of supercapacitor cells. The frequency range for the test was set from 10mHz to 100kHz.

Fig. 6. 2 The cells made were carefully labeled in zip-lock bags

6.4.2 Loading-discharging tests

After impedance testing, the charge-discharge tests were performed using an automated software-controlled system (Fig.6.15). The purpose of this test was to evaluate the cells' ability to charge and discharge and determine if they can reach the desired voltage of 3V.

Charge-discharge cycle	Parameters	Supercapacitor For a voltage of 3.6V and a current of 0.01mA		Supercapacitor For a voltage of 4.5V and a current of 0.01mA	
		R2HV1	R2HV2		
Cycle 1	ESR(ohms)	56.4	59.6	54.2	62.6
	C(mF)	407	392	521	590
Cycle 2	ESR(ohms)	59.5	65.8	54.2	65.7
	C(mF)	401	401	526	595
Cycle 3	ESR(ohms)	60.1	70.4	59.5	69.7

	C(mF)	407	407	525	597
Cycle 4	ESR(ohms)	62	70.7	60.4	73.2
	C(mF)	408	415	529	596
Cycle 5	ESR(ohms)	61.7	70.4	62	76.9
	C(mF)	409	420	532	592

Table 6. 1 Series equivalent capacitance and resistance for the 4 supercapacitors in 5 charge-discharge cycles up to 3.6V and 4.5V respectively using a current of 0.01mA

6.5. Conclusions

The results obtained represent a significant milestone in the research, as achieving a working voltage of 3.6V and 4.5V respectively is important in overcoming the limitations of commercial supercapacitors, which typically have a maximum operating voltage of 2.7V. Reaching these higher tensions opens up possibilities

Chapter 7

Development of a Flexible-Piezoelectric Supercapacitor

7.1. Introduction

This chapter aimed to explore the integration of piezoelectric elements into flexible supercapacitors, allowing energy to be harvested from mechanical deformations such as bending. The initial idea focuses on using a PVDF (polyvinylidene fluoride) membrane as a separator within the supercapacitor structure. This membrane possesses the necessary properties of porosity to facilitate the passage of ions, electrical insulation, high flexibility and a significant generative piezoelectric effect in case of deformations (see Figure 4.1).[102][106][107]

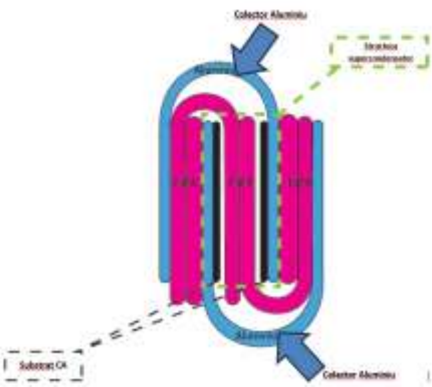

Fig. 7. 1 The structure of a piezoelectric supercapacitor using PVDF membranes. The piezoelectric harvesting effect will occur both inside the supercapacitor structure, at the separator level, and outside the structure, at the collector level.

7.2. Manufacture. Assembly

7.2.1 Manufacturing

A mixture with a concentration of 10% PVDF in NMP solution was prepared. Three membranes, respectively P11 (8.15 g), P12 (10.7 g) and P13 (14.6 g), were deposited in Petri dishes. These membranes were left to dry in the niche for 21.5 hours, then transferred to the vacuum-free oven. P11 and P12 showed signs of dryness, but after a month, only P11 dried completely.

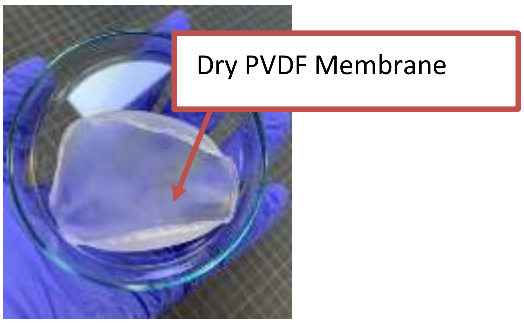

Fig. 7. 2 Completely dried PVDF P11 membrane

7.2.2 Assembly

For the assembly of the supercapacitor structures, the P11 membrane was used, which dried successfully. The membrane was cut larger than the size of the electrodes. The electrodes presented in the previous chapter, composed of 90% activated carbon and 10% PVDF, with a thickness of 30 µm on aluminum foil, were used. The electrodes were cut to the size of 4.5 x 2.5 cm. [111] [112]

