Department of Energy, Systems, Territory and Construction Engineering

Master Degree in Electrical Engineering

Construction of a setup for the evaluation of non-linear behavior in supercapacitors

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Abstract

In this thesis work we will build a setup to characterize the dynamic behaviors in the supercapacitors and in particular we will set these objectives;

- Build a voltage / current converter that allows us to obtain high currents, starting from low voltages; this device must allow the current driving of any type of load;
- Characterize this device in terms of noise and distortion in order to give indications on the goodness of the measures
- Design of a program in Labview that allows to send voltage signals to the designed current voltage converter and that allows me to process the measurements acquired by DAQ board.
- Characterize the supercapacitors by evaluating their dynamic behaviors and understanding the type of response of these devices when they work at the limits of their field of application.

Chapter 1 – Introduction to supercapacitors

The main goal of this chapter is to explain, starting from the simple capacitor, the working principle of the supercapacitor and in particular the so-called ECDL, or the double layer supercapacitors which represent, at the moment, the most used technology.

We will illustrate how these objects are characterized at a mathematical level so as to understand why these objects behave in very different ways depending on the frequencies that urge them and, finally, we will briefly illustrate the future developments of this technology.

1.1 Capacitors structure

The idea of the supercapacitor was born in 1957 in the laboratories of General Electrics which, did not give much weight to the possibility of obtaining high capacity by exploiting the porous carbon structure and, for this reason, the project fell into oblivion.

It was in 1966 that, during some studies on fuel cells, Standard Oil discovered this phenomenon again and patented it without succeeding in getting the desired benefits; for this reason the patent was sold to NEC in 1978.

From here on, the history of the supercapacitor, also thanks to the development of electronics and new studies on materials, began to evolve rapidly and, in the nineties, began to find an increasingly important use in industrial applications up to nowadays here this technology has a massive use in the field of automotive, railway systems and wind turbines.

This success is largely due to the characteristics of the supercapacitors, which offer the possibility to store large amounts of charge and to offer an unmatchable specific power for any other component on the market.

1.1.1 Working principle

We can define the capacitors as electrical components that store energy in the form of an electrostatic field by accumulating electric charge.

Their physical principle is based on the presence of two charges of opposite sign between two plates, called capacitor armatures, separated by a dielectric material, or a material that is polarized by the electric field.

The presence of the two charges determines an electrostatic field on the dielectric and consequently a potential difference between the armatures. The capacity C, in Farad [F], is described by the formula:

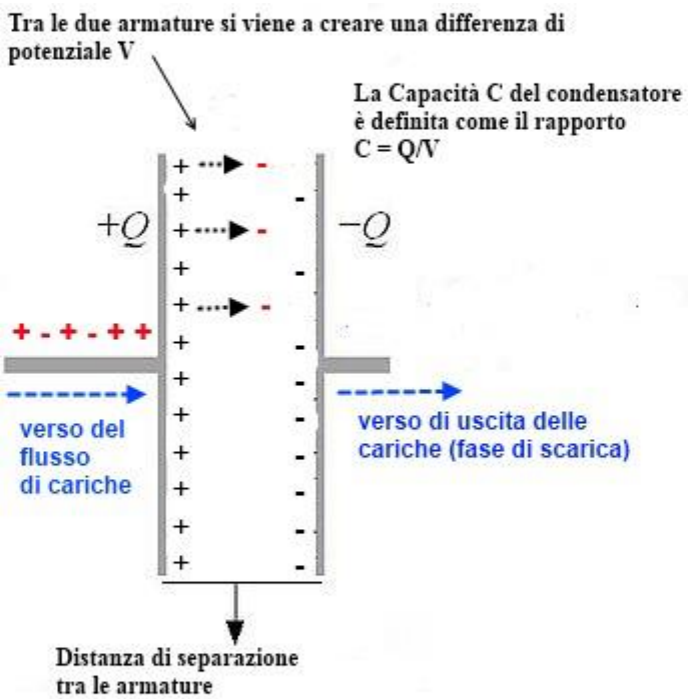


Figure 1: owrking principle of capacitor

$$C = \frac{Q}{V}$$

Where Q is the charge accumulated between the capacitor armatures and V is the potential difference created between the two armatures.

In this formula the most important parameter is given by the capacity because it can be increased or decreased simply by varying the geometric shape.

As you can guess from the picture on the side the capacity depends on the amount of charge that accumulates on the surfaces of the armor and, going to work right on the area of the armor, you can modify this parameter consistently. Let's see this thing by quickly comparing the most common structures that are flat and cylindrical:

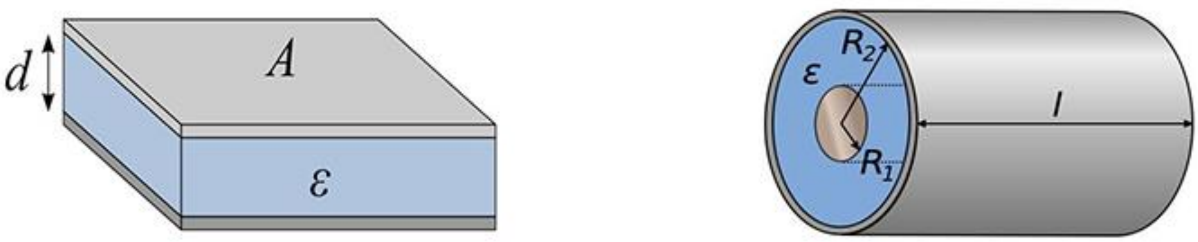


Figure 2: capacitors structures:

$$C = \mathcal{E}_0 \mathcal{E}_r \frac{A}{d}$$

$$C = 2\pi \mathcal{E}_0 \mathcal{E}_r \frac{l}{\ln\frac{R_2}{R_1}}$$

Looking at these two formulas we can understand how it is possible to increase the capacity simply by reducing the distance between the armatures, in both cases; however this simple constructive attention involve many technologic problems.

Starting from this principle, however, and taking advantage of constructive solutions and special materials, the contact area can be increased dramatically: the supercapacitors are born !

1.1.2 Electric double layer

The electrical double layer is a structure that originates from a solid-liquid interface on which an electric charge transfer is established and refers to two parallel layers of charge surrounding the object; the first layer, called surface layer, consists of ions adsorbed on the object thanks to electrochemical actions, while the second layer consists of ions attracted to the surface by exploiting the physical phenomenon described by the Coulomb law.

The second layer, being composed of free ions and not yet solidly anchored to the solid surface, is also called diffuse layer.

In an electrochemical cell the solid phase is represented by the electrode and the liquid phase by an electrolyte solution.

The electric double layer model evolved over the years in order to describe better what happens at the interface. Let's see the most important models:

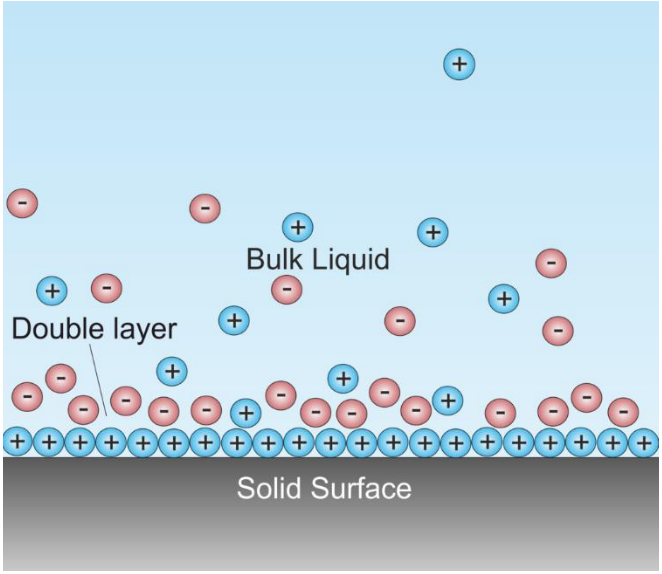


Figure 3: solid-liquid interface in an electric double layer

Helmotz model

Around 1875 he was the first to model the phenomenon of the distribution of charges at the interface and, based on electrocapillarity measurements, he assumed that the charges on the surface attract an equal number of equal charges which is distributed at a fixed distance from them like on the surface of a capacitor; according to this model, the interface behaves like a constant capacitor.

Gouy – Chapman model

In 1910 Gouy and Chapman, through more accurate measurements, understood that the constant capacity model could no longer be acceptable and therefore, assuming the ions as point charges that are distributed in the solution following the Boltzmann statistics, concluded that the charge profile it is not generally concentrated at a fixed distance but gradually spreads in the solution giving rise to a diffused layer; in addition to this they also concluded that the amount of charge that accumulates at a fixed distance from the interface is proportional to the potential difference applied.

Stern model

In 1924 Stern proposed a synthesis of the two previous models eliminating the hypothesis of thinking charges like points because that implied the possibility of having a very high number of ions at the interface and made the modeling of the phenomenon unreal.

To overcome this gap Stern predicted that the ions could not approach the surface beyond a certain distance, called precisely critical distance and delimiting what was then called the exclusion layer; beyond this layer he represented a second layer that have a linear decay, as was the case in Helmholtz's model, followed by an exponential decay, as was the case in the Gouy-Chapman model.

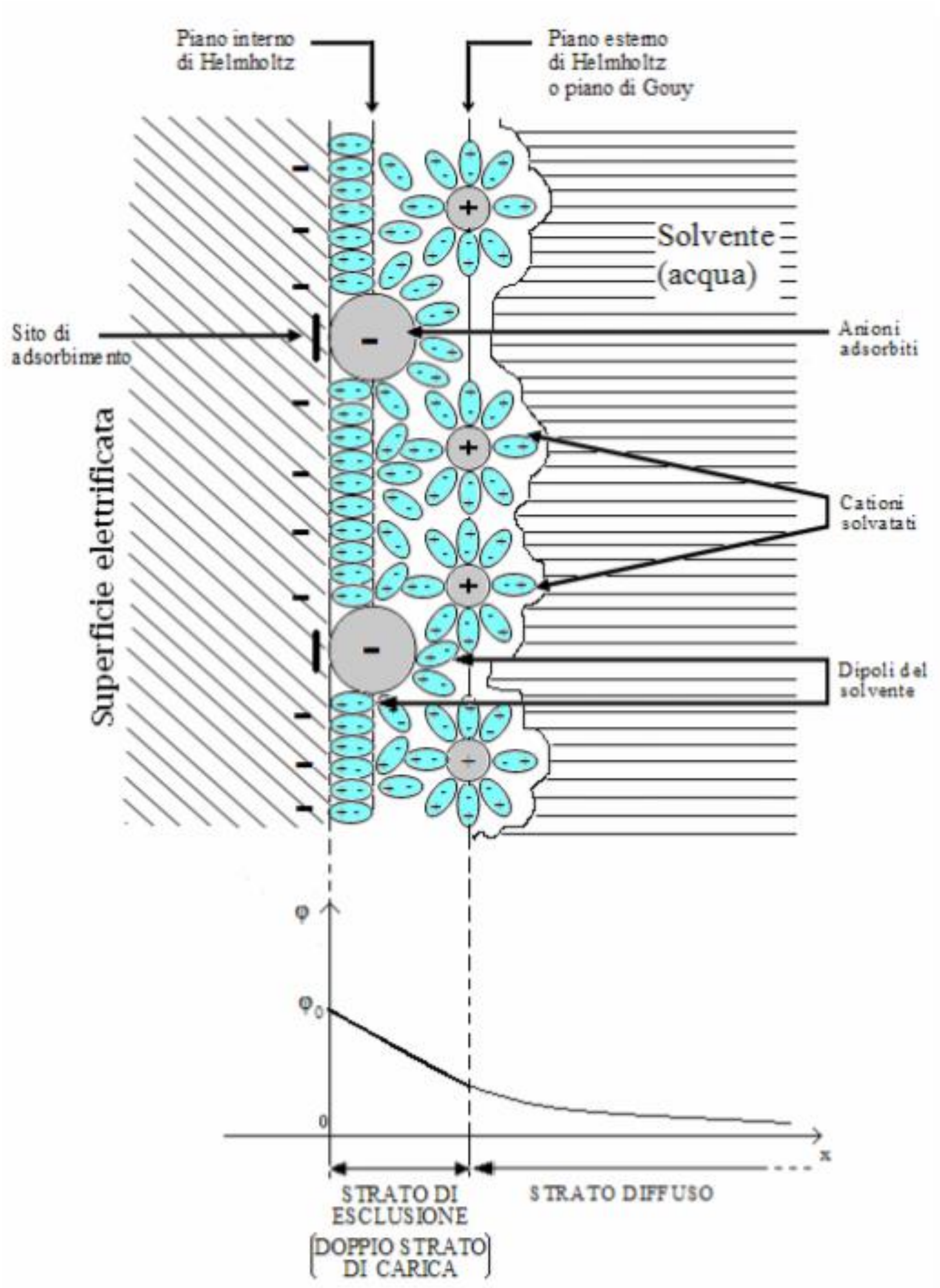


Figure 4: Stern model

The transfer of charges between the electrode and the electrolyte ions takes place in the cathode as semireation of reduction of ions, while in the anode occurs an oxidation.

1.1.3 Supercapacitor structure

The supercapacitors are composed of two electrodes, usually in aluminum, coated with active carbon or carbon nanotubes that have the important characteristic of having a surface area up to 2000 $\frac{m^2}{g}$, a separator whose purpose is to direct the flow of ions, and an electrolyte.
The operating principle on which they are based is that of the double electrical layer

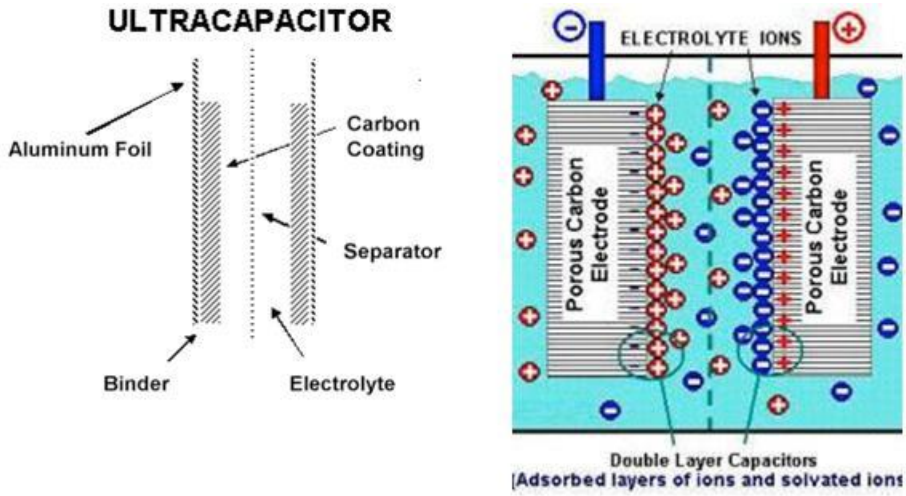


Figure 5: Supercapactirors structure

Let’s see these three components in detail:

The Electrodes

The electrode, and in particular its coating, is the crucial component of the supercapacitor, because it usually determines the extent of the area on which the charges will accumulate. The most used materials are carbon nanotubes and carbon aerogels; For the sake of completeness, it is fair to say that for several years research has been carried out to develop graphene electrodes that should guarantee the possibility of storing much higher quantities of energy, but, at least until today, this technology is not yet consolidated.

In this paper we will analyze the two most widespread and already mentioned types:

- **Carbon nanotubes electrodes:** The nanotube structures are obtained by melting two graphite electrodes from which the impurities are eliminated through chemical processes; the electrodes obtained in this way have, in addition to a high contact surface, also a low resistance which, consequently, allows to obtain a high electrical conductivity.

The carbon nanotube has a flat surface composed of micro-aggregates of hexagonal-shaped atoms that wraps itself by relaxation, forming cylindrical surfaces with a diameter of the order of 2.2 nm and much longer length.
It is possible to obtain different structures according to the orientation of the hexagons on the cylindrical surface; SWNT (Single Wall NanoTube) nanotubes that have the simple cylinder shape or MWNT (Multi Wall NanoTube), or more concentric cylinders, 0.34 nm apart, forming a single nanotube.
Usually three types of nanotubes are distinguished for the arrangement of the rolling direction of the hexagonal structure: Armchair, Zig-Zag and chiral.

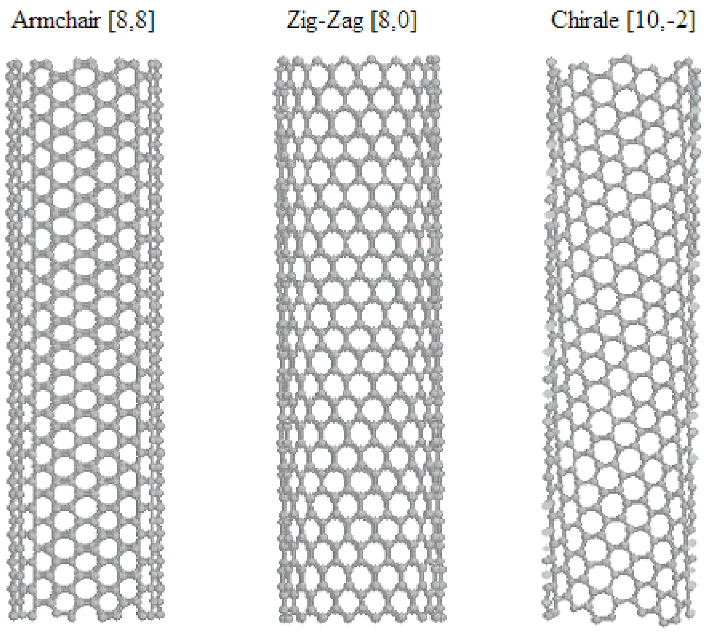


Figure 6: nanotube structures

Depending on the type of hexagonal structure the characteristics of electrical conductivity vary and, speaking specifically of the supercapacitors, the armchair structure is used because it is the only one that ensures a perfect conduction of the current thanks to its very high capillarity.

- **Aerogel carbon electrodes:** Aerogel is a gel-like mixture consisting of a solid-state substance and a gas, whereby the liquid component is replaced with gas. The result is a solid foam with many particular properties.

  The most common types of aerogel are those made of silica and carbon; silica aerogels are mainly used as an insulator because it is the field of application in which they have the best results, while carbon aerogels, having a high surface area and an equally high porosity are used as electrodes in the supercapacitors.

  In addition to the properties already mentioned, another important property of the carbon aerogels is their incredible lightness, which is then reflected in the creation of components that exploit this property, leading to a very versatile components; just think of the field of supercapacitors in which very often there are stock of hundreds of supercapactiors connected together, if they were not built with this foam, this would represent an important problem also from the point of view of the location due to the important weight that they would have to have.

Electrolytes

The choice of the electrolytic solution in a supercapacitor depends very much on the choice of the electrodes and vice versa; the limit cell voltage depends on the electrolytic dissociation voltage and the energy density, also related to the maximum applicable voltage, depends precisely on the nature of the electrolyte.

Finally, the electrolyte conductivity also influences the resistance of the supercapacitor to the current circulation and therefore also influences its power density.

Mainly two types of electrolyte are used for an electrostatic condenser:

- **Aqueous Electrolytes:** they limit the operating voltage of the cells to about 1 V, reducing the possibility of energy accumulation respect to organic electrolytes.

  They have the advantage of having greater electrical conductivity than organic electrolytes and being cheaper and easier to produce.

- **Organic Electrolytes:** they are the most adopted in commercial applications due to their higher dissociation voltage, higher than 2 V. The operating cell voltage is typically 2.7 V and is limited by the water content in the electrolyte.

  Some manufacturers have planned to increase the operating voltage up to 3.2 V, with particular low-water electrolytes and by coating the carbon electrodes with protective layers to reduce their corrosion.

  The only real disadvantage of organic electrolytes is to present a rather low electrical conductivity; this fact affects the equivalent resistance and decreases the maximum available power. It must be said, however, that this power reduction is completely compensated by the higher voltage that can be applied.

  The most used organic electrolytes are propylene carbonate and acetonitrile, to which tetraeliammonio salts are added, which then characterize the cell voltage. In the table below you can see how different types of salts affect the cell voltage:

Sali di tetraetilammonio	Range di tensione [V]	Concentrazione [M]
Et_4NBF_4	2.3 ÷-2.7	1.69
$Et_4NCF_3SO_3$	3.0÷-2.5	1.49
Et_4NCIO_4	-2.8	1.13
n-$Pr_4NCF_3SO_3$	3.0÷-3.4	2.5
n-Bu_4NCIO_4	1.5÷-2.77	2.05
n-Bu_4NBF_4	2.3÷-2.74	2.21
n-Bu_4NBr	-2.76	1.99

Figure 7: tetraeliammonium salt properties

The different electrical characteristics make the organic electrolyte more suitable for energy storage, while the aqueous one is more suitable for high powers, as can be seen from the Ragone diagram below:

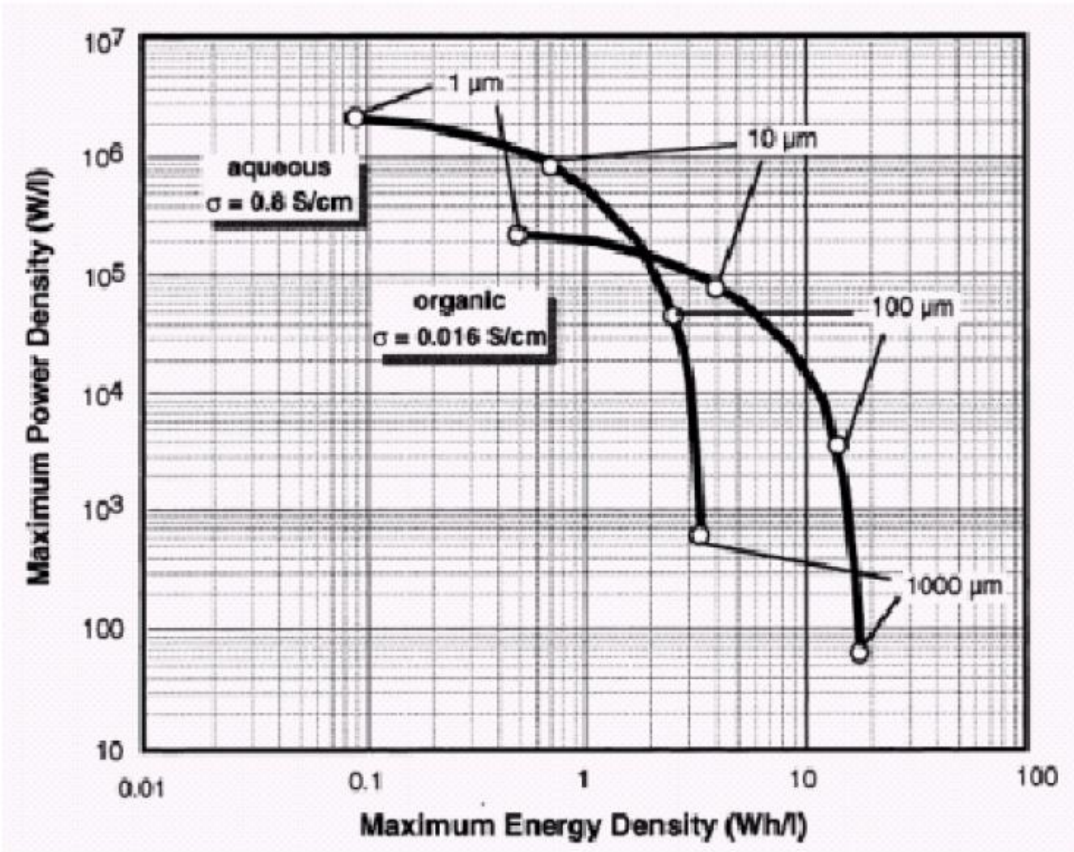


Figure 8: Ragone plot

It can therefore be noted that the choice of the electrolyte depends by the property that we want to give to our object and from the applications that we want to realize.

The separator

The third and last component of the supercapacitor is the separator; the task of this element is to allow the transit of ions through the electrolyte, preventing at the same time the occurrence of currents between the electrodes which would cause dangerous short-circuits.

Two types are used that strictly depend on the choice of the electrolyte:

- **Cellulose or polymer fiber separators:** used when the electrolyte is organic
- **Glass or ceramic fiber separators:** used when the electrolyte is an aqueous type

Beyond this difference when we choose the separator the most important parameters to consider will be the ionic conductivity and resistivity, which must be high, and the thickness that, vice versa, should be as small as possible.

1.2 Circuit models of Supercapacitors

The supercapactiror is an electrochemical storage system. Its electrical behavior is not so simple to model and, over the years, different approaches have been followed to create a model that makes virtual simulations comparable with the results obtained in laboratory.

The approaches that have been used the most are the analytical approach and the modeling through electrical circuits approach; in these last two years a third one has been added, which is the one of modeling through neural networks.

In our discussion we will first examine the various models that have been developed in the time domain and, finally, we will discuss the approach used to describe the supercapacitors in the frequency domain.

1.2.1 Circuit models in time-domain

1. **RC series model:** The first and simplest model that was created for the schematization of the supercapacitor is that which represents it as a single branch RC series circuit, where the resistance simulates the ohmic losses of the supercapacitor (ESR) and the capacitor simulates the capacity during the charge and discharge phases. This model brings with it a high degree of simplicity as an advantage, but unfortunately fails to adequately describe the behavior of the supercapacitor.

   In fact, comparing the experimental results with the simulated ones, as we can see in the figure below, we note that the model fails to reproduce the non-linearity of the supercapacitor during the charge and discharge phases and the final change of the voltage when the discharge phase occurs.

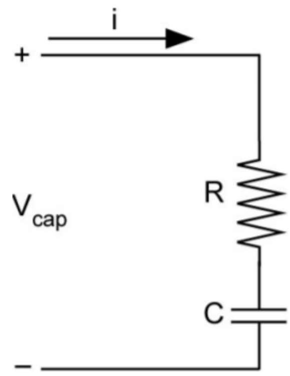
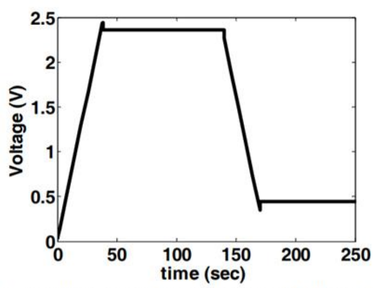
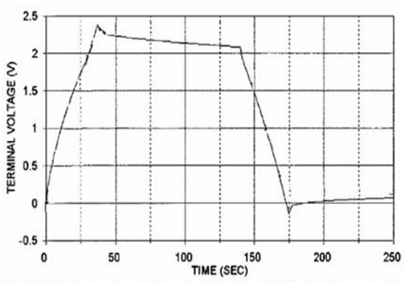


Figure 9: RC Model



Ultracapacitor constant current charge and discharge simple model simulation (30A).



Ultracapacitor constant current charge and discharge experimental test results (30A)

Figure 10: real and ideal behavior comparison

For the disadvantages mentioned above more complex models have been developed:

2. **Model with n parallel RC branches:** this model was born with the aim of being able to simulate the behavior of the supercapacitor in the points where the simple RC model diverged a lot from reality; is intended to simulate the non-linearity of the charge and discharge and the fact that when the discharge ends the supercondenser restart charging for a short period of time. To do this the basic idea is to insert three RC branches in parallel with different time constants that go to simulate respectively the behavior of the supercapacitor in the long term (Rf and Cf), in the medium term (Rm and Cm) and in the short term (Rs and Cs)

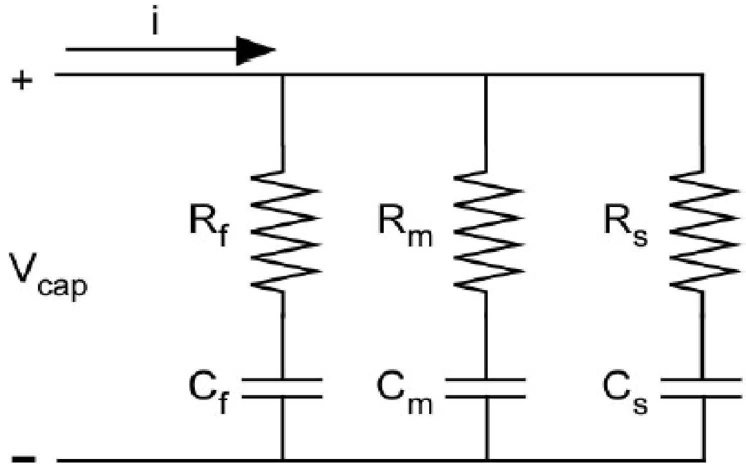


Figure 11: Model with n parallel RC branches

The rightmost branch simulates the behavior of the supercapacitor during the first seconds, the second branch for the time from minute to 10 minutes and the leftmost branch simulates the behavior over 10 minutes.

With this model it is indeed possible to reproduce the trend of the supercapacitor dynamically in a very good way and with a degree of accuracy much higher than the previous model.

The biggest defect of this model is at low voltages where the deviation from real data reaches up to 10%.

The definition of the parameters is determined by constant current tests carried out on the supercapacitor; finally, the time constants are chosen arbitrarily and corrected through an iterative process on the result of the measurements made.

This model can be further implemented by introducing further parallel branches which model the behavior of the supercapacitor in a more detailed manner; ideally, in fact, if we had infinite RC branches that model the described circuit the obtained trend would be perfect but, due to the countless mathematical complications of a model of this type, many studies agree that the optimal number is the one proposed above with 3 branches in parallel.

3. **RC transmission line model:** this model is born from the porous electrode theory developed by Levie from which we can think at the supercapacitor as a transmission line.

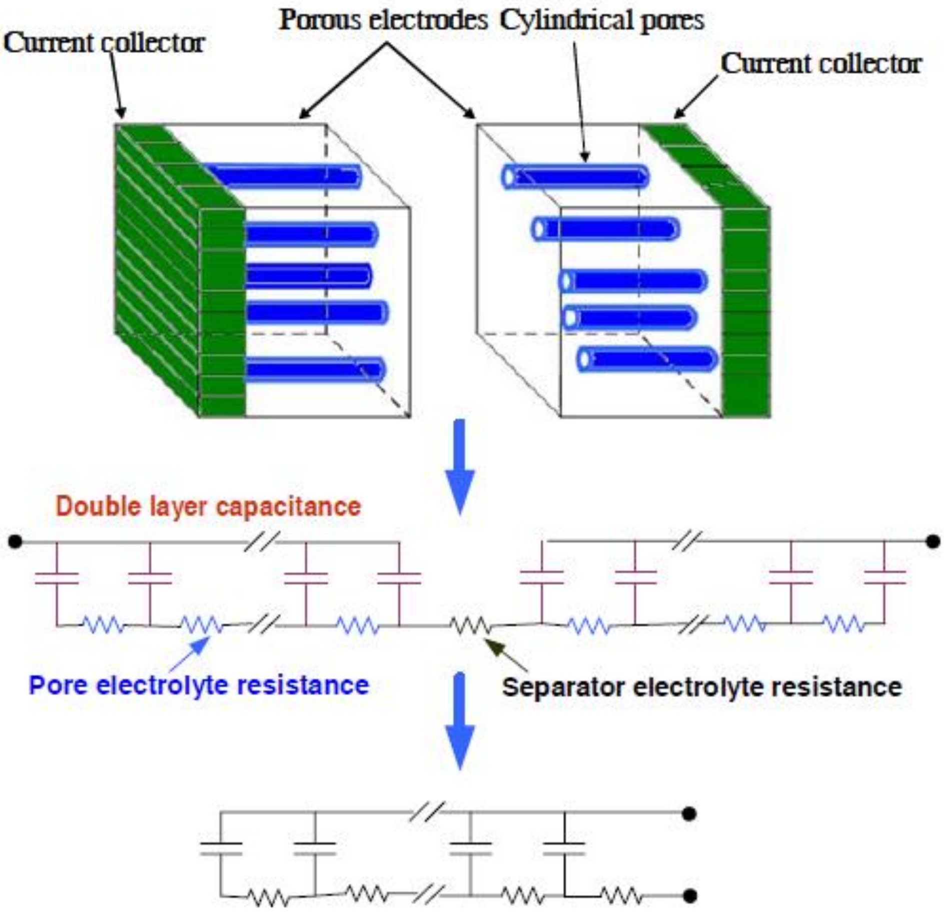


Figure 12: Levie model

On a physical level, what is done is to schematize each pore of the porous electrodes as a transmission line, assuming that the electrodes are perfectly cylindrical.

Without these assumptions we arrive at a model made up of blocks with different RC branches as seen in the figure below.

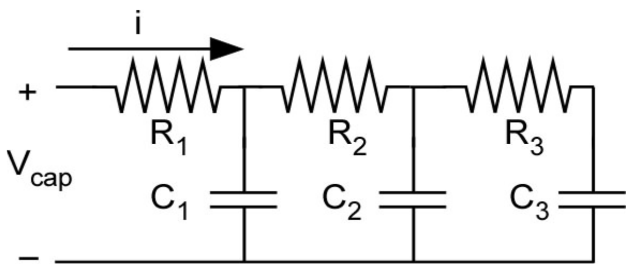


Figure 13: electric scheme of Levie model

However, since this model is subject to the equations of transmission lines, which are differential equations, it is not widely used in circuit modeling, while it is mentioned a few times when it comes to analytical modelling.

4. **RC model with series/parallel brench:** this circuit is a sort of hybrid with a branch in series and two in parallel. The resistance Ra represents the overall ohmic losses while the other resistances and capacities represent the overall impedance of the entire porous structure. To further develop the model, all parameters can be made dependent on temperature, voltage and frequency.

   Finally, impedance spectroscopy can also be used to obtain the parameters.

   A further improvement which has been obtained in the circuits presented is the insertion of an inductor upstream of the first element which simulates the behavior of the supercapacitor in the case of impulsive applications; in the same way it has been shown that the insertion of this inductor is completely useless in the case of any other type of application.

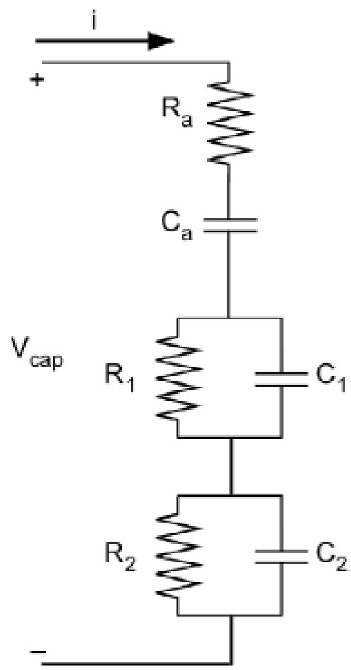


Figure 14: RC model serie/parallel

1.2.2 Circuit models in frequency-domanin

The frequency modeling is used because it more accurately describes the dynamic behavior of the supercapacitor, allowing to appreciate the variations of the parameters that describe it over a wide frequency range.

This description is therefore more usable because in many applications in which the supercapacitors are used, we have to pay attention to the dynamic aspects.

As we have seen, the structure of EDLC is very complex; usually when these objects are studied in the frequency domain, the temporal model from which we start is that relating to the modeling of supercapacitors as transmission lines.

Starting from this model, the equivalent Impedance we find is:

$$Z(j\omega) = R_{sol} + R_{sep} + R_{con} + Z(\omega) = R_s + Z(\omega)$$

Where the resistances take into account the electrolyte solution, the separator and the connections with the electrodes, while the impedance takes into account the variations in capacity and internal resistance as a function of frequency.

The measurements made on this impedance allow us to observe how, for intermediate frequency values, this is a straight slope of 45 ° with an Ohmic - Capacitive behavior: at low frequencies, however, the capacitive behavior is predominant.

The high frequencies finally deserve a separate discussion; in this range, in fact, it happens that the ions in the electrolyte solution cannot spread adequately within the porous structure of the electrodes, causing a drastic reduction of the available area which causes a reduction of the internal resistance and the cancellation of the capacitive behavior of the device

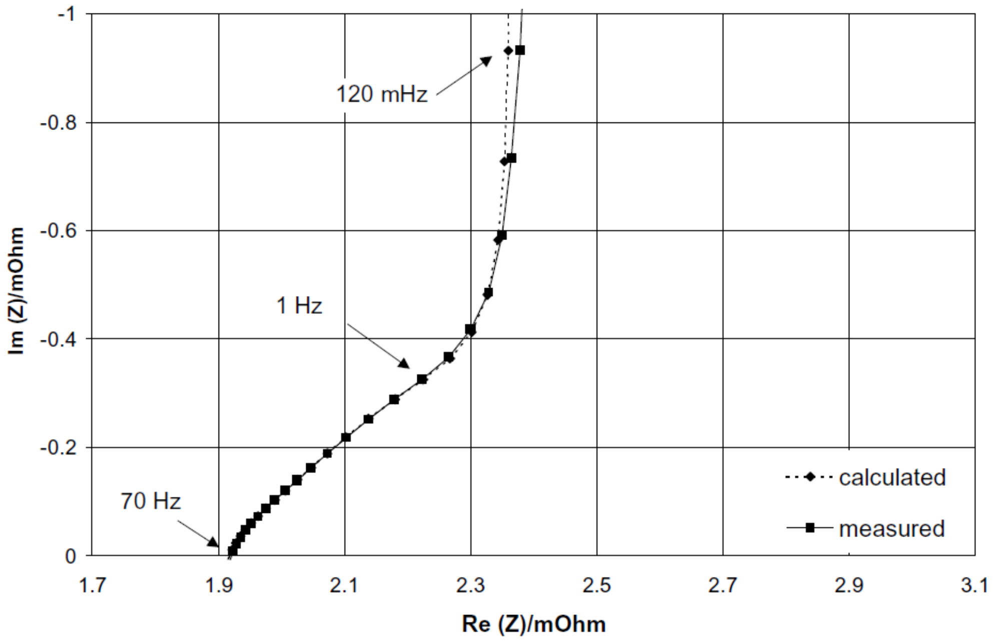


Figure 15: Impedance behaviour n supercapacitors

The expression that describes the trend of this impedance is the following:

$$Z(j\omega) = \frac{\tau * coth\sqrt{j\omega\tau}}{C * \sqrt{j\omega\tau}}$$

Excluding therefore the internal resistance, which is usually supplied by the constructors, the parameters τ and C are obtained by extrapolation from the impedance spectroscopy; carrying out subsequent experiments in the laboratory it has also been shown that the time constant τ presents a dependence on voltage and temperature.

Equivalent parallel admittance *Y*: absolute value and phase vs. *f*.

f (Hz)	|Y| (S)	Phase (Y) (deg)
0.001	0.7562	82.4012
0.002	1.4122	85.9395
0.005	3.2765	86.5005
0.01	6.3618	84.5882
0.02	12.3738	81.1673
0.05	28.9672	69.3828
0.1	49.0973	54.2286
0.3	80.0417	27.1849
0.5	85.7622	17.2604
0.7	88.6836	14.6511
0.9	90.1113	10.8514
1.1	90.9796	9.6209
1.3	91.5878	9.2377

Figure 16: Phase and Amplitude of the impedance

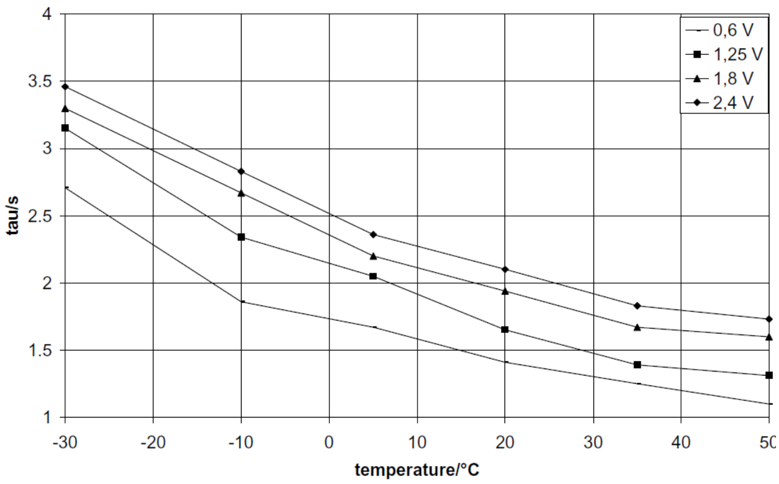


Figure 17: Time constant dependence by temperature and time

Observing the level of detail of the parameters that is obtained thanks to this type of approach we can understand why it is used a lot.

Chapter 2 - Designing a Howland Pump for the detection of dynamic behaviors in supercapacitors

2.1 Theoretical overview of Howland pumps

In electronics it is known that the positive and negative pins of an operational amplifier can be exploited to create a high impedance current generator; in addition, by creating a current generator in this way, it is possible to obtain positive and negative currents.

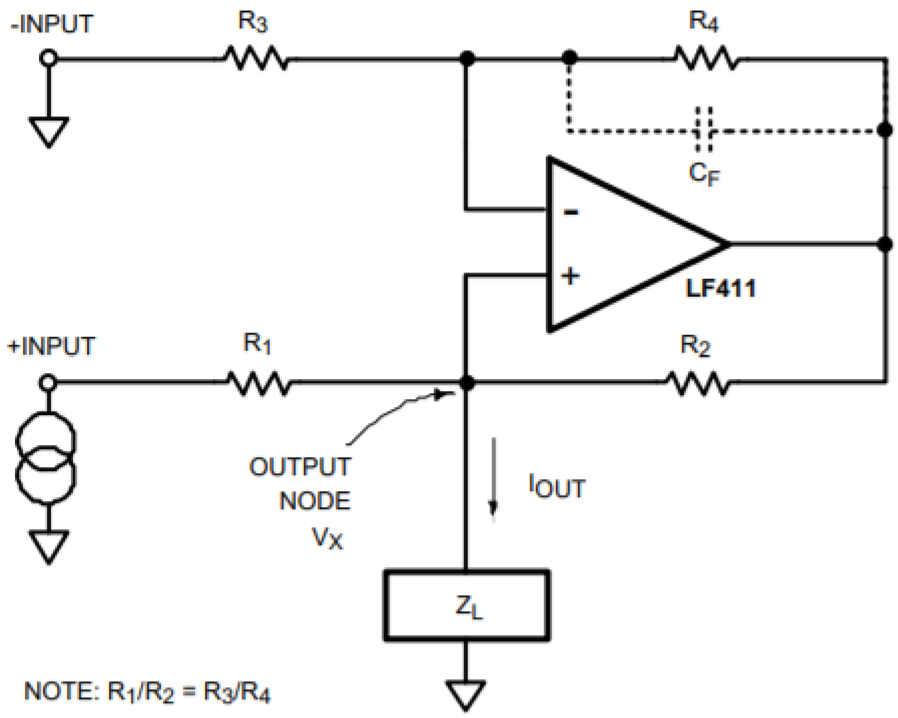


Figure 18: Howland pump basic version

Practically we are going to create is a voltage / current converter, which can be obtained combining transistors to the resistive bridge of the Howland pump. The advantage of this object is given by the bidirectionality of the current and by the possibility of exploiting any waveform.

But let's start from the beginning; the idea to which we refer was born from the mind of Bradford Howland in 1962; to explain how it works, we can refer to the "Figure 1" circuit.

Writing the equations for the currents with the numbers of the currents referred to the resistances we have:

$$I_1 = I_2 + I_{OUT} \qquad\qquad I_3 = I_4$$

By replacing the currents with the relationship between voltages and associated resistances we have:

$$\frac{V_{IN+} - V_X}{R_1} = \frac{V_X - V_0}{R_2} + I_{OUT} \qquad \frac{V_{IN-} - V_X}{R_3} = \frac{V_X - V_0}{R_4}$$

Replacing $V_X - V_0 = A$, we obtain:

$$\frac{V_{IN-} - V_X}{R_3} = \frac{A}{R_4} \frac{V_{IN+} - V_X}{R_1} = \frac{A}{R_2} + I_{OUT}$$

And introducing the bridge condition related to resistances:

$$\frac{R_2}{R_1} = \frac{R_4}{R_3}$$

And replacing also this expression:

$$\frac{V_{IN-} - V_X}{R_1} = \frac{A}{R_2}$$

Finally we can compare the two equations with the term $\frac{A}{R_2}$ to find that:

$$I_{OUT} = \frac{V_{IN+} - V_{IN-}}{R_1}$$

And we have shown that the gain of the Howland pump is $\frac{1}{R_1}$.

The biggest problem of this object, however, is that of not being able to drive high loads; in fact, if a resistance as load is used, as soon as the value of the voltage across a resistive load increases beyond the value of the supply voltage, the operational amplifier saturate, and the device become unusable;

Another problem is that the value of the current is limited to maximum voltage that could be tolerate by the operational amplifier and that the bridge resistance is at least 1000 Ω; for this reason the output current is limited to mA.

For this reason we have moved from this basic device to what is called "Improved Howland pump", designed to remedy these problems.

To improve the device, has been developed e model called "Improved Howland pump" which, thanks to the trimming of a resistance and the insertion of electrolytic capacitors, improves the general functioning of the voltage / current converter.

Now let's take a closer look at the changes that these constructive innovations bring to the device:

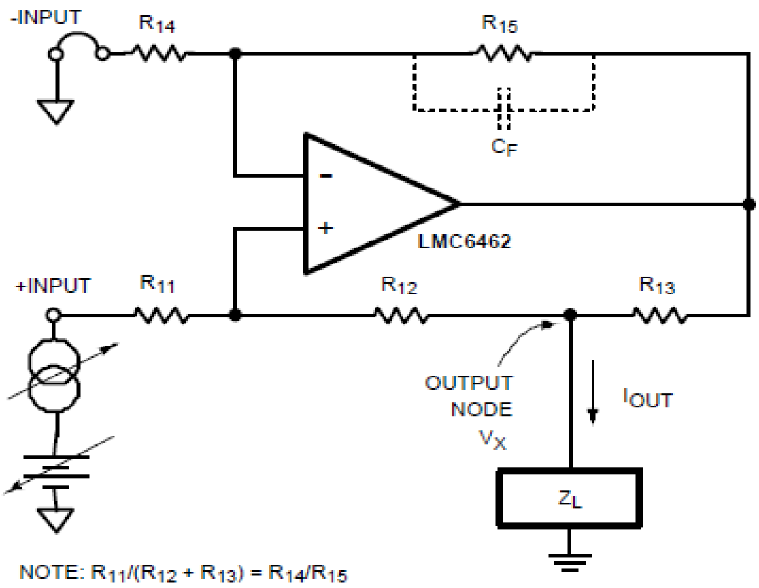


Figure 19: Improved Howland Pump

In this circuit we can immediately see that the relationship between the resistances of the bridge is different:

$$\frac{R_{11}}{(R_{12}+R_{13})}=\frac{R_{14}}{R_{15}}$$

Il generatore di Howland infine possiede due difetti di cui dobbiamo necessariamente tenere di conto:

In this way, properly choosing R_{12} *and* R_{13}, the output current can be increased.

Another interesting thing that has been done in this advanced version of the Howland generator is the introduction of a capacity in parallel to the R_{15} resistance; placing this resistance in fact compensates the oscillations in high frequency due to the pole of the operational amplifier.

As far as the choice of amplifiers is concerned, it depends very much on the voltage values that we need as a power supply; in fact all the amplifiers can be fine but, in the case of applications that intend to exploit AC currents with various wave forms, we need Rail-to-Rail amplifiers.

With this type of amplifiers it's possible to work with both positive and negative voltages, which is obviously useful for bidirectional currents.

The Howland generator finally has two defects that we must necessarily take into account:

- The voltage at the output node of the amplifier (in the case of a generator with four equal resistors) is $V_x = \frac{V_0}{2}$. This relationship makes it possible to conclude that, when the input voltage at the operational is about 7.5 V there is an output saturation because the limit of 15 V is reached. If we need higher voltages this becomes a limit because usually the operational amplifiers do not have powers higher than these values.

  As we saw in the advanced configuration to partially obviate this thing we could think of varying the relationships between the resistances of the bridge keeping them the same two by two (in this case carrying out all accounts of sees that manages to increase the voltage on V0; in this way you get a lot more noise and you risk unbalancing the bridge creating problems of accuracy to the whole system.

- The power dissipated by the Joule effect: this power is equal to $V = R * I^2$; if the voltage to be reached is around 0.5 V, we see that the wasted power is very low (we obtain currents of the order of mA) but, if we rise to voltages of the order of volts then things change and the wasted power is very important and the system become inefficient

Now that we have learned how our device works we can try to understand the better way to connect it with our supercapacitor; we should think at something like the object below:

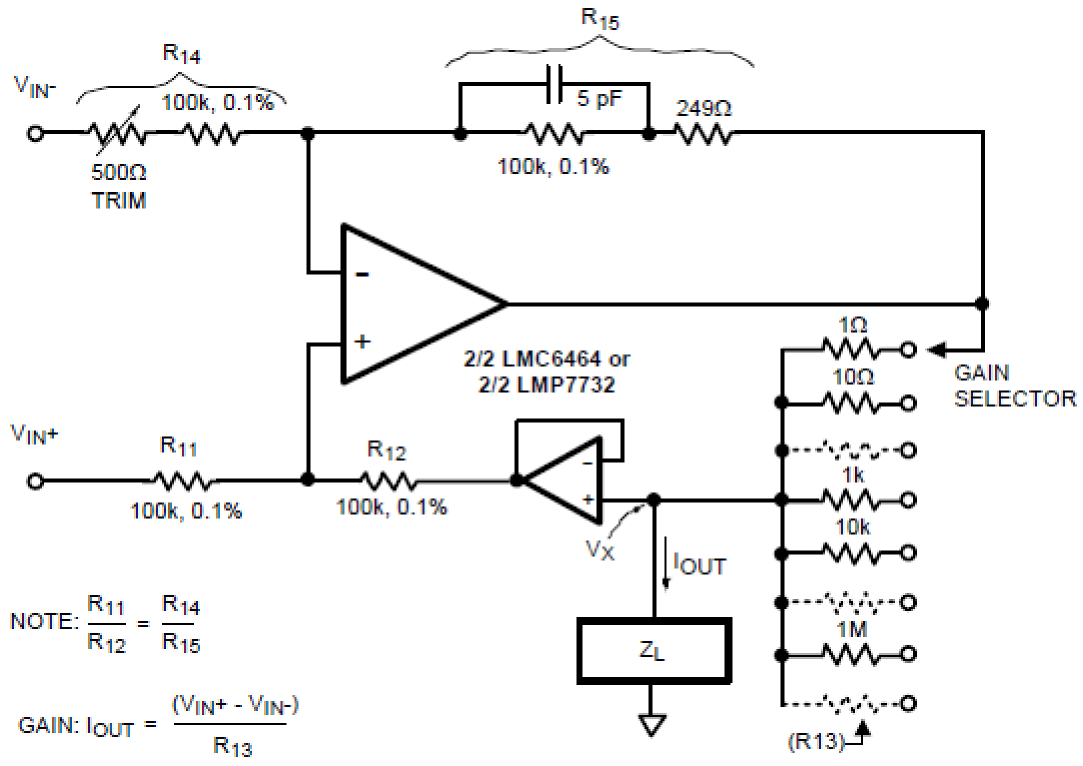


Figure 21: Howland pump with variable current

In this device the output current is equal to:

$$I_{OUT} = \frac{V_{IN+} - V_{IN-}}{R_{13}}$$

Where the resistance can be varied so as to obtain different current values useful for the most disparate applications.