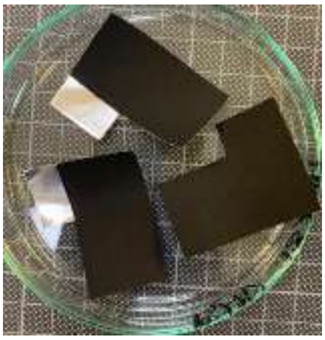

Fig. 7. 3 90% Activated Carbon and 10% PVDF electrodes deposited on aluminum manifold, cut to size 4.5x2.5 cm (11.25 cm^2)

To ensure the integrity and quality of the supercapacitor structures, the assembly was done in the Glove-Box.

A smaller cell, MP2, measuring 2x2.5cm (5cm2) was also fabricated using the same process described above.

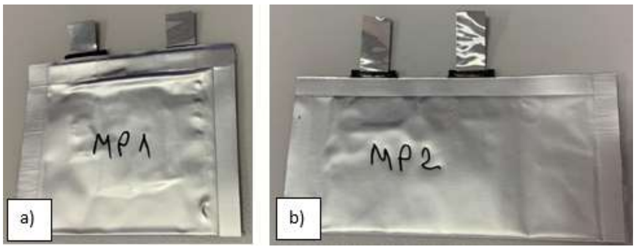

Fig. 7. 4 Supercapacitor cells a) MP1 and b) MP2 completely vacuumed and sealed

7.3. Experimental methods

In this section, the test methods used to evaluate the performance and characteristics of manufactured supercapacitor cells will be presented. The same test procedures described in Chapter 6.4 were used to ensure consistency and comparability of results.

7.4. Experimental results

After processing and analyzing the data, it was observed that the ESR (Equivalent Resistance in Series) values as well as the capacitance do not have favorable values, as can be seen in Table 7.1.

Supercapacitor	ESR	Capacity
MP1	196,37 Ω	0.2108 F
MP2	0,9 Ω	0.093 F

Table 7.1. Calculated values for the ESR and Capacitance values for the 2 assembled supercapacitors, MP1 and MP2

7.5. Conclusions

The experimental results obtained from the analysis of the fabricated supercapacitor cells revealed the limitations imposed by the PVDF membrane chosen as a separator. The insufficient porosity of the membrane prevented the formation of the conventional supercapacitor structure, leading to high values of Equivalent Series Resistance (ESR) and resulting in reduced capacitance values.

To overcome this limitation and achieve the desired performance of supercapacitors, future research will focus on replacing the current PVDF separator with an industrially manufactured alternative, a PVDF separator manufactured by electrospinning having controlled pore size.

Chapter 8

Conclusions

The experiments carried out demonstrated a significant impact of temperature on the parameters of supercapacitors. The changes in ESR and capacity observed in commercial variants underline the need for increased attention to the variability of parameters under real operating conditions.

Two supercapacitors with impressive capabilities have also been developed using exclusively environmentally friendly materials. The conclusions on PDMS-based nanocomposites showed that a sample with CB at 10% by weight showed the most favorable electrical properties. This represents a significant achievement for the development of flexible electrodes in supercapacitor structures, with the potential for impact in portable and flexible applications.

The successful development of operational supercapacitors at 3V voltages is an important step in overcoming the limitations imposed by commercial variants. Even though ESR and capacitance showed significant differences between the variants, these results open new horizons for the use of supercapacitors in applications requiring higher voltages.

Research in the field of flexible piezoelectric supercapacitors has revealed the current limitations of the PVDF membrane used as a separator, identifying the need to explore industrial alternatives to improve the behavior and performance of these supercapacitors.

8.1. Results obtained

In chapter 2, an introduction to supercapacitor technology was made, analyzing the necessary properties of the materials intended for their construction through the detailed study of the literature. Electrolyte types, electrode structure and requirements for an efficient separator were investigated, and the essential parameters of supercapacitors, such as capacitance, series equivalent resistance and Warburg impedance, were explained in detail.