Note: In an application of this type, a second operational amplifier connected is required, so as to work as a buffer and to avoid stress on the bridge due to voltage alterations that could compromise the device. Starting from this idea, we add two transistor and we create a device able to drive currents up to 10 A

2.2 Design and simulation of an Howland pump

Starting from the idea of a Howland pump with variable gain we decide to create a V/I converter able to pass from very low voltages (below 1 Volt) to high current (speaking in electronic terms) up to 10 A:

In order to achieve this effect, we simulated a device with an electrical circuit of this type:

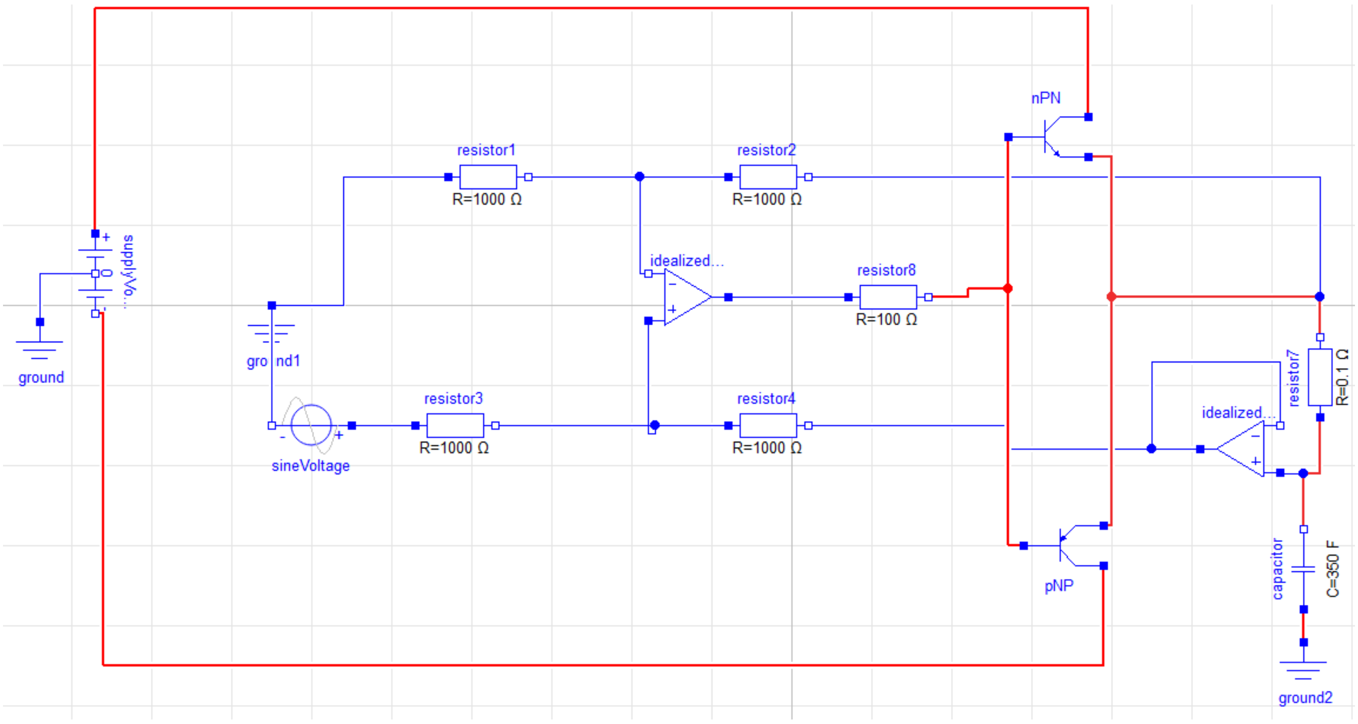


Figure 21: Howland Pump scheme

In our case we have joined the signal part of the Howland source to a part of power, consisting of transistors, which allows to obtain the desired effect and to create high currents starting from low input voltage values.

The output current of this device will in fact be given by:

$$I_{OUT} = \frac{V_{IN+} - V_{IN-}}{0,1}$$

Where the value of the current is given by "resistor7"; in our case the value of this resistor is about 0,1Ω and with a difference of 0,1 V between $V_{IN+} e\ V_{IN-}$ we are able to obtain a current of 1 A !

The technical limit of this circuit is given by the characteristics of the transistors and of the operational amplifier and is related to maximum voltage that you the component can have at their input.

To understand what happens inside the device we are going to simulate the behavior of our device by we evaluate a situazione with a resistive load and with a sinusoidal voltage input of 1 V; let's go and see what happens:

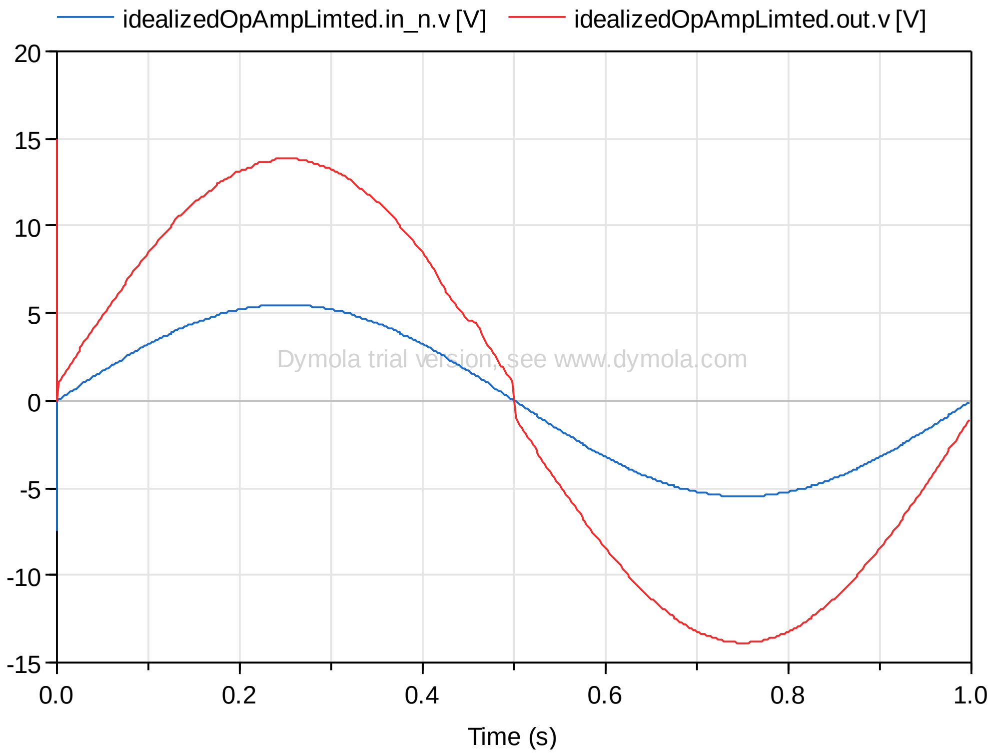


Figure 22: Simulation 1

From this first graph we can see that the theory is confirmed because the relationship between Vin e Vout is maintained:

$$V_{OUT} = 2V_X$$

Except for a voltage step introduce by the transistors when there is the inversion of polarity.

Proceeding to the right of the circuit, we find the transistors; here we see how the positive part of the sine wave is passed through the PNP transistor, while the negative part through the NPN transistor. Here too, as far as values are concerned, we are in line with what we expected.

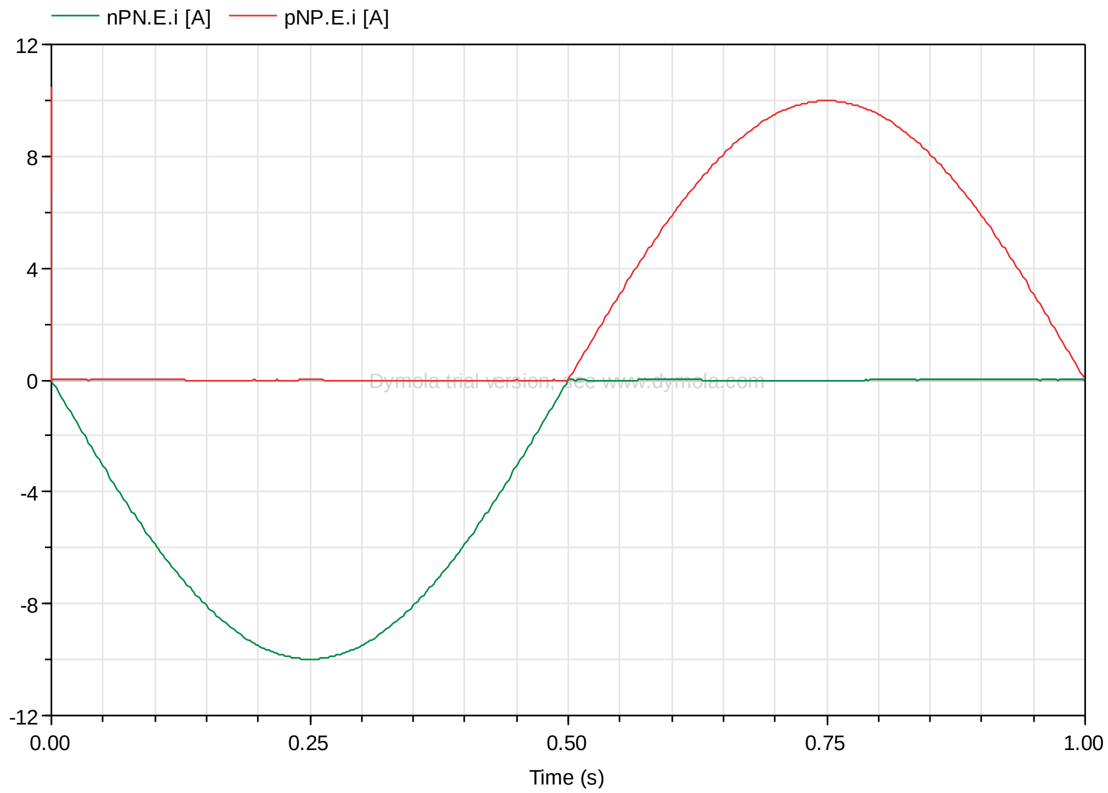


Figure 23: Simulation 2

Regarding the output current we can observe that the current on the "resistor7" which manage the gain of our device is 10 A, as we expect.

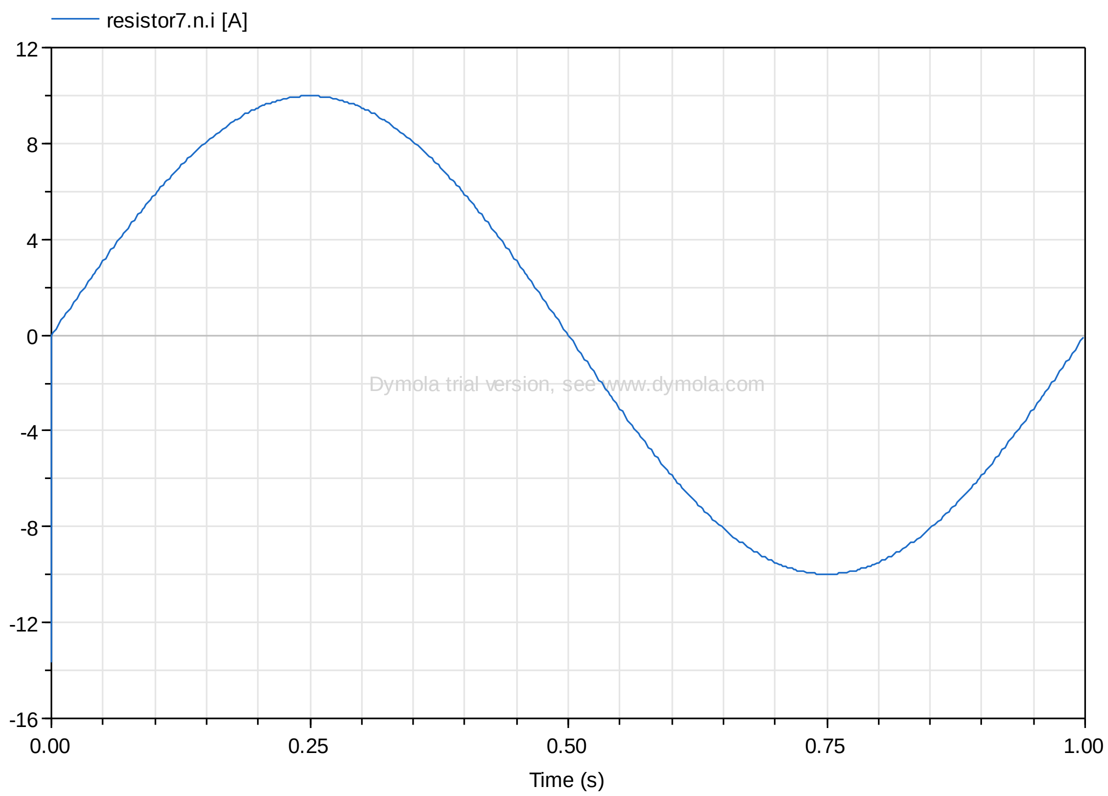


Figure 24: Simulation 3

Finally also the current on the resistive load is about 10 A, so our device work really well:

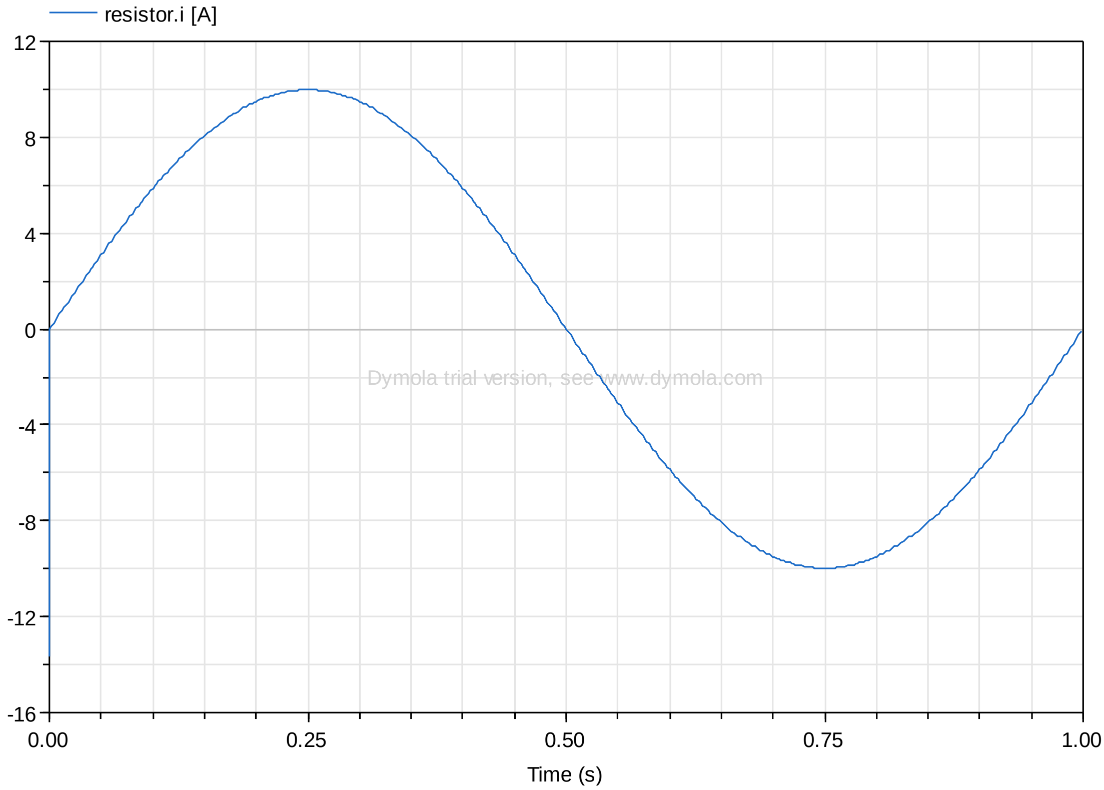


Figure 25: Simulation 4

Even if you replace the resistance at the output with a 350 F capacitor, which is what we're going to do in practice, the behavior remains the same:

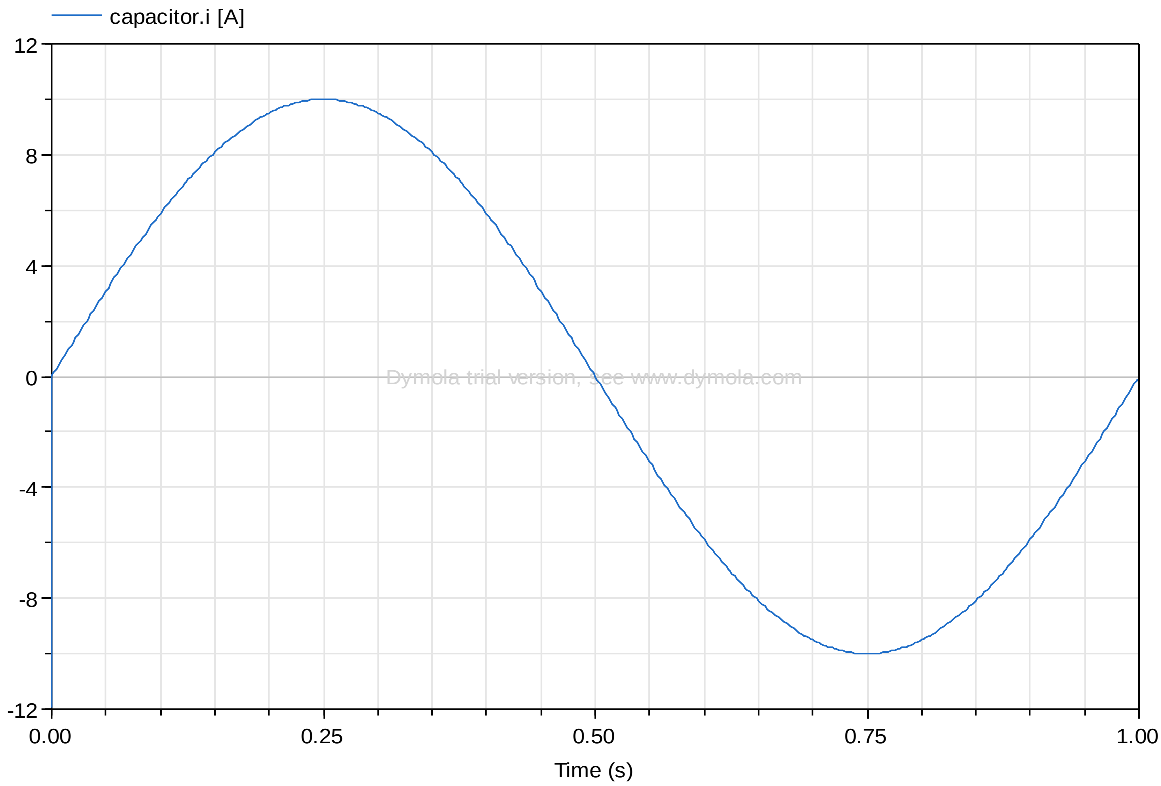


Figure 26: Simulation 5

This is also in line with the theory because with such a short period it is not possible to see the charge in the capacitor; to do this it would be useful to introduce a voltage signal at very low frequencies but this generates a problem in compilers such as Dymola and therefore we can not do this on a theoretical level.

To complete our simulations let's see what happens if the input signal is no longer sinusoidal but rather constant over time !

In this case we have only one transistor conducting at a time; in case of a positive signal, the NPN transistor in the only one that works, as shown in the graph below:

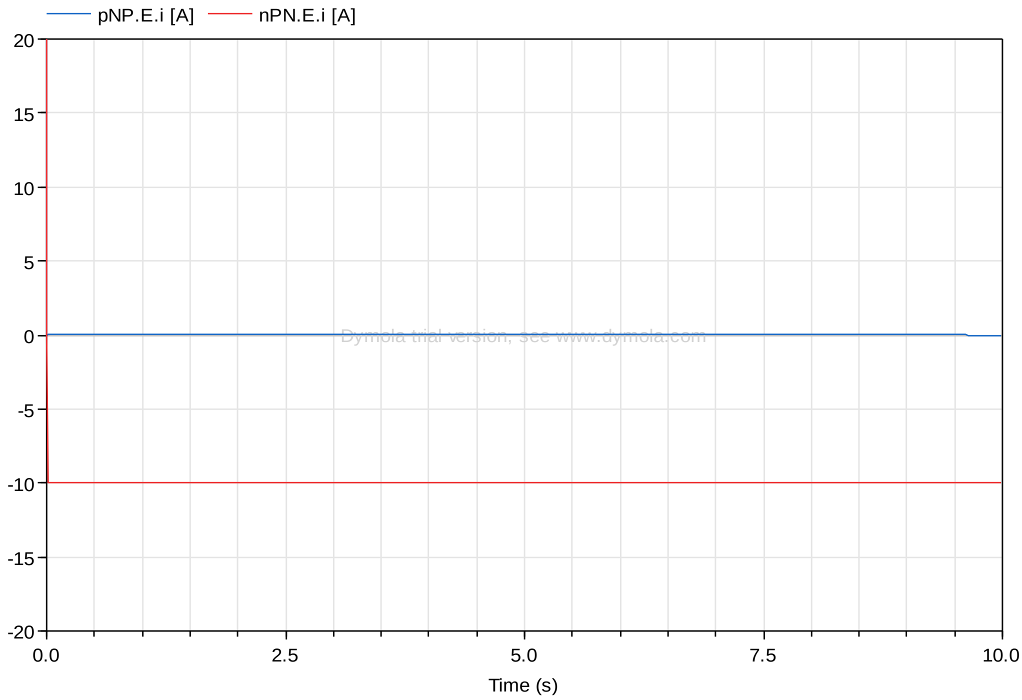


Figure 26: Simulation 6

This current, negative on the Emitter of the NPN transistor for circuit construction, on the load assumes a positive value, as it must be from the relation:

$$I_{OUT} = \frac{V_{IN+} - V_{IN-}}{0,1} = \frac{1}{0,1} = 10A$$

Let’s now see voltage and current on the supercapacitor:

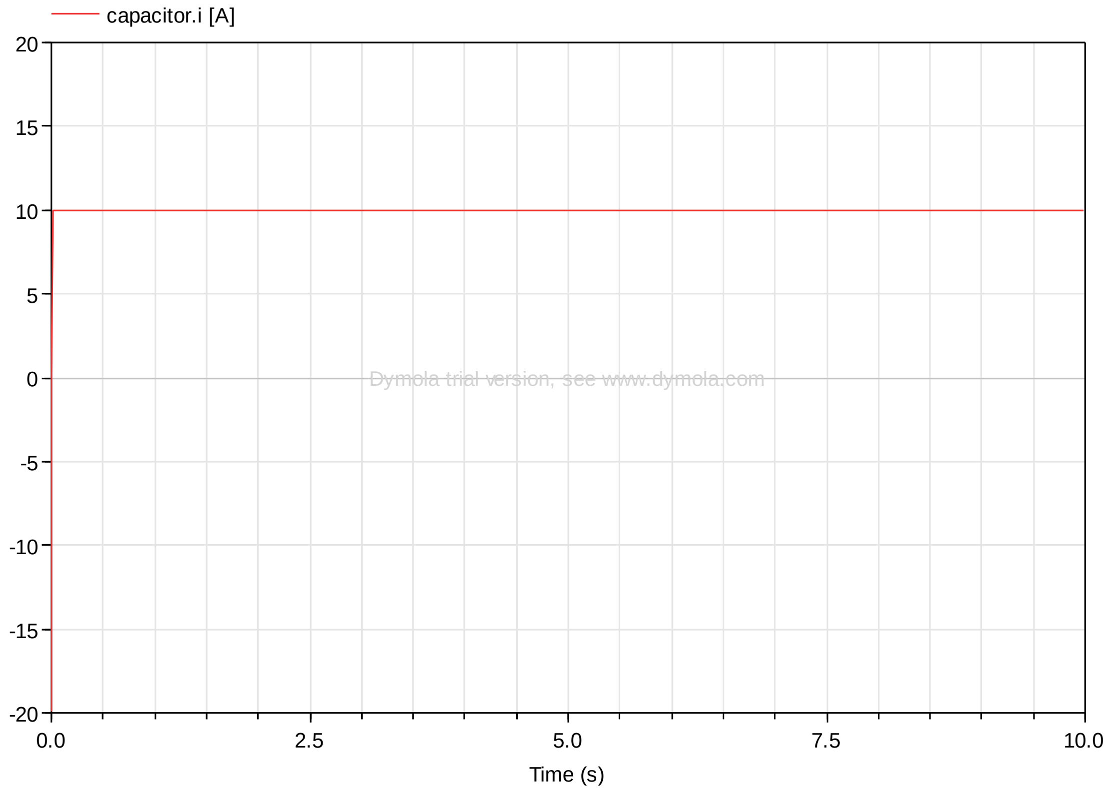


Figure 27: Simulation 7

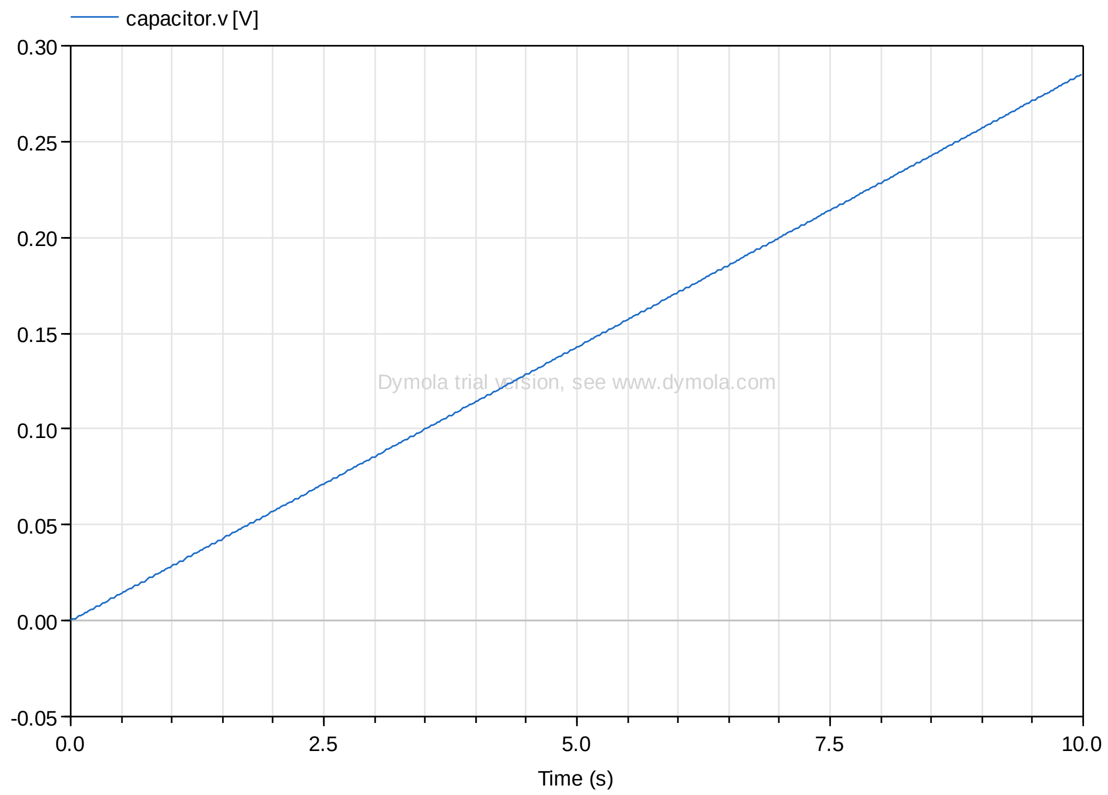


Figure 28: Simulation 8

We can now observe how the supercapacitor is able to charge itself and so we can conclude that our device works well and that everything is ready to take our measurement data.

2.2.1 Operating Limits

The operating limits of the device are substantially divided into two categories:

- Technological Limits
- Thermal Limits

The technological limits are those introduced by the voltage and current limits of the operational amplifier and transistors respectively. In fact, when the current exceeds 10 amps or the voltage exceeds 15 V, the components either break (transistor) or go into saturation, making the device unusable.

However, these limits also depend on the size and the type of the load; so let's see the 2 most common types of load and analyze what happens:

- Resistive load: in the case of resistive load, when the resistance increases, the voltage at the ends of the operational amplifier increases and therefore when exceeded 15 V, the amplifier go into saturation:

  Considering this fact in case of resistive load the resistance maximum value are:

Vin	Rmin	Rmax
0.1	0.001 Ω	15 Ω
1	0.001 Ω	1Ω

- Capacitive loads: for these two types of loads we have not encountered any problems and we have seen that the device works without problems for capacitors ranging from 1 to 350 F in a frequency range ranging from 1 mHz to 1000 Hz.

Finally it is right to talk about the thermal limits of our object; it has been seen that, after 25 minutes of uninterrupted operation, the transistors exceed the maximum operating temperature and the break themselves after a shortcircuit; to solve this problem we inserted a 20 W fan downstream of the transistors that drastically increase convective exchanges and replace natural convection with forced convection.

In this way it has been verified that the device is able to work continuously for 120 minutes (longer test run than we have done) without reporting any sign of failure to the components.

2.3 Components choice

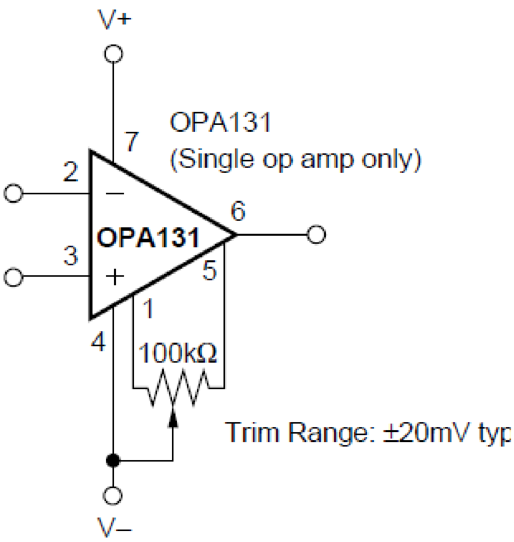
Each component has been chosen following precise criteria; so let's see them briefly and list them;

Bridge resistance: in our case, a slight imbalance of the bridge is not a very serious problem because our measurement application does not require absolute precision; on the other hand it is also important not to have an excessive imbalance of the bridge.

The compromise is found going to choose resistances with tolerances of 1%. In this way a bridge is created that does not present imbalances and that meets the required requirements.

Operational Amplifier: this component has to be able to transmit a bidirectional voltage and therefore for this it is necessary a Rail to Rail amplifier. In our case we have used the model OPA131 because in its category is one of the best with a power supply up to ± 18V.

In addition to this the OPA131 offers a very wide operating temperature range (up to 85 ° C) and a very high impedance; finally, it is possible to trim channels 1 and 5 so as to cancel any offsets (and we do that in this application) by following the instructions given in the manual and using a 100kΩ resistor.



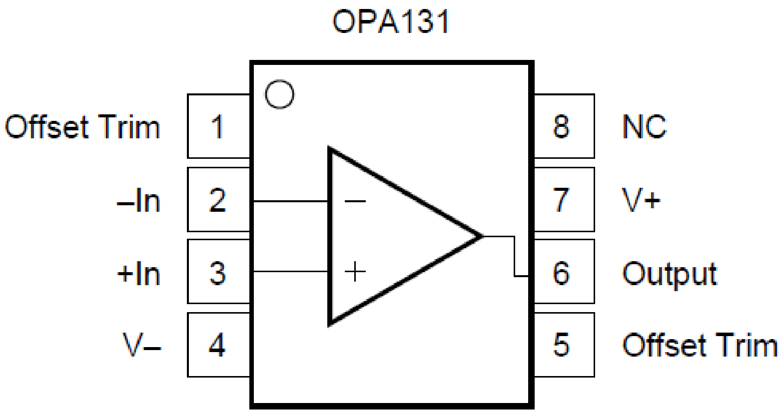
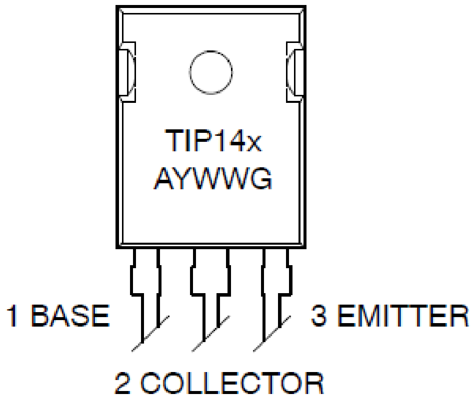


Figure 29: Operational Amplifier

Darlington transistor: Darlington-type transistors are formed by two bipolar junction transistors in cascade; the choice of these transistors is due to their characteristics of use which allows them to withstand much higher currents than the classical transistors.

In our case we chose the pair TIP142 / TIP147 because, among the transistors on the market, they possess one of the highest values of sustainable current, equal to 10 A in continuous mode and 15 A as peak current.



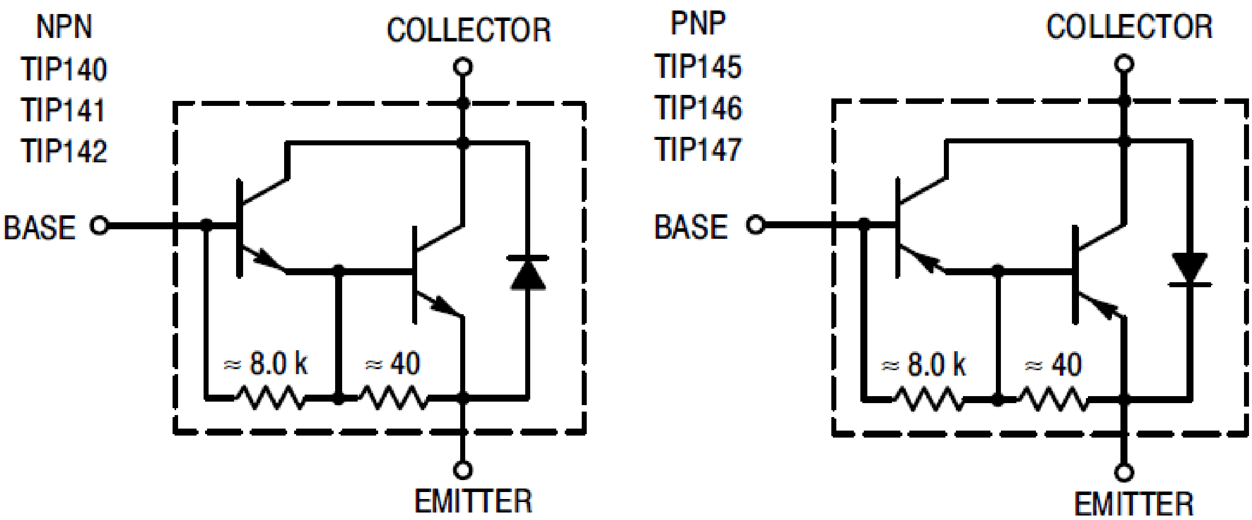


Figure 30: Transistor

These transistors have been mounted as indicated in the circuit a the beginning of this chapter.

Power resistance: The output resistance is the one which defines the gain of my Howland pump and therefore must be chosen appropriately; in the designed circuit the biggest problem related to this resistance was related to heat dissipation; the problem was that the current is in a quadratic relationship with the power and, with a current of 10 A, assuming a resistance of 1 Ω, we would have had a heat dissipation equal to 100 W and this would have greatly complicated everything because, given the proximity of the components, this heat would have broken down both the resistance itself and the neighboring components.

Figure 31: Power resistance

For this reason the solution was to choose a resistance of the smallest available value that would effectively dampen the value of the dissipated heat.

So we opted for a 100 mΩ THS resistor with a possibility to dissipate up to 25 W; considering the maximum design current in this way we will have a heat dissipation equal to 10 W, a value much more reasonable than before.

2.4 Test and Characterization

After choosing the components we assembled our device measuring before the output resistance with a 4-wire method so as to identify the value as precisely as possible:

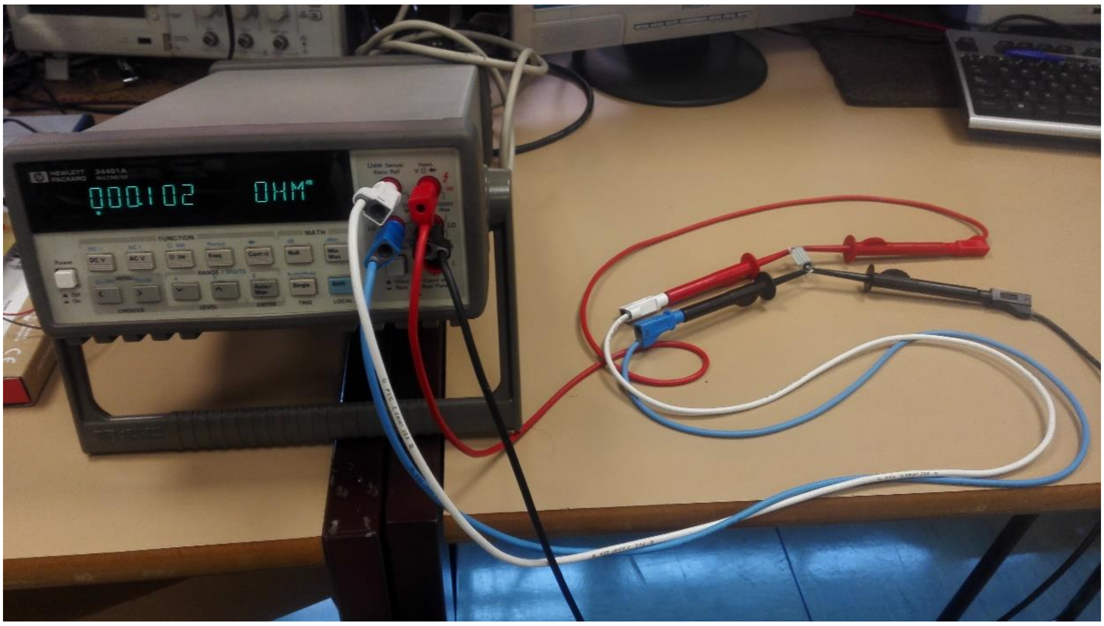


Figure 32: 4 wire characterization

We then inserted a resistance of 1 Ω as a load, also calibrated with the 4-wire method, and then we carried out several tests with various currents to see if the values at the terminals of the operational amplifiers and of the transistors were in line with the theoretical results (all this was done using a probe connected to the oscilloscope).

Once these basic data have been verified, we have moved on to the device characterization: to perform it we have done two types of tests:

- **Distortion Test:** this test was made by sending to the device sinusoidal waveforms at various frequencies and going to detect the difference between the waveform sent in input and the resulting waveform at the output with a resistive load of 1 Ω;
- **Noise Test:** this test was performed in two successive steps: initially we connected our device to a noise spectrum analyzer and we evaluated its response by testing it first without power and then with positive and negative power of 500 mA. In the second place we repeated the usual test inserting the device in an anechoic chamber so as to remove all the external noise due to laboratory equipment and other experiments in progress.

Let's go to see the two tests in detail:

2.4.1 Distortion Test

The distortion test has been made in this way:

- We sent sinusoidal waveforms with different frequencies to our device
- We evaluate the resulting waveform on the load
- Using Labview we acquire the measurement datas of the two waveforms
- We elaborate the data through Matlba measuring the THD and concluding about the distortion introduced by our device.

Technical scheme used for the test

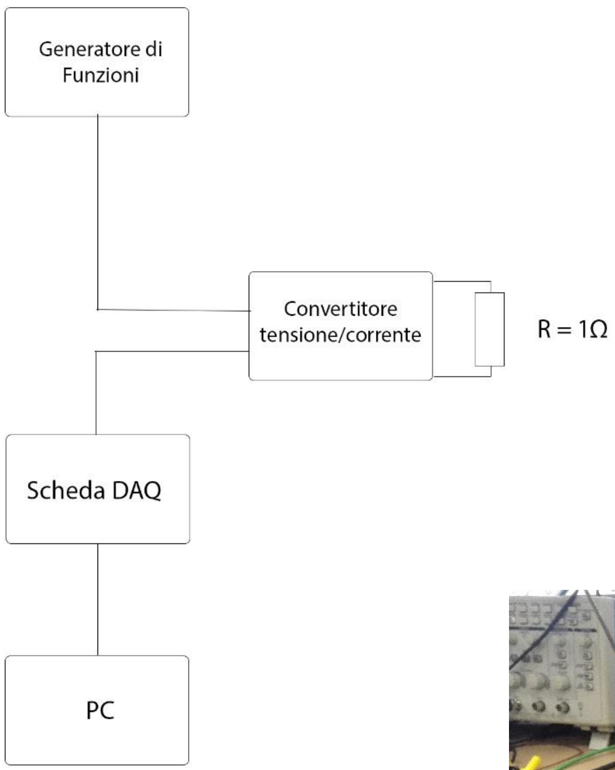
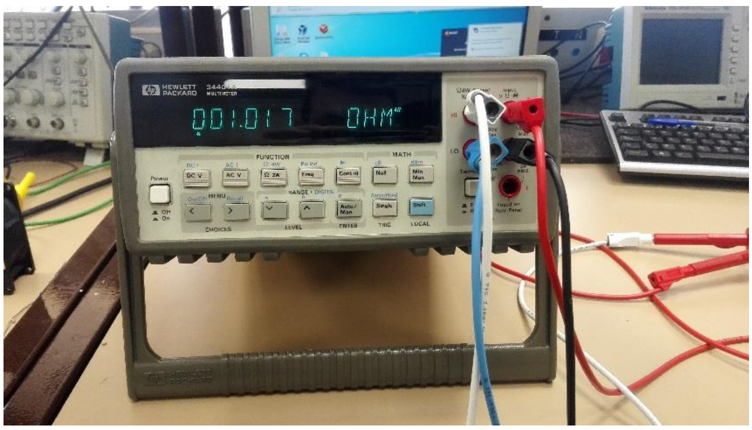


Figure 33: Technical scheme

To perform this test, we connected our Howland pump to a generator of functions able to create sinusoidal signals up to a frequency of 500 kHz and, with proper connections to the DAQ board, and to the PC we acquire data in real time.

Finally, to complete the setup and to close the circuit, we connected a 1 Ohm resistor, also measured with the 4-wire method.

In this way we have carried out measurements at 0.5, 1, 10 and 50 Hz so as to see the distortion in the field of interest and we have elaborated them through a program with MatLab.



Matlab code Description;

```
clc, clear, close all


A = importdata('sinusoide 50 Hz.lvm');

x = A(:,1);
y = A(:,2); %2 uscita 4 ingresso

signal = plot(x,y);

B = y;
fs=1000;
ts=1/fs;

%Lunghezza del segnale in secondi:
Tmax=ts*(length(B)-1);

%Costruzione asse delle frequenze:
f=[-fs/2:1/Tmax:fs/2];
```

The Matlab program has to process the data and give the signal distortion percentage as a last result; To do this, we import the data from the Labview file that we have obtained and from this we extrapolate the axis of the times (x) and the axis of the voltages (y).

Having fixed these two values we are going to introduce the sampling frequency, given by the parameters of our DAQ, and the sampling time that is nothing but the inverse of fs.

Once these values have been defined, we can proceed by constructing the time axis and, subsequently, the frequency axis.

This second axis is translated by fs / 2 because, as we know from the theory, the frequency spectrum is symmetrical with a symmetry axis centered precisely at fs / 2.

```
periodogram(y,kaiser(length(y),38),[],fs,'power') %power spectrum

r = thd(y,fs,7); %thd in decibel

thdperc = 10^(r/20)*100 %thd in percentage
```

Once the parameters have been defined, we can plot the power spectrum of our signal; the command "periodogram" evaluate the FFT of the inserted data and then create the power spectrum; finally we evaluate the THD (Total Harmonic Distortion), that is the total harmonic distortion, in decibels and in percentage.

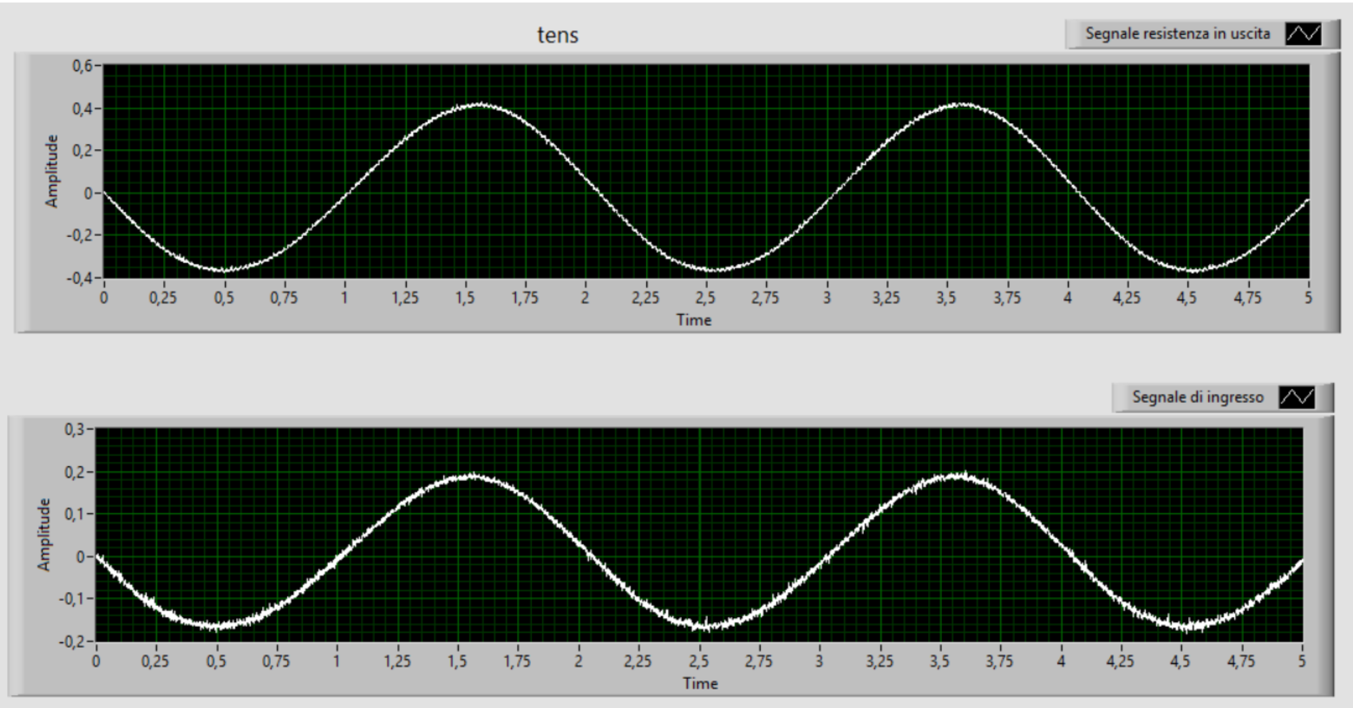
We evaluate this parameter in two different ways because they are both important; the absolute value of this parameter allow us to understand the magnitude of the harmonic distortion and the difference between the harmonic distortion on the input and on the output so as to understand if the signal, passing through the components of the device, has been distorted.

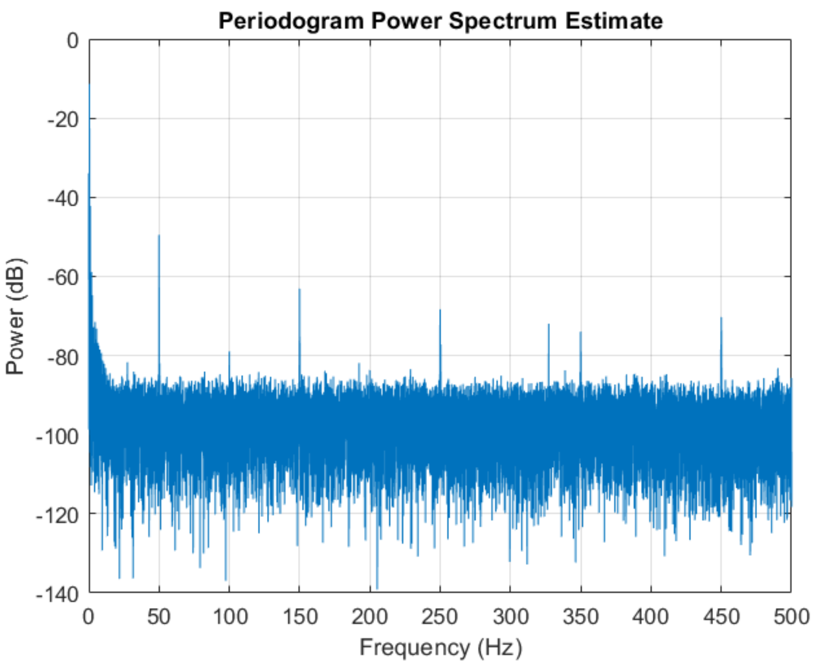
In this way we are able to determine the magnitude of these values and we can understand how reliably our measurement datas are.

Test results

We now report the results of the 4 tests carried out to see the power spectrum in different situations and the results in terms of percentage of THD on the input and on the output.

0.5 Hz Test





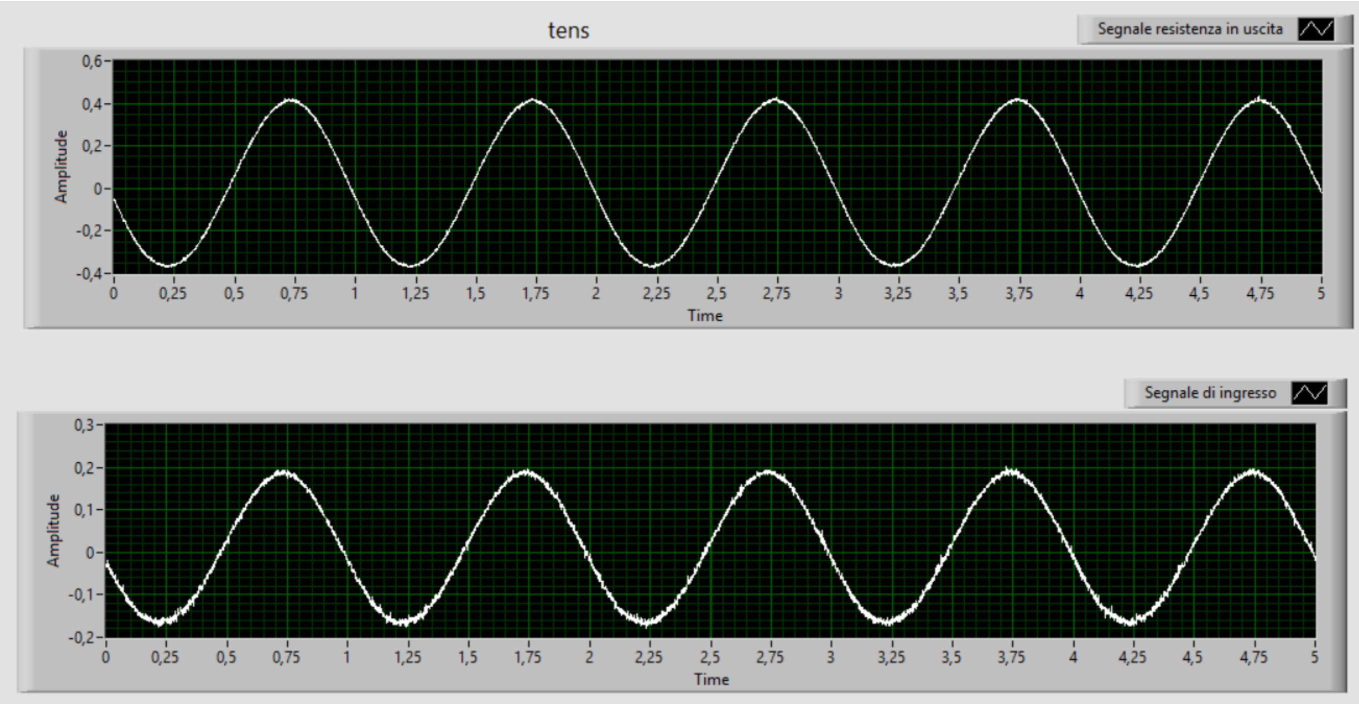
At first glance it might seem that the input voltage is more distorted than the output voltage; in fact, as will be seen from the results given by the power spectrum, this is only an optical effect due to the fact that the amplitude of the output signal is twice that of the input signal and less details are shown in the graph.