In Chapter 3, tests were carried out on three commercial supercapacitors with identical catalog parameters, purchased from different suppliers. The test was carried out in a range of extended temperatures (-20°C–60°C), according to the catalog specifications, and, by means of a method developed by me, the ESR parameters and capacity were determined at various temperatures and at different current levels. The concluding observations revealed significant variations in the parameters depending on the temperature and current used, also highlighting the direction of variation between them, depending on the manufacturer.

In Chapter 4, several PDMS-based nanocomposite samples were characterized, with the aim of later using them as flexible electrodes in supercapacitor structures. The analysis included determining the strength and conductivity of the samples. The results showed that the samples based on MWCNT and CB showed low conductivity values, associated with the formation of agglomerates in the structure of the nanocomposite, with a negative impact on the conductive properties. The interpretation of the data led to the conclusion that the PDMS sample with 10% CB showed the most favorable electrical properties among the tested samples.

In chapter 5, the development of cost-effective and sustainable methods for the manufacture of supercapacitors was investigated, building two experimental supercapacitors using affordable and environmentally friendly materials. The impressive parameters, with a capacitance of 61F and 20F in an area of 12cm2, were achieved by using materials such as aqueous KOH electrolyte, nickel collectors, PVA binder and activated carbon. However, further improvements are needed to optimise the value of the ESR.

In chapter 6, a series of CR2023 coin supercapacitors with an operating voltage of 3 V were developed using ionic liquid electrolytes. Of course, reaching this voltage is a significant advance, but key parameters such as ESR have suffered because of the materials chosen. The results provide valuable insights for overcoming the limits of commercial supercapacitors in higher voltage applications.

In Chapter 7, the development of a flexible piezoelectric supercapacitor was explored, in which the piezoelectric element simultaneously fulfilled the role of separator. The process of creating the cells took place in the laboratory, including the development of a PVDF membrane. Following the processing and analysis of the data obtained, it was found that the values of the equivalent resistance in series (ESR) are very high and the values of the capacitance are reduced.

This increased ESR value posed a significant challenge in accurately assessing the capacity of supercapacitor cells. A possible cause of this limitation lies in the characteristics of the PVDF membrane used as a separator in the supercapacitor structure. As a result, the exact determination of cell capacity has become difficult due to the predominance of high ESR values.

8.2. Original contributions

[3.1.9] Development of an original method for testing and determining the parameters of supercapacitors.

[3.2.9] Identification of the real values of commercial supercapacitors under simulating conditions of the real environment, where extreme temperature variations can considerably influence the parameters compared to the catalog specifications.

[4.1.8] Evaluation of the parameters of the PDMS samples and identification of the most suitable configuration as a flexible collector for supercapacitor structures.

[4.2] Creation and testing of two innovative supercapacitor recipes, supercapacitors that have outstanding capacitance values in a small area.

[4.3.7] Development and testing of supercapacitors with working voltages of 3V, representing a significant advance in overcoming the limitations of common commercial supercapacitors.

[4.4] Innovation in the field of flexible piezoelectric supercapacitors, including the development of two distinct concepts for piezoelectric supercapacitors, opening up new perspectives in wearable devices.

[7.1] Development of concept models for the structure of flexible piezoelectric supercapacitors (Fig.7.1 and Fig.7.2).

8.3. List of original works

This list includes only the published/communicated works for which the doctoral student is an author or co-author. To these are added the research reports from the doctoral program and the contracts on which the doctoral student has worked. All these works can also be found in the Bibliography. All the mentioned works must have a content related to the topic of the doctoral thesis.