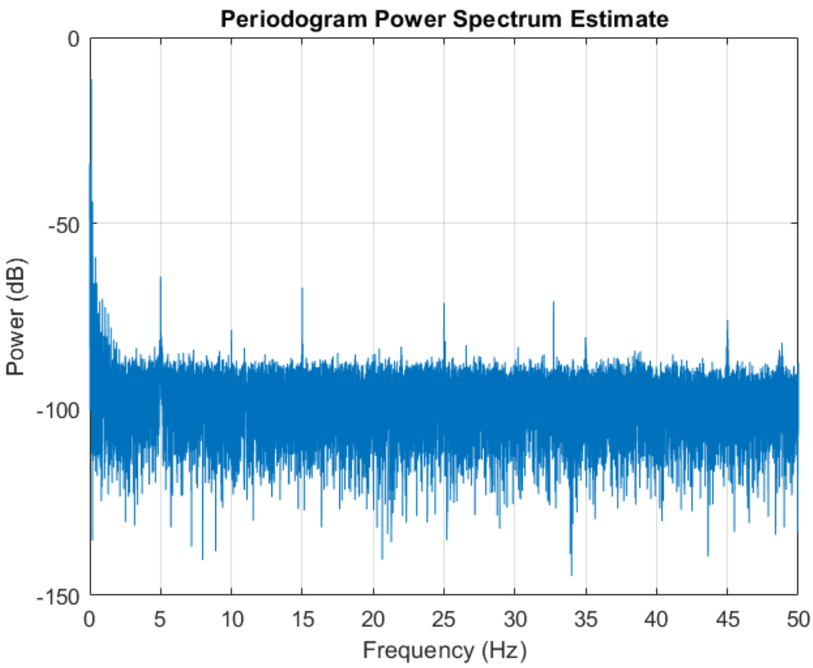
Going to process the data we see instead that:

	Input Voltage	Output Voltage
THD	2.0848 %	2.0912 %

So we see that we have a small distortion and therefore acceptable in the most absolute way; also the difference between the input and output distortion is less than 0.01% and therefore we can also consider this an excellent result.

1 Hz Test

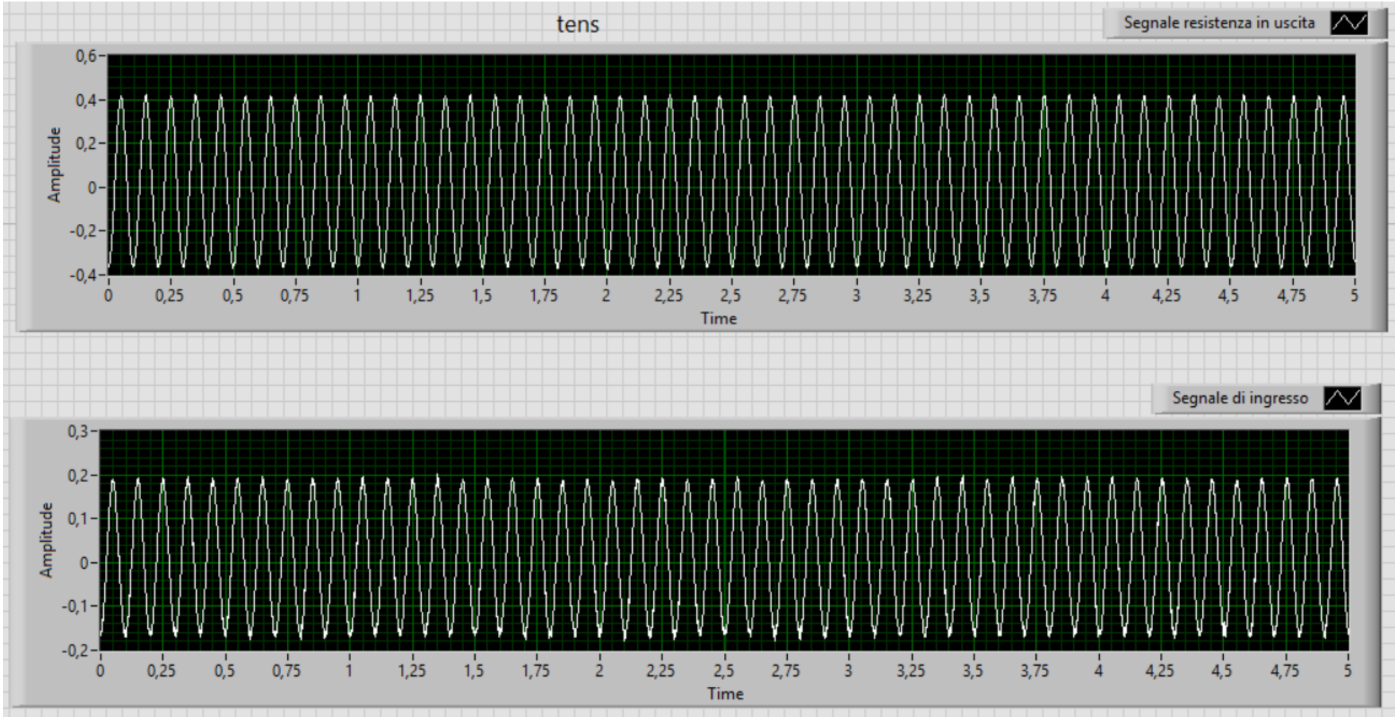


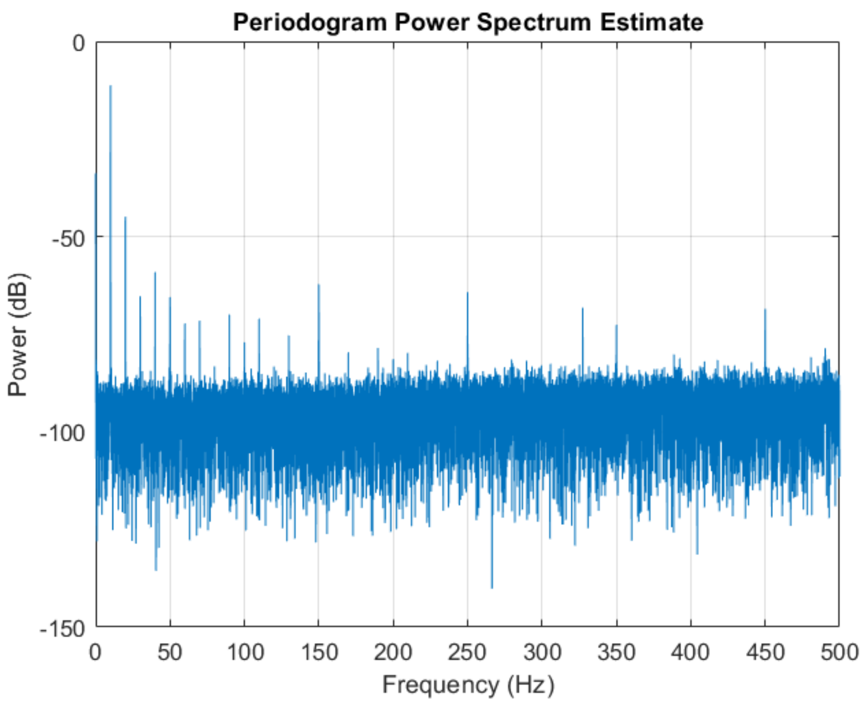


In this second measure we can see that the harmonic distortion increases by 14% compared to the previous one, while still remaining on acceptable levels; the difference between the input and output distortion values remains practically unchanged.

	Input Voltage	Output Voltage
THD	2. 3591 %	2.3629 %

10 Hz Test



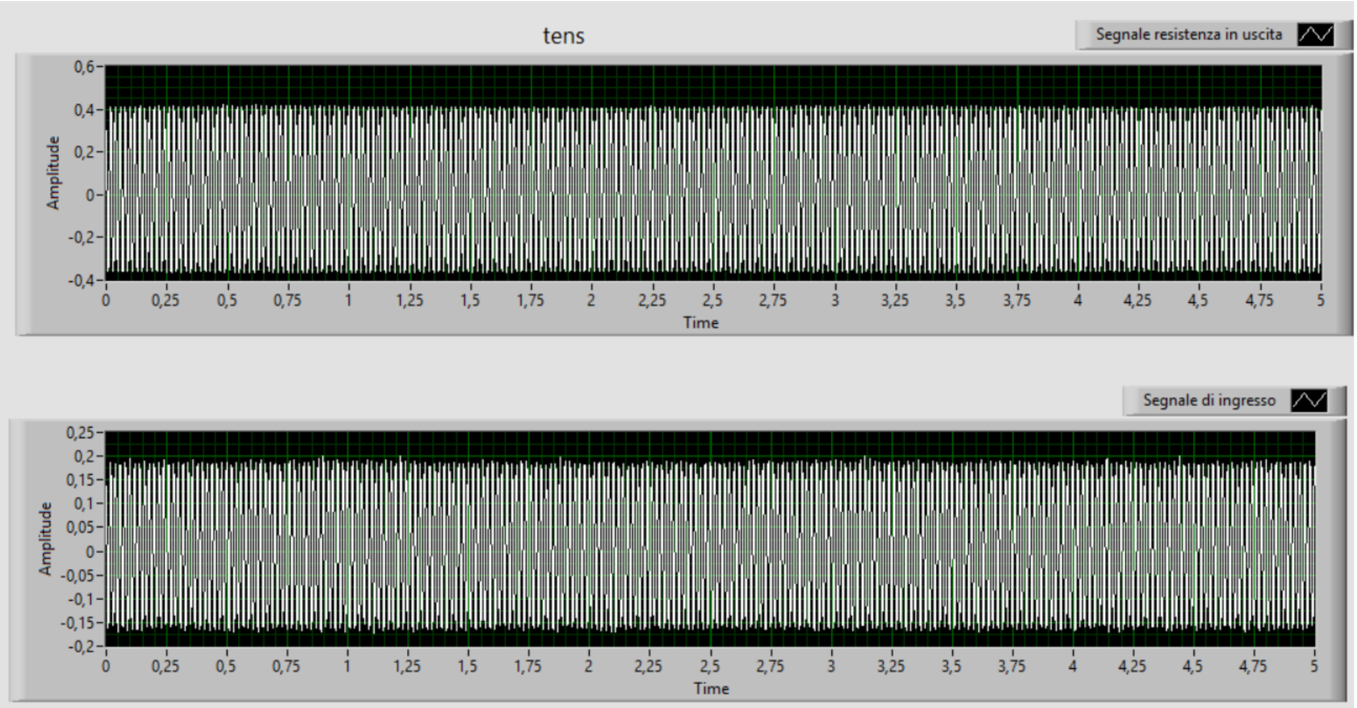


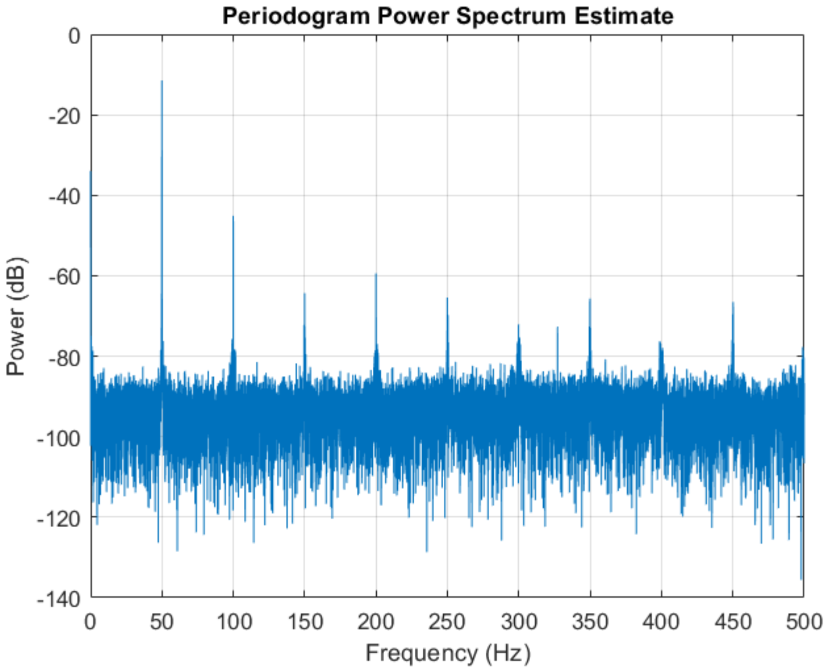
Also in this case we can see that the harmonic distortion remains very similar to that obtained from the previous tests.

The difference between the distortions in this test turns out to be almost nil, but this value is also in line with that obtained in the previous tests.

	Input Voltage	Output voltage
THD	2. 1367 %	2.1370 %

50 Hz Test



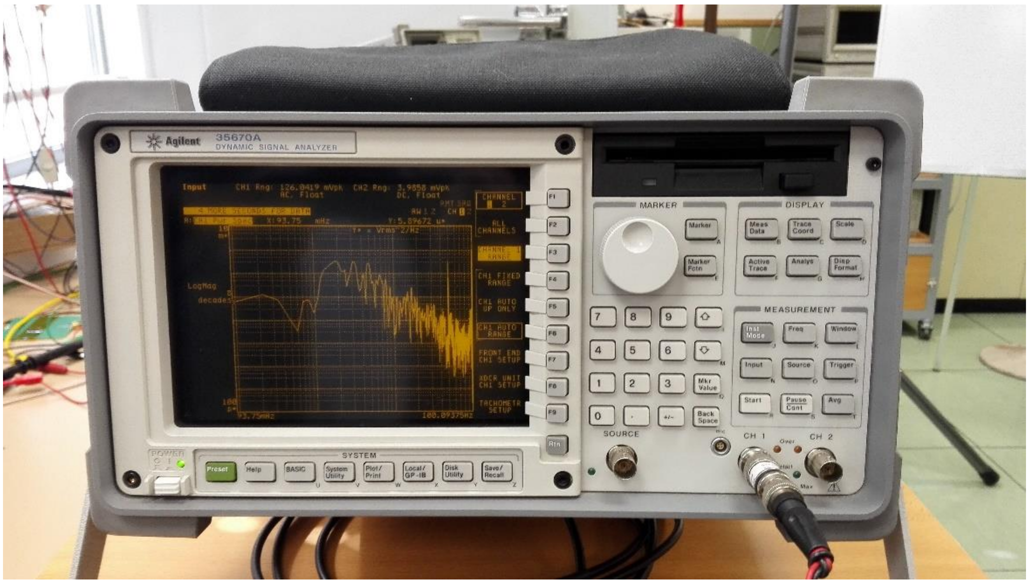


Also in this test we can conclude as we have done for the previous tests with the values that remain in line with what we saw in the previous tests.

	Input Voltage	Output Voltage
THD	2. 0849 %	2.0912 %

We can therefore conclude by saying that the device has provided excellent responses to the distortion test highlighting a low alteration of the measurements and an almost zero difference between input and output distortion, and this is a positive indication that indicates that our device produced remarkable results with a really low distortion.

2.4.2 Noise Test



The noise measurement test was made using a special instrument, connected to the external resistance, that was able to permorm a frequency analysis, to determine the noise on a given frequency band.

We set the parameters as the frequency band, the number of measurements to averaged before going to do the FFT and the measurement time; obviously, the longer the measurement time will be, the better measurements will take.

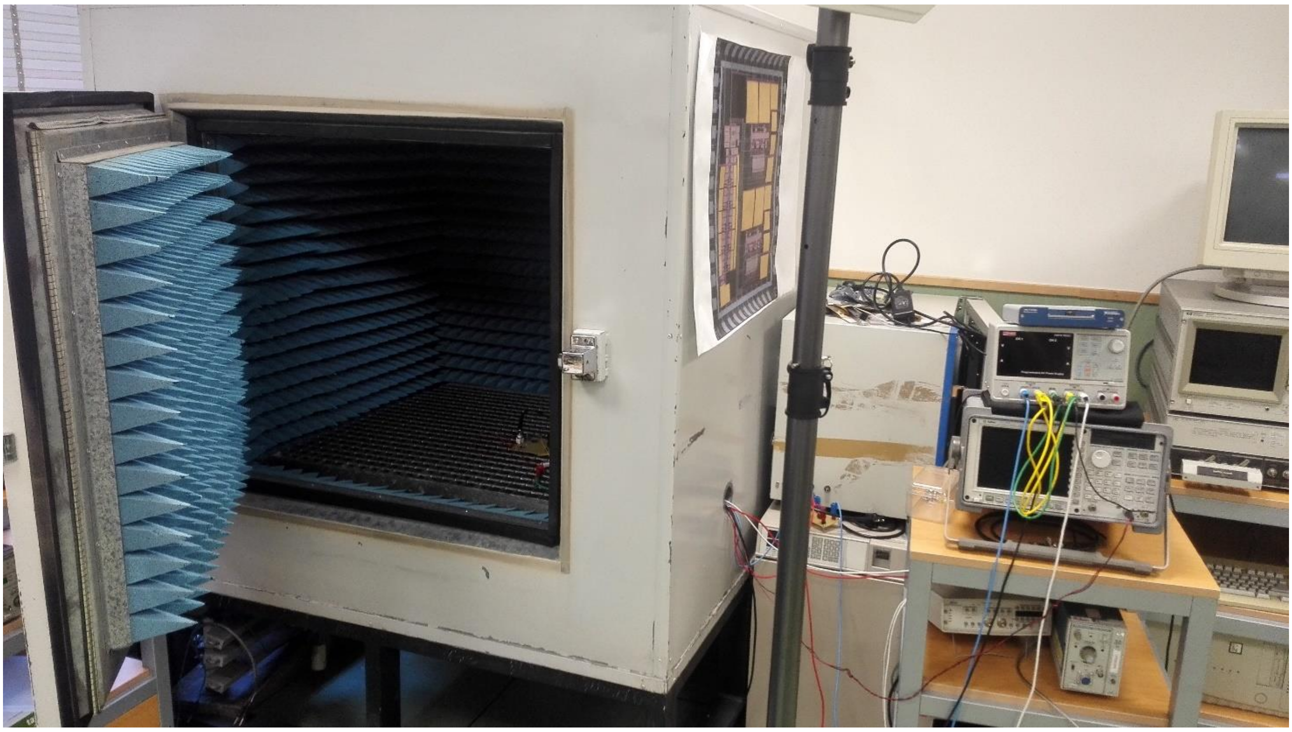
Our test was conducted by referring to three basic conditions:

- Howland pump not powered: this test is mainly used to measure the white noise
- Howland pump with positive current
- Howland pump with negative current

The fact of making positive and negative current measurements allows us to verify the symmetry of our object related to the noise allowing us to verify that there are no measures with a noise rate significantly greater than the others.

The usual measures were finally repeated in two conditions:

- On the laboratory bench
- In the Anechoic chamber



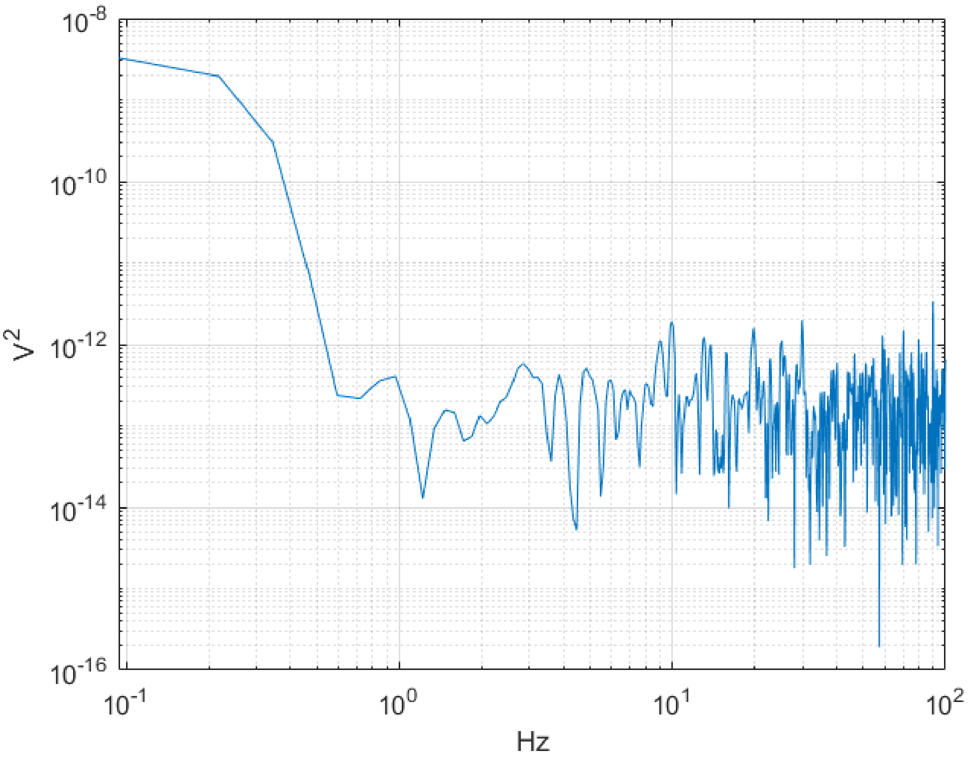
This was done to verify the differences in the two cases and to understand in an indicative way which part of the noise was due to external equipment and which one come directly from our device.

The results of the test are expressed through bilogarithmic graphs which show the frequency andthe V^2; this makes sense because in the electronic field noise can be expressed as a function of the average quadratic voltage:

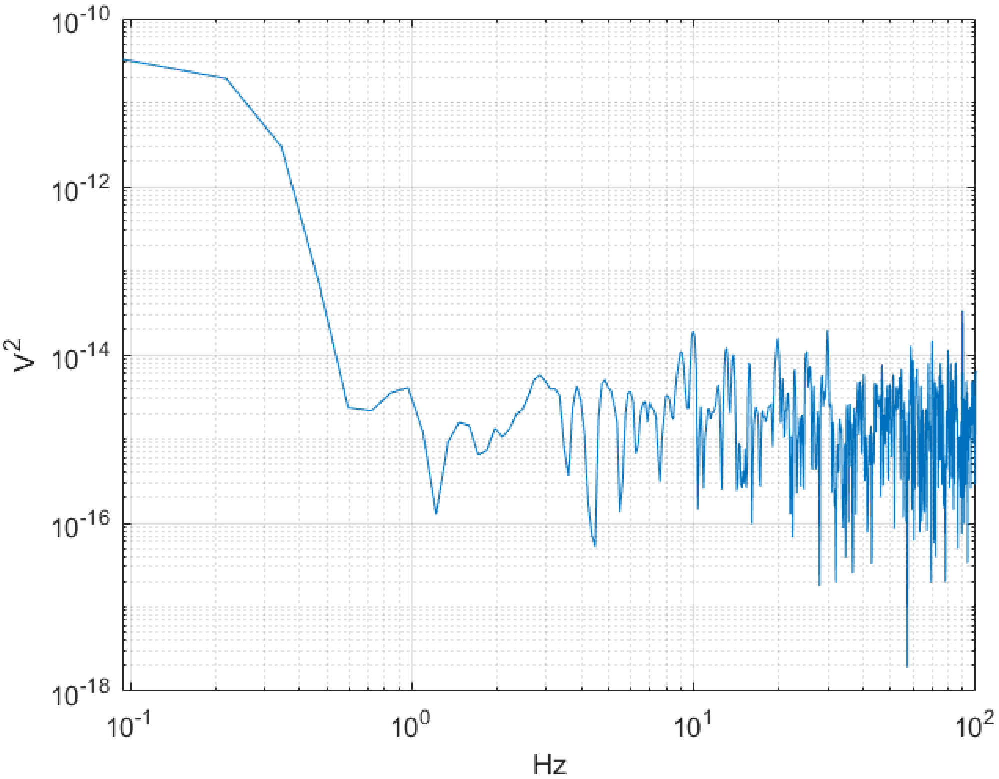
To complete this chapter we will discuss the results by comparing what has been obtained by measuring the noise directly on the workbench and the results obtained in the anechoic chamber;

Measurement without the power supply

Measurements took on the workbench



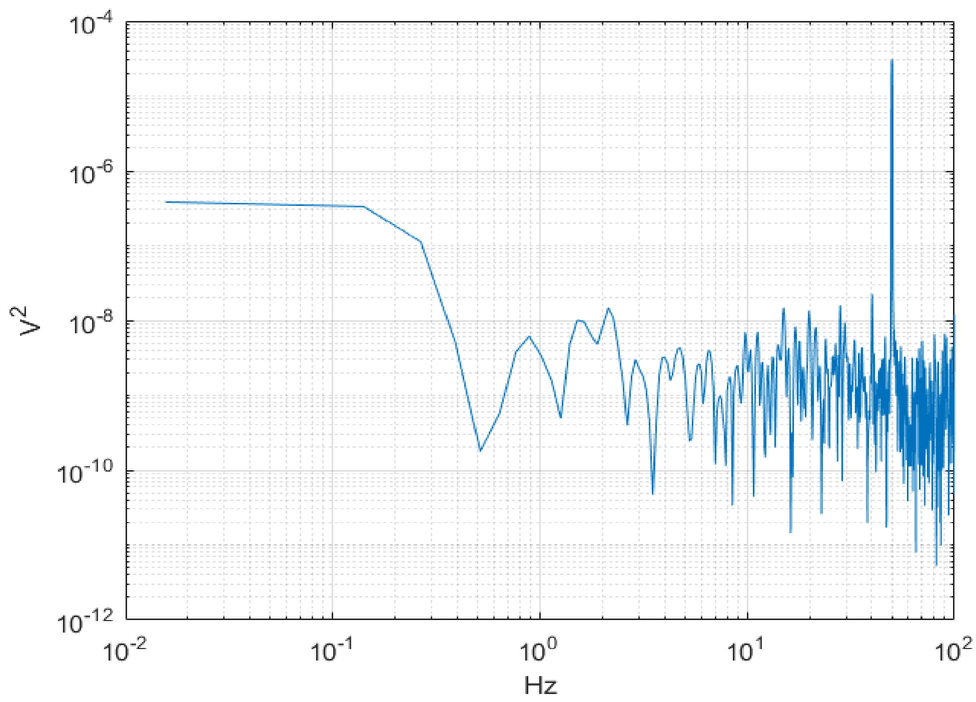
Measurements took in the anechoic chamber



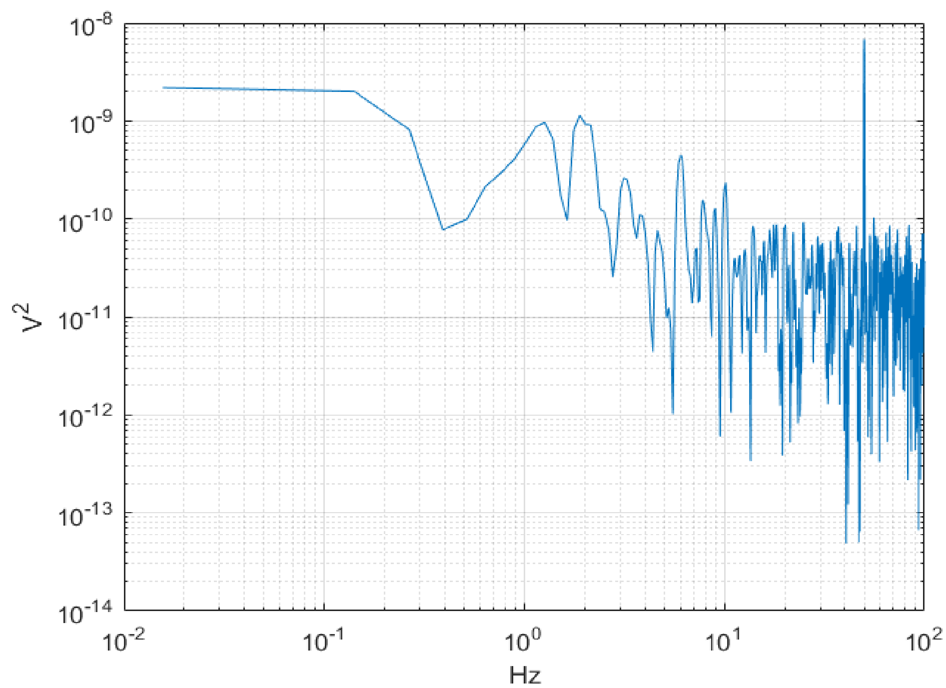
Comparing the two measures, it can be seen that, although maintaining the usual trend, the measurements in an anechoic chamber are practically translated along the y axis of $10^{-2}\ V^2$, which probably is the noise level introduced from the surrounding environment.

Measurements with the circuit fed positively

Measure took on the workbench



Measurements took in the anechoic chamber

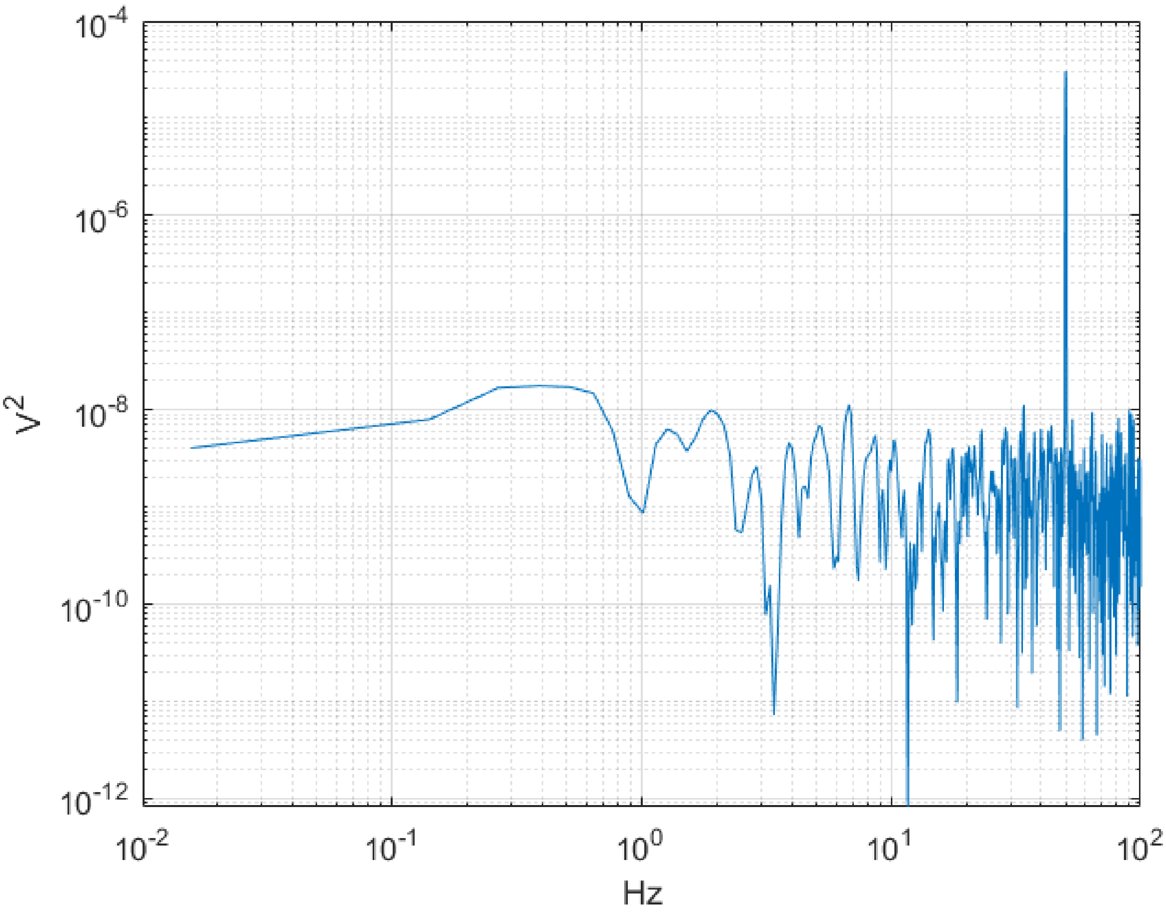


Also in this case it is noted how the effect of the anechoic chamber positively affects the behavior of our device by reducing noise when there is a current.

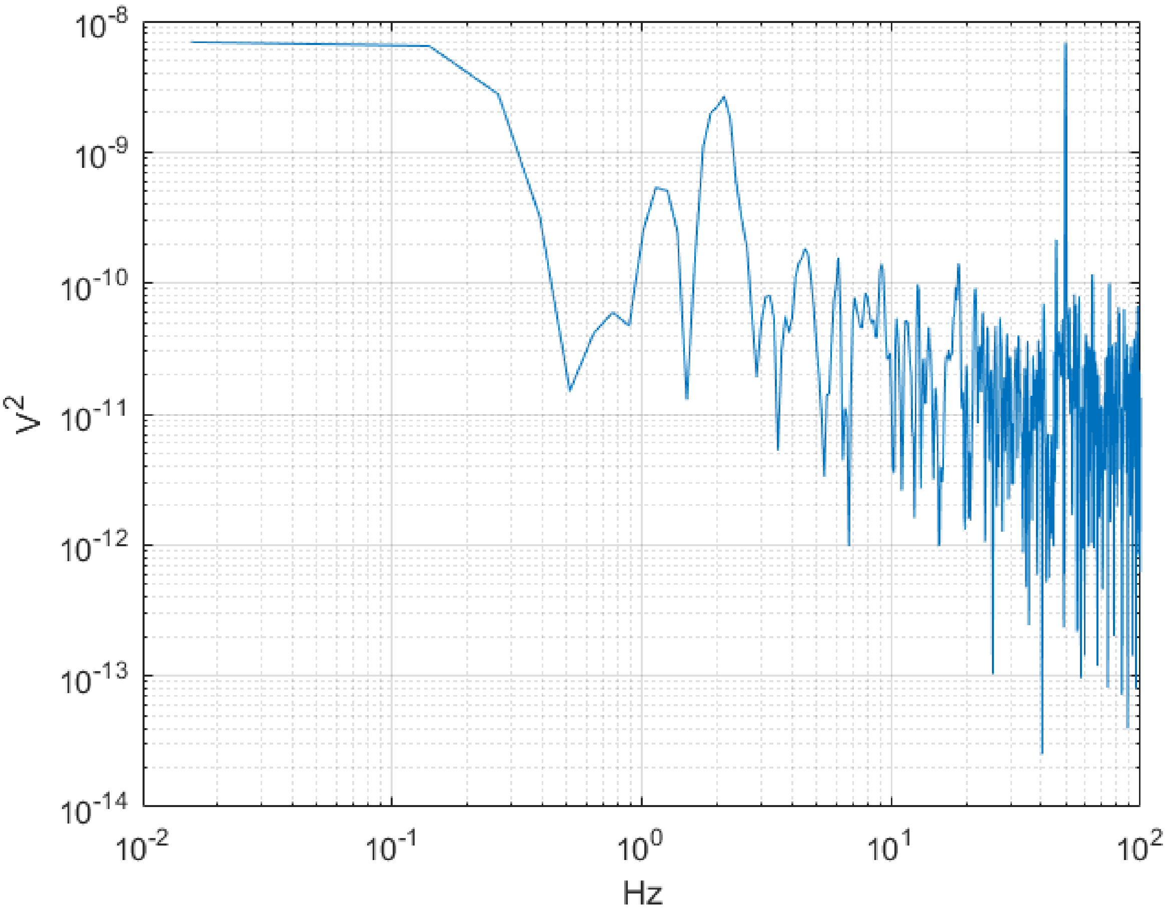
Similarly, let's see what happens if the device is powered negatively to see if there is a sort of "symmetry" of noise, especially related to orders of magnitude.

Measurements with the circuit fed negatively

Measurements took on the workbench



Measurement took in the anechoic chamber



Chapter 3 –Labview program to acquire and process measurement data

In this chapter we will examine the Labview code to understand the process followed to acquire and process measurement data. The choice of the program to use is mainly due to the fact that our DAQ card was built by Texas Instrument and therefore Labview is one of the best solutions since it offers many tools to manage the data acquisition boards.

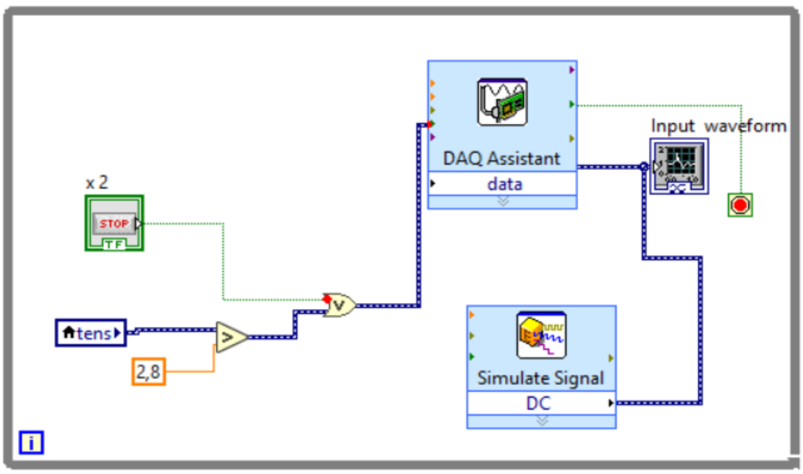
3.1 Structure of the data acquisition program

The data acquisition part was created to perform two distinct operations:

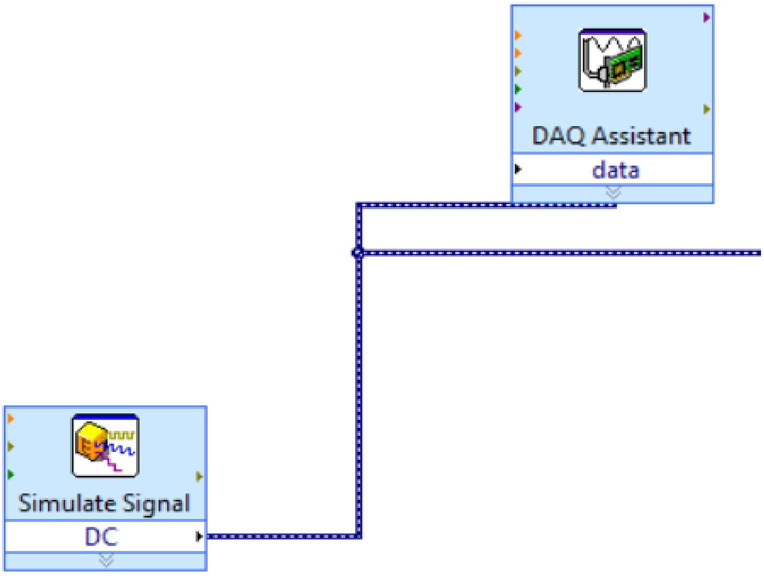
- Send a simulated signal of arbitrary form to the voltage / current converter output from the DAQ card.
- Acquire the voltage on a resistor and on the supercapacitor for a defined and limited and store this informations in a text file that will then be elaborated by the second part of the program.

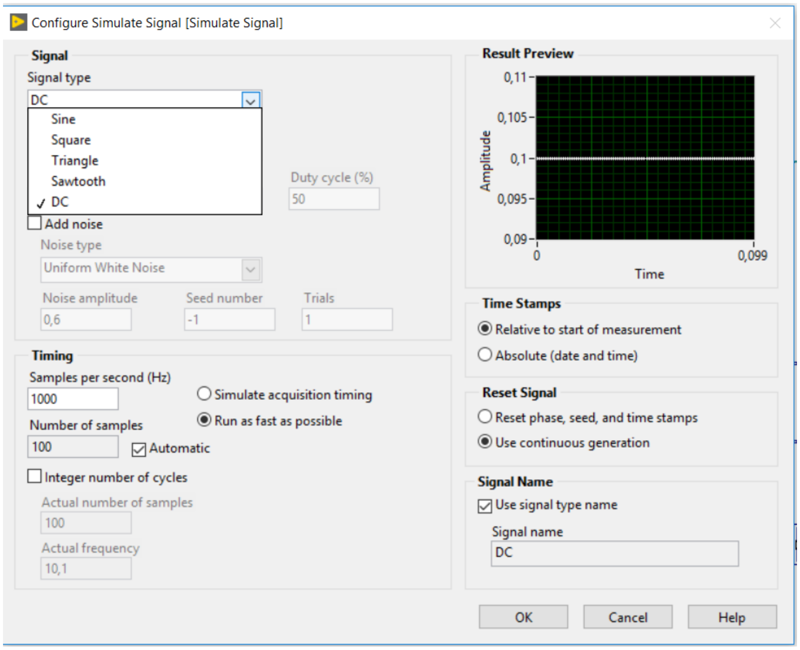
So let's start from the first of two tasks:

3.2.1 Send signal of arbitrary form



The most important block that allows to carry out this operation is the "Simulate Signal" block which, combined with the "DAQ Assistant" block, allows us to generate the desired signal. Let's see it in detail:





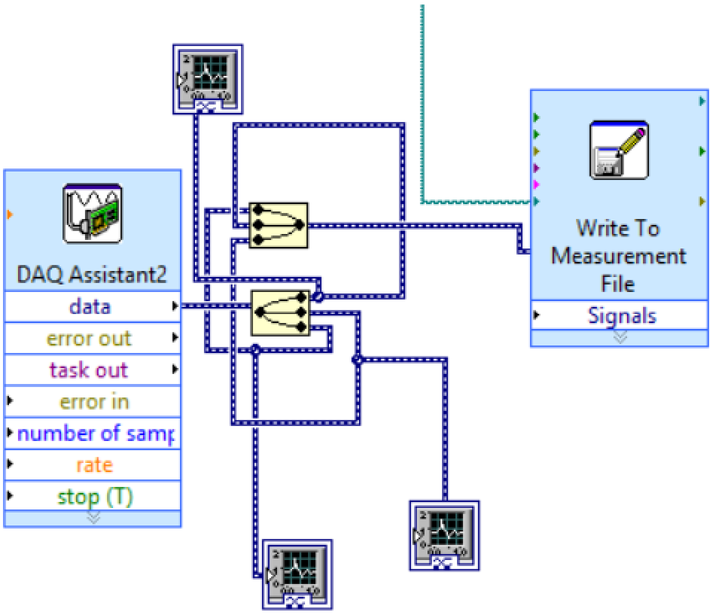
In the figure on the side you can see how the DAQ Assistant, combined with a signal generator, allows us to generate signals of any shape and at any frequency as long as we remain within the linearity limits of our DAQ board (which is specifically shown to be ± 10 V for the voltage and between 1Hz 100kHz for frequency).

In the options related to the simulated signal we can also introduce the white noise; this option has been exploited in several articles to give an element of randomness to the measures made but, in our case, being aware of the noise introduced by our Howland pump, we did not consider it interesting to insert it.

As far as the number of samples per second is concerned, in this case they do not have a fundamental value because, by setting the continuous generation, once the signal is started, this stops only when one of the two stop conditions is satisfied, ie the push of the button “stop” or when we reach a predetermined voltage on the supercapacitor (this mechanism is explained in more detail in paragraph 2.1.2).

3.2.2 Acquire voltage data and store it in a text file

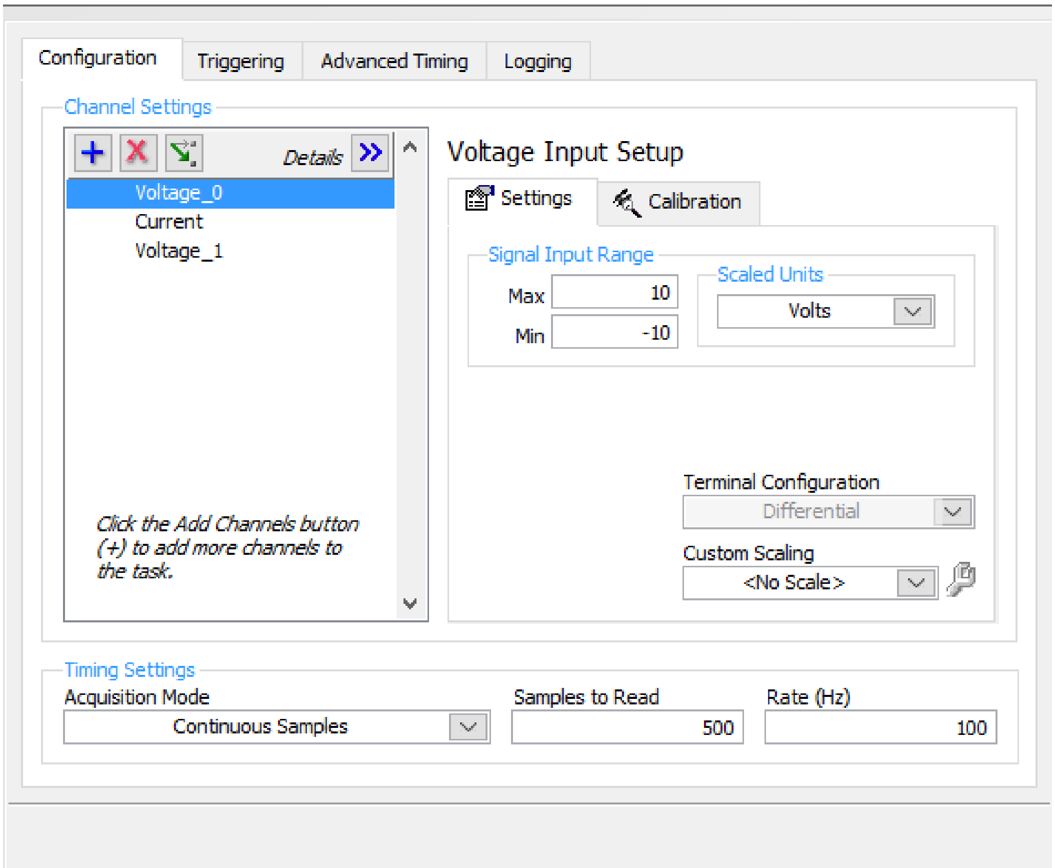
In this second operation the program will have to acquire the voltage data on a resistor (in our case the R of our voltage / current converter) and on the object connected to the converter output (in our case the supercapacitor). To make it the logical scheme set is the one below:



In this second task the "DAQ Assistant" has a greater importance because, by varying the number of samples per second, the accuracy of the measurement is improved; we also have to set the types of measures we want to do.

In this case we need a small clarification concerning the measurement of the current on the resistance because. To create the graph Q-V it would be better to have a direct current measurement but this measurement is impossible because the DAQ card in current is limited to a few mA, while in our measurements we have currents of the order of the Ampere, that is larger than a factor of 1000.

We overcame this problem by measuring the voltage on the resistance and obtaining the current during the processing phase by entering the precise value of the resistance measured by a multimeter with the 4-wire method.

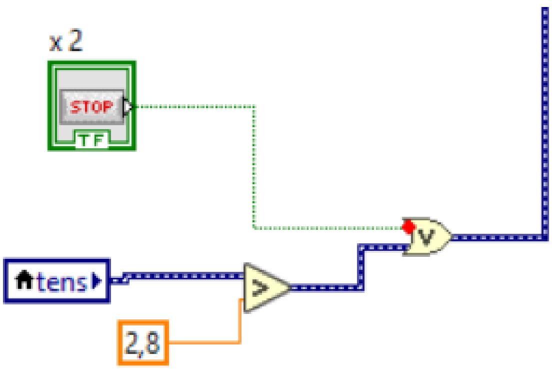


As we can see we have the current and voltage measurements that interest us, the limits of the Input signal (which are always relative to the range in which our DAQ board is linear and that are predefined), the configuration with which our measurements are taken (in our case in a differential way) and finally the question of timing;

For this options the best setting is that of "continuous mode": this mode is obtained by inserting all our system of acquisition and sending of data within a while loop and, in so doing, you can create a system which acts in loop until the stop criterion is satisfied.

In our case we chose to create a loop that updates every 500 samples read at a frequency of 100 Hz, that is every 5 seconds.

All this is done, as already mentioned, until the stop criterion is met, as we see below:

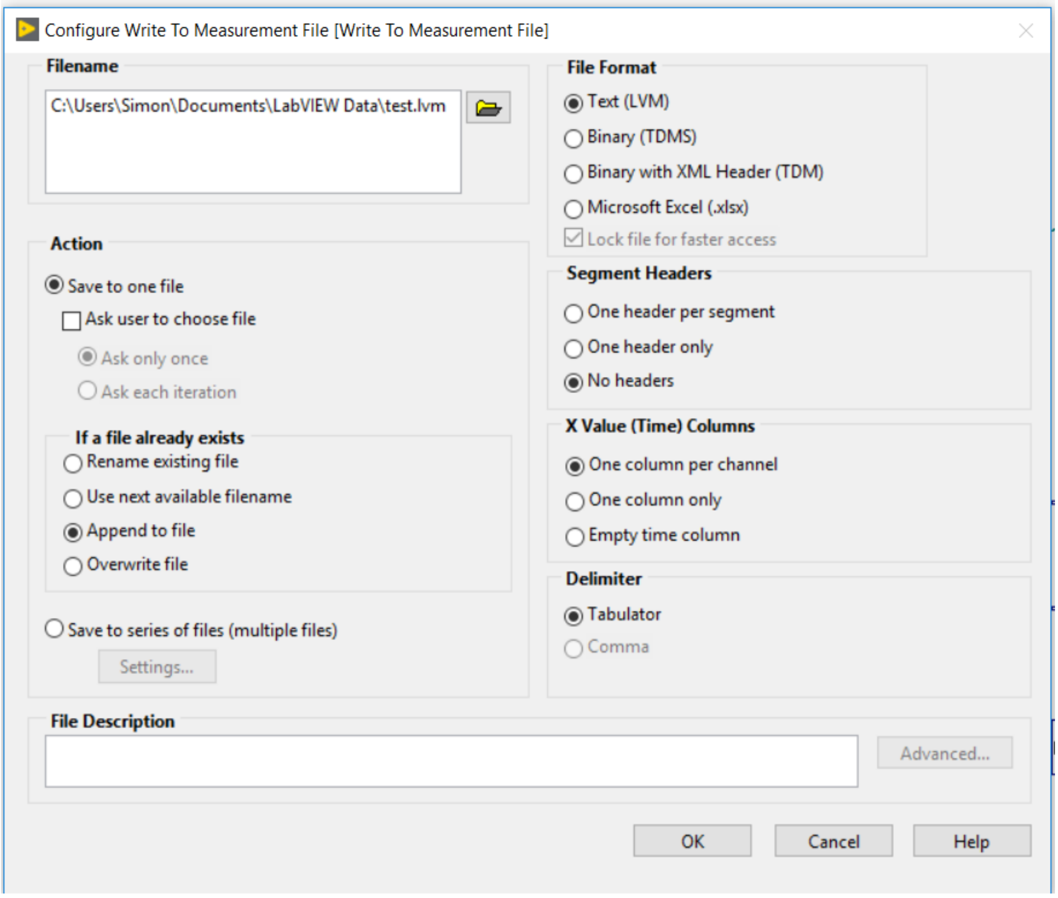


This criterion has a very simple logic and use the voltage graph to make a comparison in real time between the voltage values coming out from the graph and the threshold value (in the image set at 2.8 V). if the comparison give “true” as value the system automatically stops eitherwise it continues to take measurement data.