1. First Scientific Research Report
2. Scientific Research Report II
3. Scientific Research Report III
4. Scientific Research Report IV
5. Rodica Negroiu;Paul Svasta;Irina Madalina Burcea;Cosmin Ungureanu;Mihaela-Ramona Buga, "Investigations on experimental data obtained by Electrochemical Impedance Spectroscopy on Supercapacitors Structures", September 2022, DOI:10.1109/ESTC55720.2022.9939414, Conference: 2022 IEEE 9th Electronics System-Integration Technology Conference (ESTC)
6. Rodica Negroiu; Paul Svasta; Irina Madalina Burcea; Cosmin Ungureanu; Mihaela-Ramona Buga, "Investigations regarding the increase of the nominal voltage of the supercapacitors", October 2022, DOI: 10.1109/SIITME56728.2022.9988309, Conference: 2022 IEEE 28th International Symposium for Design and Technology in Electronic Packaging (SIITME)
7. Rodica-Cristina NEGROIU, Cristina-Ioana MARGHESCU, RamonaMihaela BUGA, Cosmin UNGUREANU, Irina-Bristena BACIS, Madaliana-Irina BURCEA, Vasile Madalin MOISE, "High-voltage supercapacitors, a viable alternative to conventional electrical energy storage devices", January 2023, DOI 10.37410/EMERG.2023.2.05
8. Irina Madalina Burcea; Rodica Negroiu; Attila Bonyár; Róbert Huszánk; Ciprian Ionescu; Cristina Marghescu, Paul Svasta , "Comparison of Nanocomposites based on PDMS and Conductive Nanomaterials for the realization of Supercapacitors", May 2023, DOI: 10.1109/ISSE57496.2023.10168474, Conference: 2023 46th International Spring Seminar on Electronics Technology (ISSE)
9. Irina Madalina Burcea; Paul Svasta; Rodica Negroiu , "The Influence of the Equivalent Series Resistance (ESR) on the Functional Behaviour of Electrochemical Double Layer Capacitors (EDLCs)", May 2023, DOI: 10.1109/ISSE57496.2023.10168419, Conference: 2023 46th International Spring Seminar on Electronics Technology (ISSE)
10. Irina Madalina Burcea, Rodica Negroiu, Paul Svasta, "Development of Cost Effective and Environmentally Friendly Supercapacitors", 2023 IEEE 29th International Symposium for Design and Technology in Electronic Packaging (SIITME), Craiova, Romania, 2023, pp. 142-146, doi: 10.1109/SIITME59799.2023.10431223.
11. Rodica Negroiu, Irina Madalina Burcea, Paul Svasta, C. Marghescu, M.R. Buga, A. Spanu Zaulet, C. Ungureanu, "Comparison between the electrical parameters of high voltage supercapacitor cells", 2023 IEEE 29th International Symposium for Design and Technology in Electronic Packaging (SIITME), Craiova, Romania, 2023, pp. 277-280, doi: 10.1109/SIITME59799.2023.10431353
12. RĂDULESCU, Ion Răzvan; PERDUM, Elena; LUPESCU, Caesar; DINCĂ, Laurențiu; VISILEANU, Emilia; BACIS, Irina; NEGROIU, Rodica; BURCEA, Irina Madalina; SVASTA, Paul, "SYNTHESIS OF GRAPHENE OXIDE ON COTTON FABRIC FOR MANUFACTURING FLEXIBLE SUPERCAPACITOR ELECTRODE.", EMERG: Energy. Environment. Efficiency. Resources. Globalization, 2023, Vol 9, Issue 4, p92, ISSN 2457-5011
13. Irina Madalina Burcea, Rodica Cristina Negroiu, Bogdan Mihailescu, Paul Svasta, Madalin Vasile Moise, Cristina Marghescu, "Reliable Fabrication Methodology for Consistent Supercapacitor Performance", 2024 IEEE 10th Electronics System-Integration Technology Conference (ESTC), Berlin, Germany, 2024, pp. 1-5, doi: 10.1109/ESTC60143.2024.10712106.

14. Burcea Irina Madalina; Rodica Negroiu; Paul Svasta; Adnana Zaulet; Mihaela Buga; Cosmin Ungureanu; "Synthesis, Characterization, and Application of PVDF thin film separator for supercapacitors", Confference: 48th International Spring Seminar on Electronics Technology, 2025

8.4. Prospects for further development

Within this thesis, multiple research directions have been identified, opening broad perspectives for further development.

First of all, an important direction would be the exploration and implementation of innovative methods for the efficient determination of supercapacitor parameters, adapted to the various requirements of different industries.

Also, another important objective of the research is the development of supercapacitors with working voltages greater than 3V, with the aim of simultaneously achieving a low ESR and a promising capacity. This approach would lead to a significant improvement in current performance, with the potential to revolutionise technological applications.

Another research area of great interest is the development of supercapacitors with outstanding capacitance in a small volume, in parallel with the improvement of ESR parameters. This approach focuses on optimizing space and efficiency, providing innovative solutions for space-constrained applications.

Finally, an exciting research goal is to create a flexible piezoelectric supercapacitor that meets criteria such as low internal resistance and adequate capacities, thus facilitating its integration into the circuits of wearable devices. This direction could lead to the development of advanced and adaptable technologies, with significant implications in the field of wearable devices.