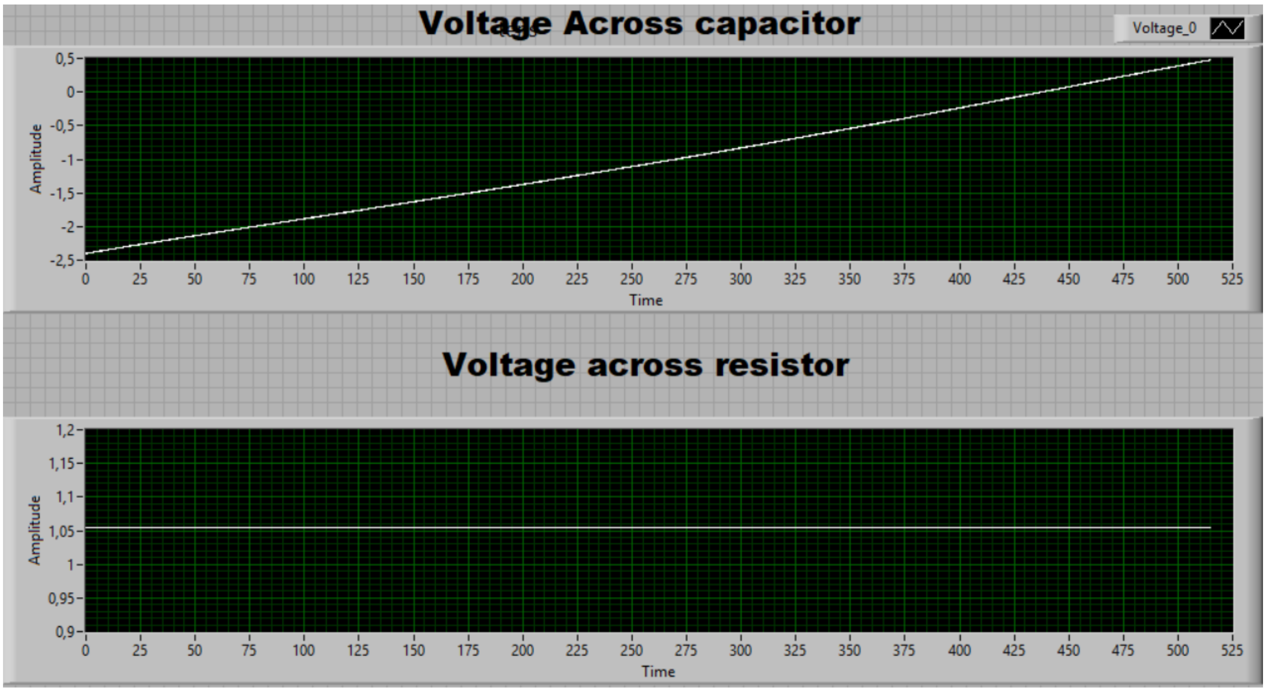
Finally, we also evaluate the possibility of manually interrupting the work cycle introducing a manual stop and a block with logical operator "or" which blocks the program in case the threshold voltage is exceeded or manually press the stop button.

The last block is nothing but a block that allows us to save the data in a text format so as to process them.

It should be noted that in the acquisition we have chosen the "Append to file" mode that allows us to practically put the results of different measures in the column instead of going to replace them; this choice allows us, in case we need the combined result of many tests, to wait a few minutes between tests, so as not to push the electronic circuit components beyond limits.



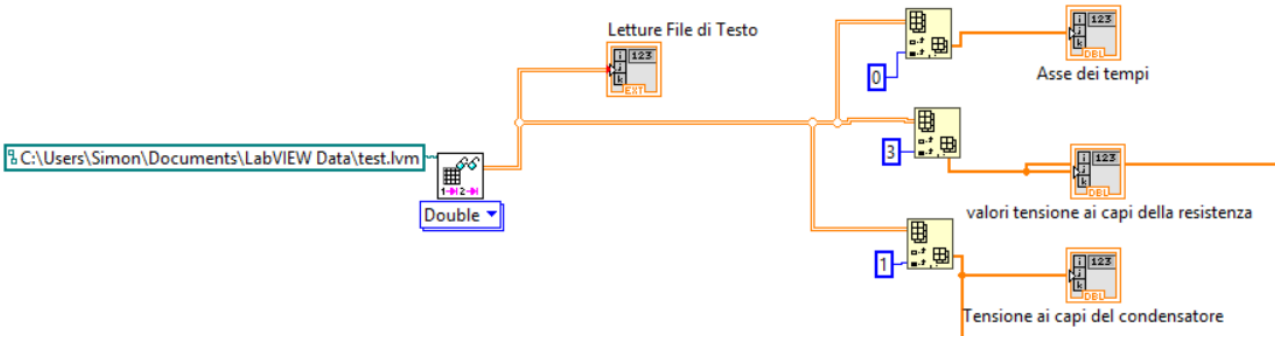
Finally the front panel was simply organized with the two graphs of voltage in order to keep an eye on the values in real time and notice any anomalies.


Voltage Across capacitor
Voltage_0
Amplitude
Time
Voltage across resistor
Amplitude
Time

3.2 Structure of the data processing program

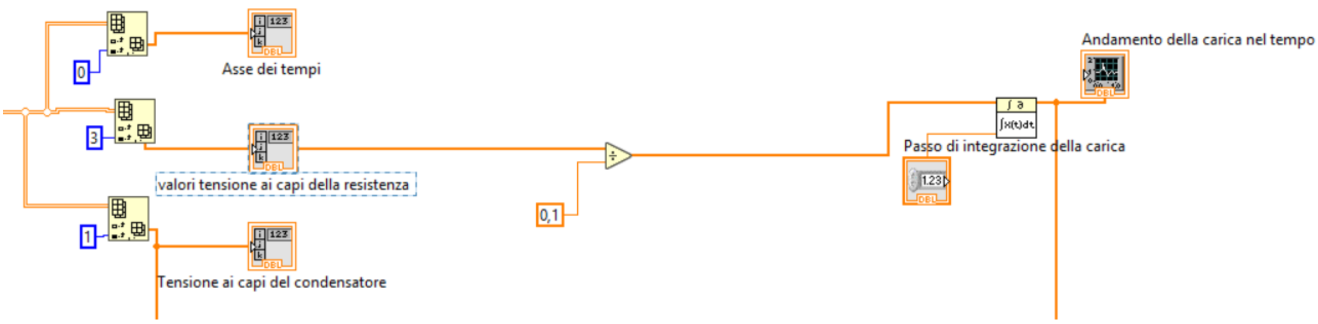
The data processing program allows us to analyze the results of the tests in a graphical way.

This program starts by reading the data file with which the acquisition program ended and proceeds to reorder the data using the "Index array" block.



In this way, by selecting the appropriate columns, we create the vector of the voltage values of the resistance, which will be used to supply the current, and the voltage values at on the capacitor.

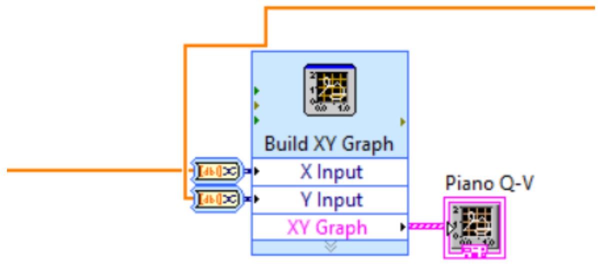
Note: as previously explained at the end of the resistance we have acquired the voltage values because our DAQ board is able to process current values up to 1 mA; in our case the currents are much greater and therefore, in order not to damage the board, we have detected the values of tension and then we have divided them by the value of the resistance, so as to obtain precisely the matrix of the currents.



From the values of the currents we make an integration and we have obtained the array of Q that we are going to plot together with the voltage above the supercapacitor. The integration step is given by the inverse of the number of samples that we have in a second.

Per realizzare i nostri grafici abbiamo utilizzato il blocco "Graph XY" che ci permette appunto di ottenere un grafico partendo da matrici di grandezze definite, che nel nostro caso sono carica a tensione.

To realize our graphs we have used the block "Graph XY" that allows us to obtain a graph starting from matrices of defined quantities, which in our case are charge and voltage.

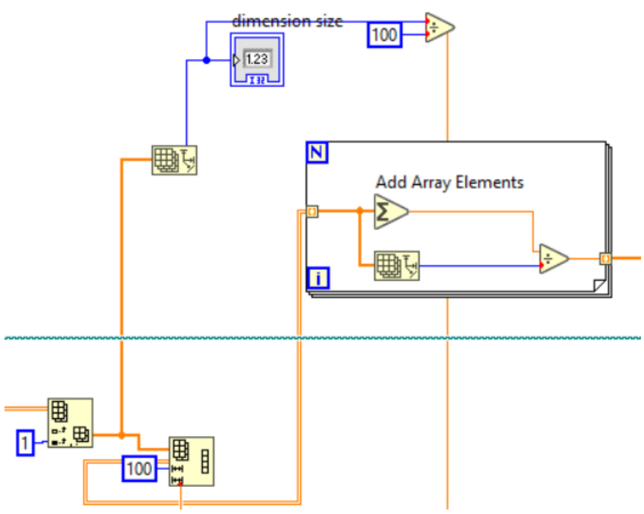


The graph create the right trend inserting 1000 points per second which is the sampling rate we entered in the part of data acquisition. However, the graph generated in this way has some irregularities due to the fact that it has many values for each moment of time.

To improve the reading of the Q-V chart, we proceed as follows:

We divide the measurements into groups of 100 points going to exploit the power of the "Reshape array" block and creating a new matrix that has as rows the number of values we want to average (in our case 100) and as columns the number of the points acquired / 100.

From this new matrix we are going to make the average row by row obtaining a final matrix that has only 1 row and N / 100 columns where each value represents the geometric mean of 100 values.



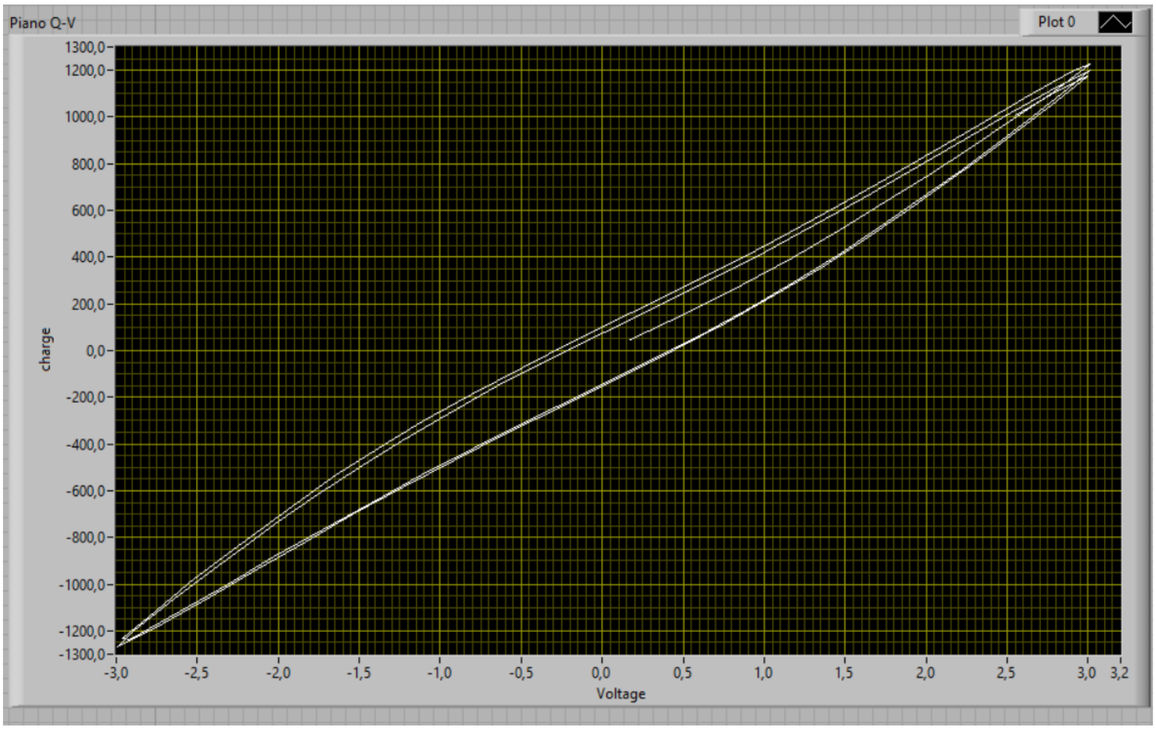
In this way we obtain a graph Q-V composed by the average values of groups of 100 measures which more clearly represents the obtained results.

The for loop allows to iterate the process of adding and dividing by 100 for N times where N depends on the number of columns of the inserted text block and is detected by the block "Size".

This fact is very useful because it allows us every time to iterate the cycle for the "right" number of measures because each trial, having a different duration, will have a different number of points that will correspond to N.

The program will read this number automatically and will make it equal to N, making it completely automatic.

Regarding the front panel of this second part, it was organized in a very simple way so as to be able to see immediately the results on the Q-V plan and the trend of the charge over time to verify if the test has gone as planned.



Chapter 4: Evaluation of dynamic and nonlinear behaviour of supercapacitor

4.1 The supercapacitor

The object where we are going to take our measurement is a Maxwell supercapacitor of 350 F. We used 6 supercapacitors and we tested them for observe different parameters; the only thing we evaluate in every device is that the supercapacitor present the same behavior in between the maximum nominal value.

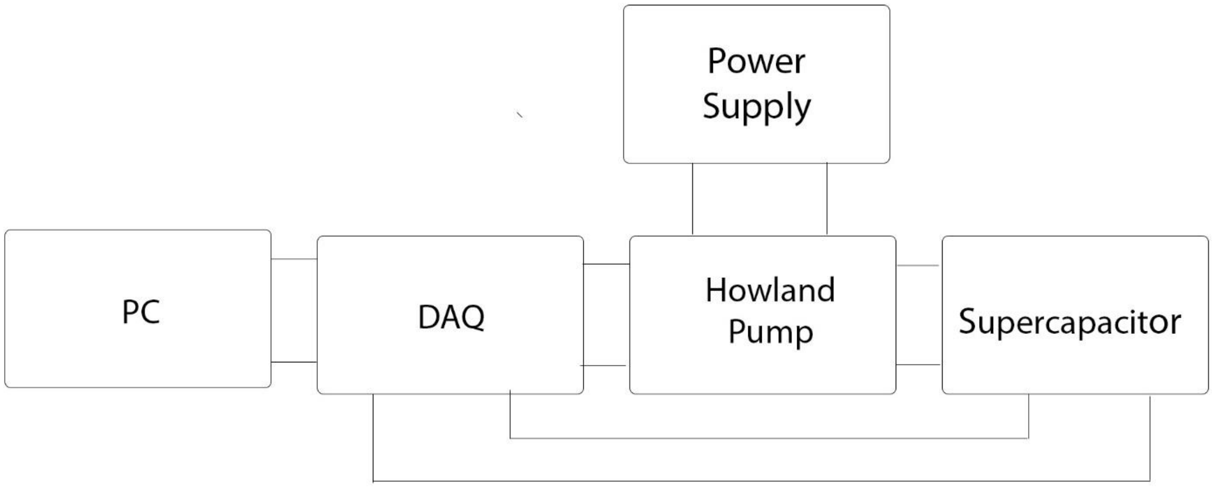
Once we verified the homogeneity of behavior within the limits we proceeded by doing different tests on each supercapacitor so that the results of a test did not influence the results of another (we have in fact considered that tests that stressed the supercapacitor beyond its limits could create micro-alterations that could invalidate subsequent tests). In terms of technical characteristics, the supercapacitor has these values:

ELECTRICAL	BCAP0310	BCAP0350
Rated Capacitance[1]	310 F	350 F
Minimum Capacitance, initial[1]	310 F	350 F
Maximum $ESR_{DC,}$ initial[1]	2.2 mΩ	3.2 mΩ
Test Current for Capacitance and ESR_{DC}[1]	31 A	35 A
Rated Voltage	2.70 V	2.70 V / 2.50 V
Absolute Maximum Voltage[2]	2.85 V	2.85 V
Absolute Maximum Current	250 A	170 A
Leakage Current at 25°C, maximum [3]	0.45 mA	0.30 mA

One thing to point out is that the type of supercapacitor used has a maximum operating voltage of 2.7 V and that the maximum recommended maximum voltage (2.85 V) is recommended for a time no longer than 1 s. We also have that the electrolyte solution inside the supercapacitor is composed of tetanethiamonium tetrafluoroborate acetonitrile.

4.2 Measurement setup

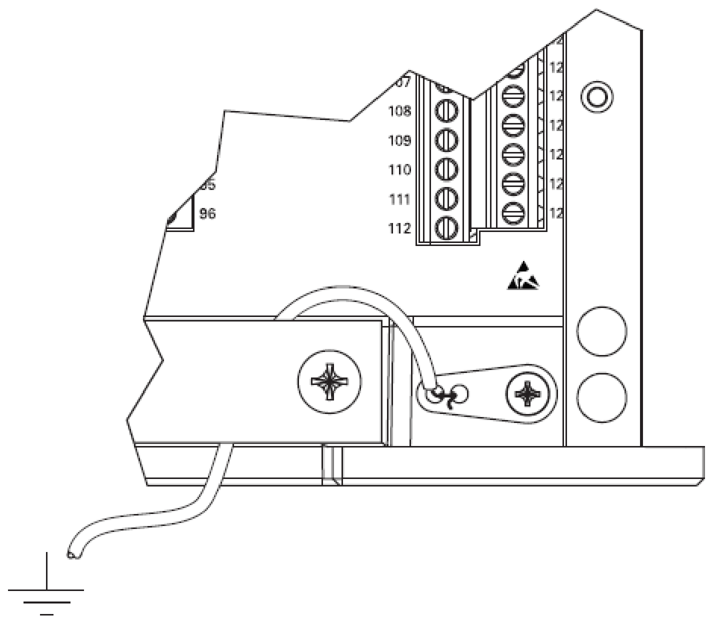
The measurement setup we used was:



Till now we have been able to observe the entire measurement chain describing in detail the part related to the PC, the Howland pump and the supercapacitor. The DAQ board and the generator are the components that we have not yet seen that complete my setup; let's go to describe them briefly:

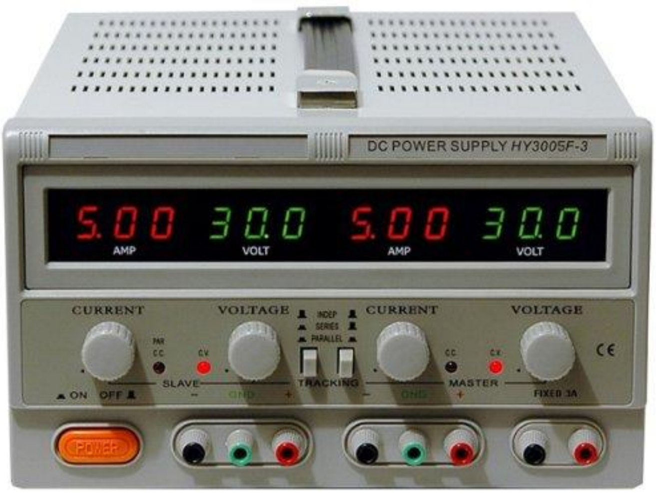
DAQ board: the DAQ board was a USB6361 card: this card has 8 analog inputs, 2 analog outputs and 16 digital channels.

The part we used by is the one related to analog inputs and outputs; as recommended by the TI manual the connections have been made with shielded cables and the DAQ board has been grounded as indicated by the manual through the appropriate connection. As far as the operating limits are concerned, this board can evaluate voltages up to 10 V and currents up to 10 mA; as we have already mentioned in the previous paragraphs the voltages sent will vary between 0.1 and 0.5 V, while the voltages measured on the resistance of the Howland generator and on the supercapacitor will not go above 4 V.

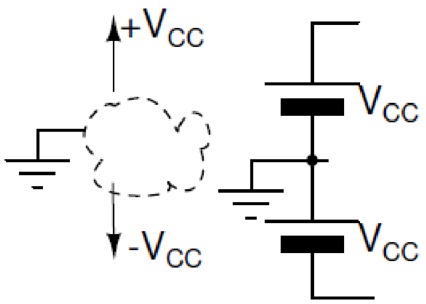


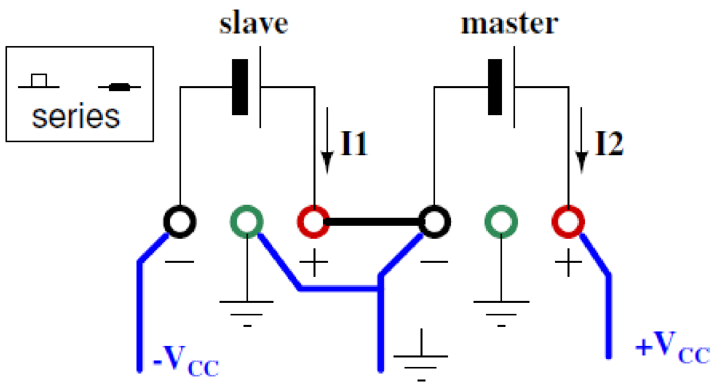
We are therefore perfectly within the linearity limits of our data acquisition card.

Voltage generator: the voltage generator used is a HY300SF type generator with a voltage range up to 30 V and a current range up to 5 A. This generator has two channels that we have configured in series by setting channel 2 as "master" and the channel 1 as "slave"; this configuration in our application is necessary because we need bidirectional currents that can only be obtained through this type of connection.



With this little digression, we have also illustrated the missing components and seen





how, considering the constraints imposed, we can say that we are working in a linear area of our setup. So now let's see and comment on the measures we have obtained from this configuration.

4.3 Measurements and Results

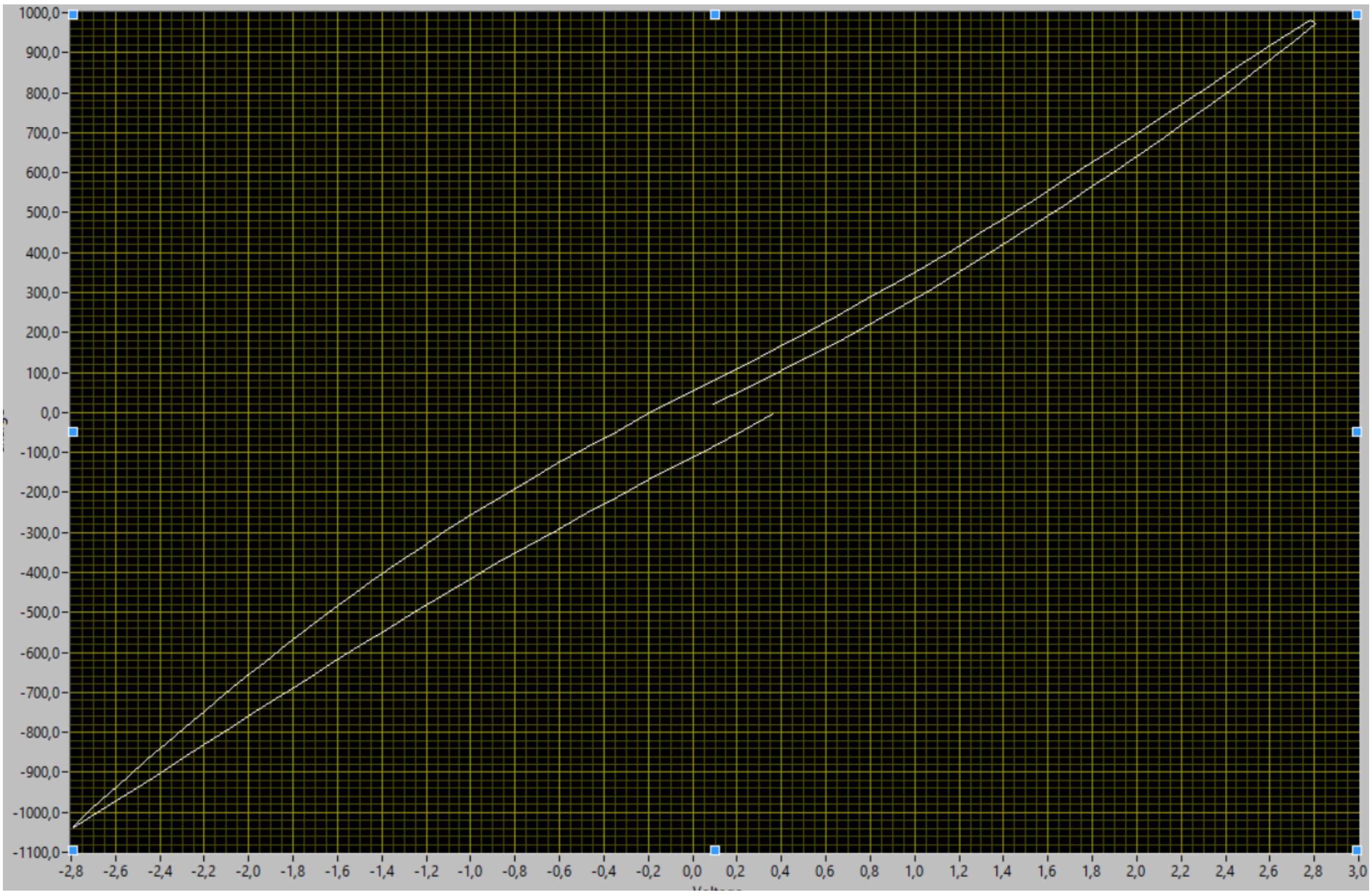
We are going now to examine the test we did on supercapacitor; for each test we will first list the methods with which it was made and the parameters that we wanted to evaluate, and then we will present and comments the resulting graphs.

1°st test: Dynamic behavior of supercapacitor: the basic hypothesis from which this work is born is the idea that the supercapacitor is a component that loses its linear behavior when we push it towards the limits of functioning. For this reason, the first test will be used to identify the behavior in this zone.

Test Conditions: supercapacitor charged up to a voltage of 2.8 V that is the declared absolute limit, and then discharged up to -2.8 V.

Parameters to evaluate: type of behavior and simmetry.

Resulting graph:



Conclusions: from the graph obtained in this test we can draw multiple conclusions:

• The supercapacitor, subject to charge and uninterrupted discharge, presents a non-linear behavior that has the characteristic shape of a cycle of hysteresis, even if very tight; this result is important and, in some

way, completes previous studies that affirmed that the behavior of supercapacitors is linear between -2.5 V and 2.5 V.
This linearity is lost as soon as we work closer to the limit.

- Another interesting conclusion is that the resulting curve is not a closed curve (it becomes if we re-charge the device up to 2.8V). This leads to the conclusion that even the supercapacitor, like all hysteretic phenomena, presents a sort of "first magnetization curve" that further characterizes the curve found as a hysteresis curve

- The supercapacitor is not completely symmetrical; in fact, it can be noted that the accumulated charge is slightly different at the two maximum voltages (negative and positive). This fact will then be further verified by subsequent tests.

- At the point where there is an inversion of the polarity we can note a sort of voltage drop; this fall is due to the internal resistance of the supercondenator and therefore, starting from the graph and knowing the charge current, we can also evaluate this value.

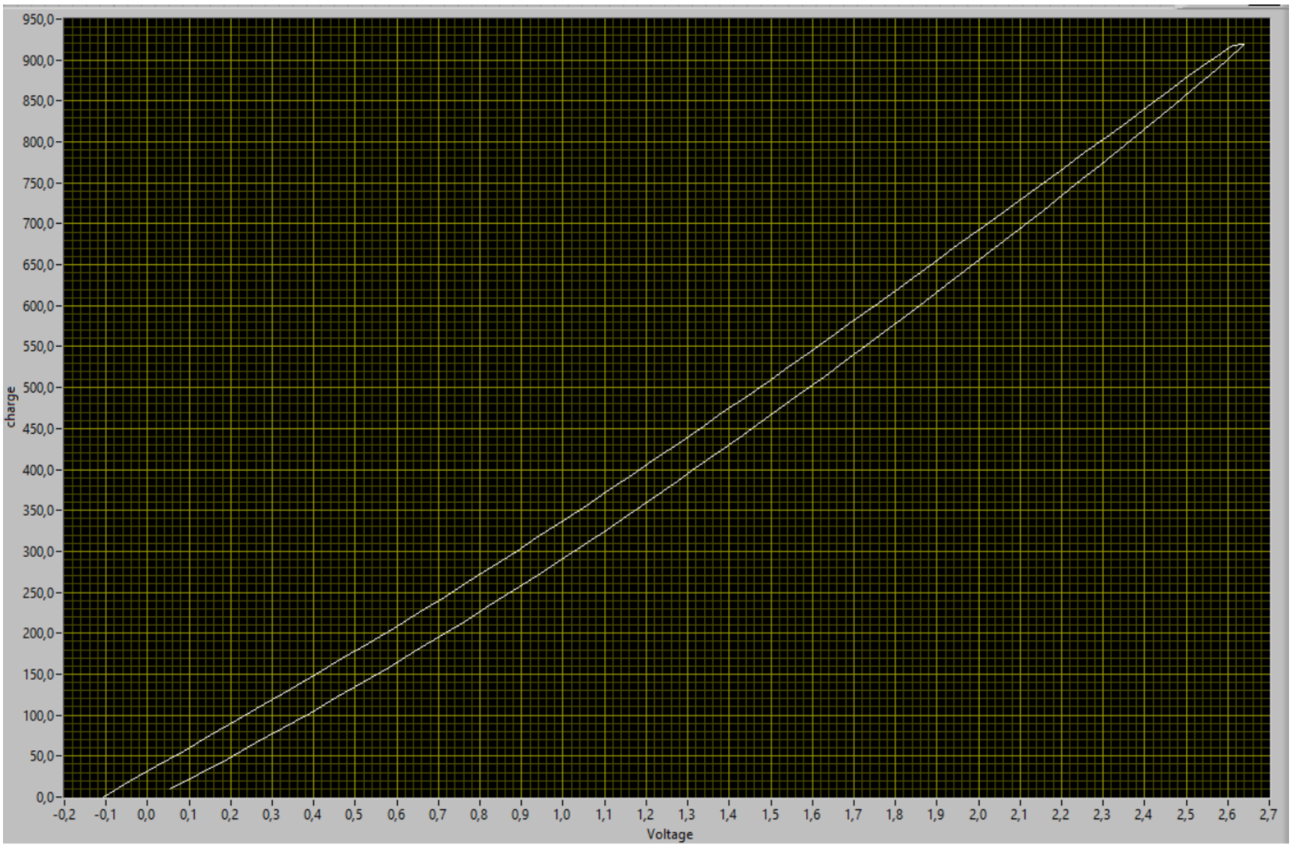
2°nd test: dependence of the hysteresis curve by the intensity of the charging currents: the idea of this test is to go to evaluate the voltage drop that occurs when you reverse the current direction so as to see the value of the internal resistance, to understand if this varies or not, and check the effect of the current on the hysteresis curve (which should become significantly larger with the increase of I).

Test conditions: supercapacitor charged and discharged up to ±2.7 V.

Parameters to be evaluated: value of the internal resistance and its behavior.

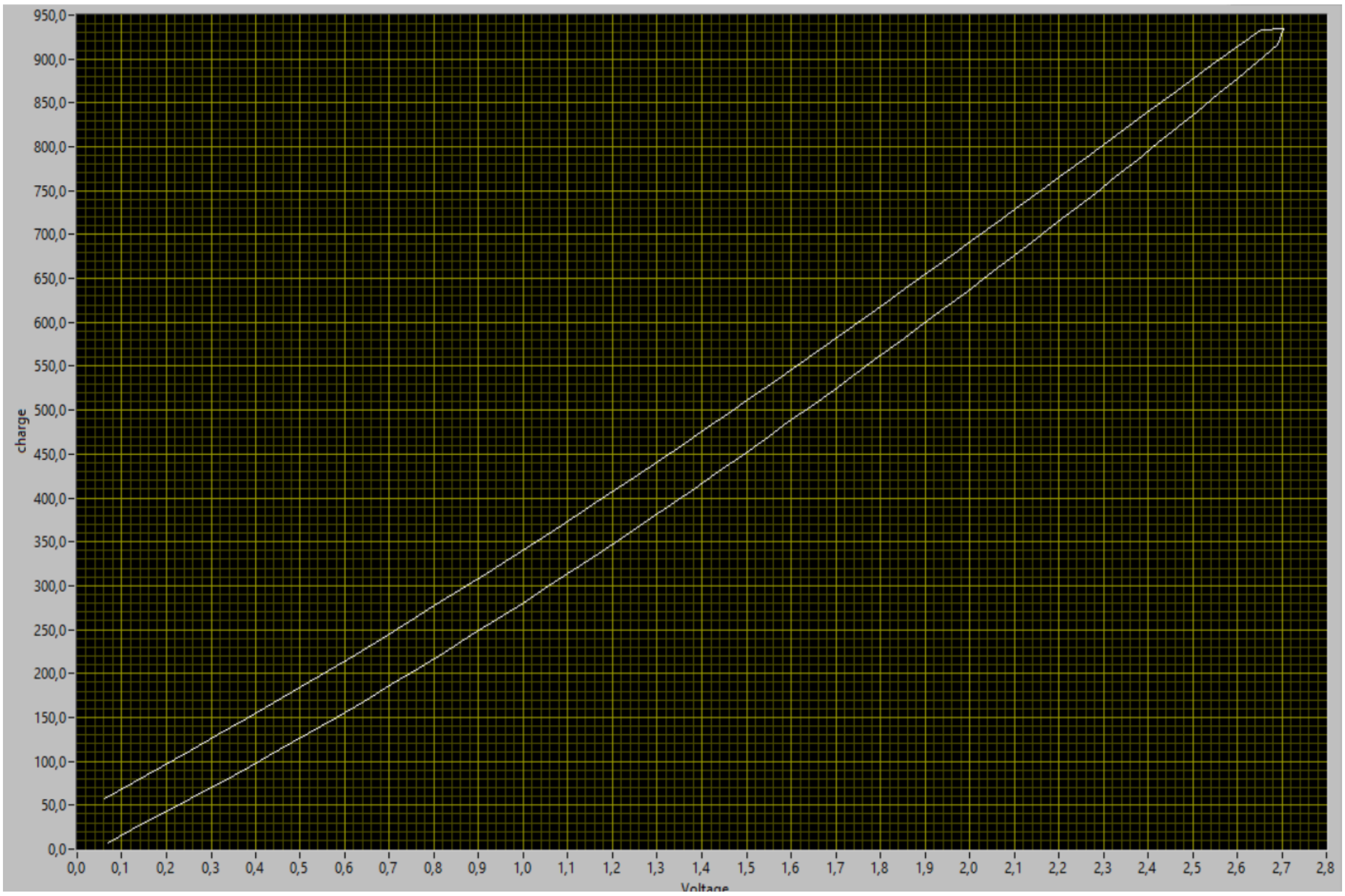
1 A test: in this first test it can be observed that, at a current of 1 A, corresponds a voltage drop equal to 0.02 V; from these two data we can conclude that the internal resistance of our supercapacitor is equal to:

$$\frac{V}{I} = R = \frac{0,02}{1} = 0,02\ \Omega$$



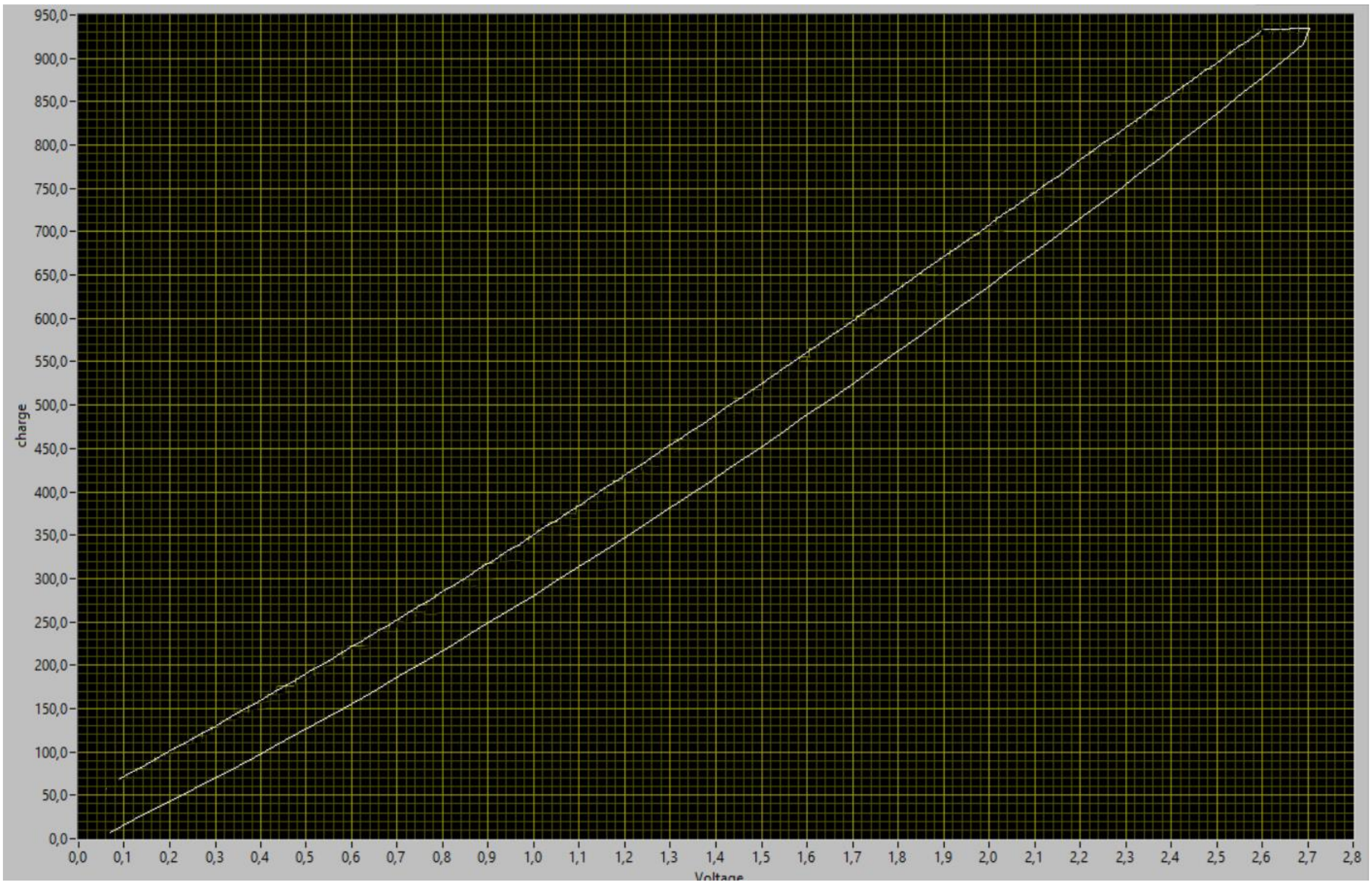
3 A test: in the 3 A test the voltage drop is about 0.06 V; knowing the current the internal resistance is equal to:

$$\frac{V}{I} = R = \frac{0,06}{3} = 0,02\ \Omega$$



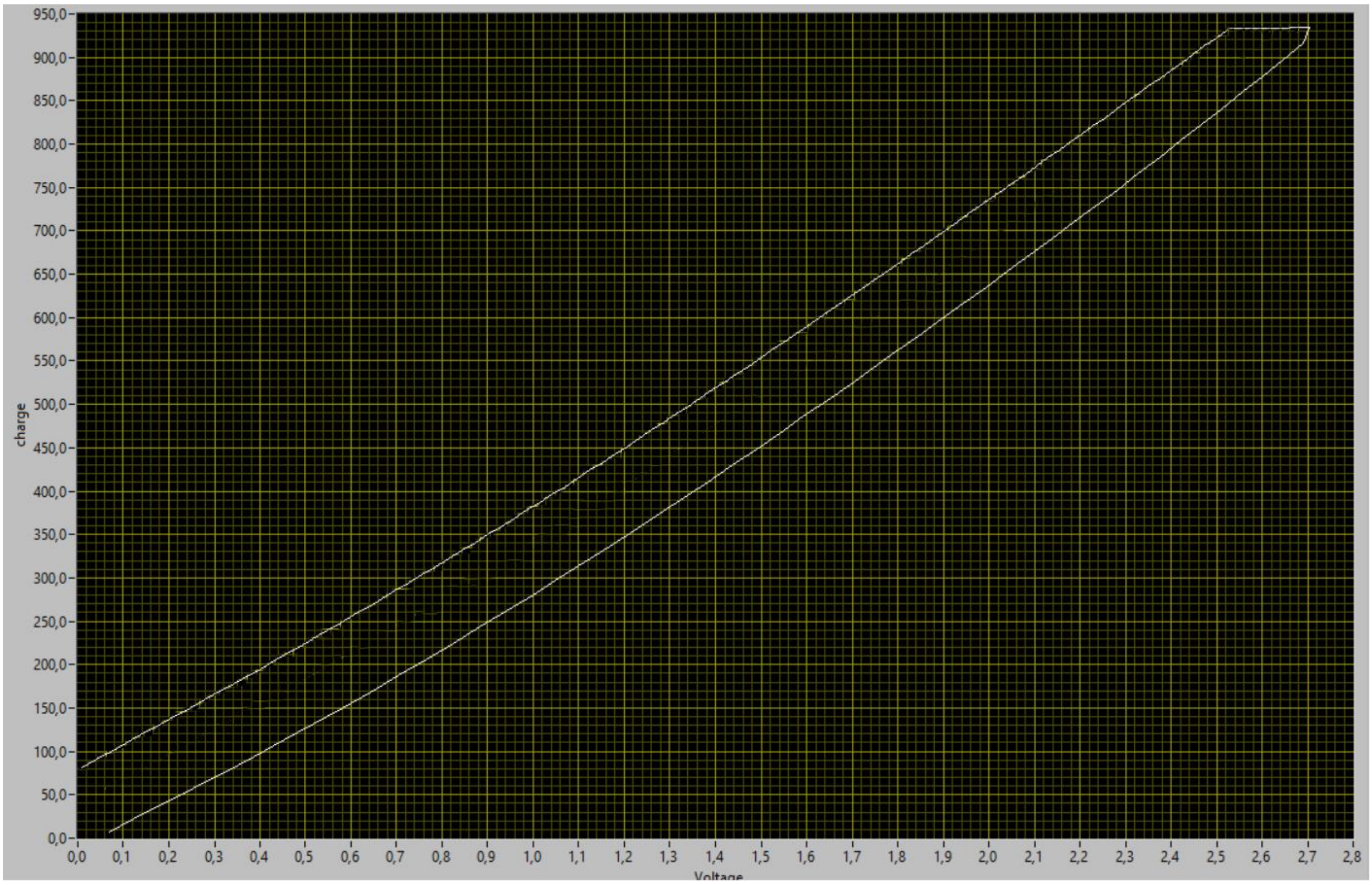
5 A test: in the 5 A test the voltage drop is about 0.11 V; knowing the current the internal resistance is equal to:

$$\frac{V}{I} = R = \frac{0,11}{5} = 0,022\ \Omega$$



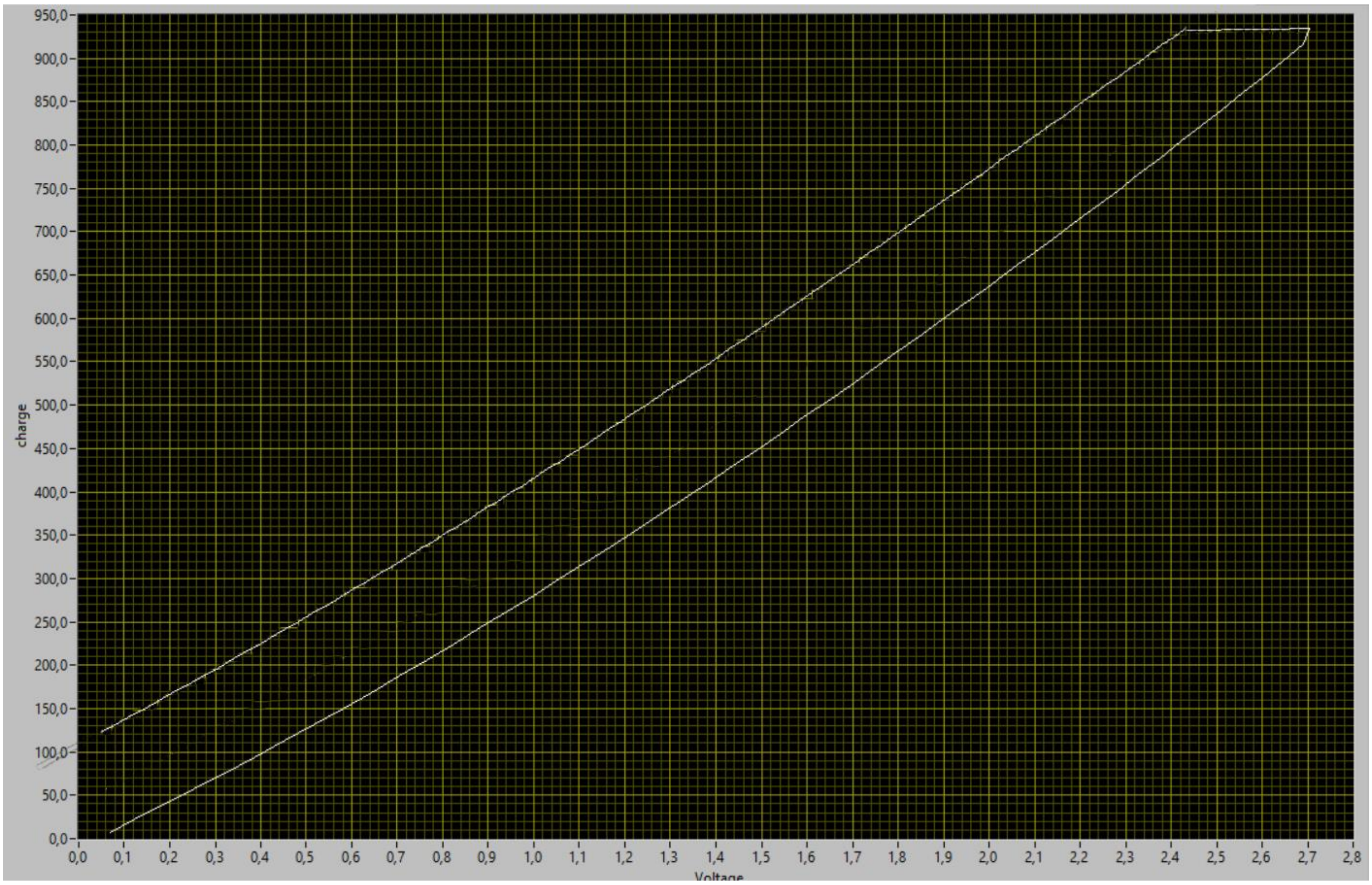
7 A test: in the 7 A test the voltage drop is about 0.14 V; knowing the current the internal resistance is equal to:

$$\frac{V}{I} = R = \frac{0{,}14}{7} = 0{,}02\ \Omega$$



9 A Test: in the 9 A test the voltage drop is about 0.18 V; knowing the current the internal resistance is equal to:

$$\frac{V}{I} = R = \frac{0{,}18}{9} = 0{,}02\ \Omega$$



The tests can be summarized in a table that shows the resistance values obtained from the 5 tests performed. This is what we obtain:

	ΔV(V)	I(A)	R(Ω)
1 A Test	0,02	1	0,02
3 A Test	0,06	3	0,02
5 A Test	0,11	5	0,022
7 A Test	0,14	7	0,02
9 A Test	0,18	9	0,02

Conclusions: from the proof obtained, we can conclude that:

- The supercapacitor has an hysteresis curve which, as we expected, increases its area as the current increases due to the fact that the supercapacitor has a resistive part.

- The internal resistance of the supercapacitor is a practically constant resistance of 20 mΩ. We can argue about the meaning of this resistance but, at least till now, we can just think that this resistance simulate the behavior of supercapacitor whene there is a step current as an input.

3rd Test: tests on supercapacitors beyond the limits of operation: this test is of interest to us to understand what it means to push a supercapacitor beyond its limits in terms of hysteresis cycle and in terms of behavior.

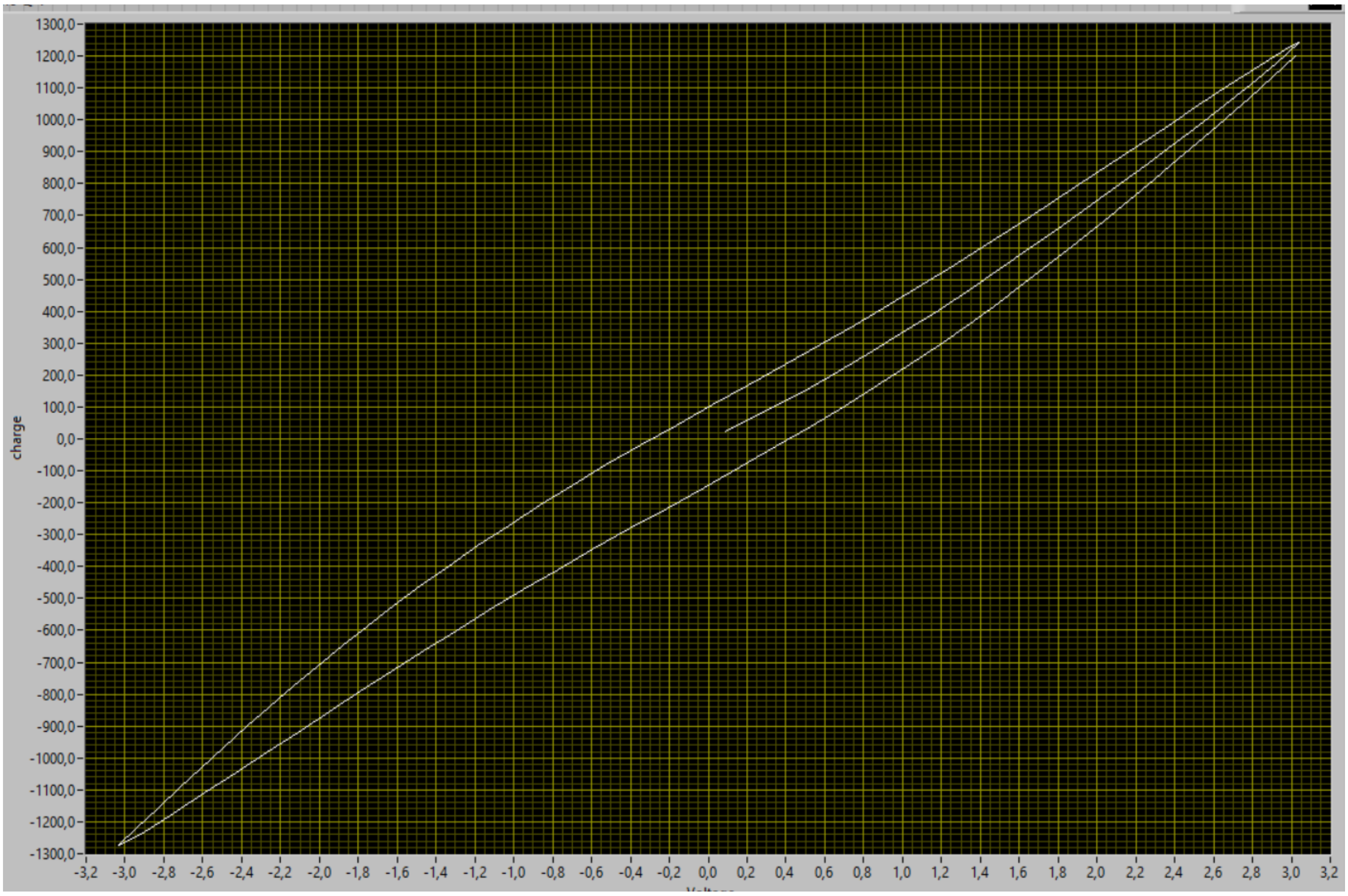
Test conditions: the tests carried out in this case were two out of two different supercapacitors:

• **Test 3.1:** we carried out a complete charge and discharge cycle with a current of 3 A up to ± 3V so as to bring the capacitor above its operating limit and, subsequently, we charged it and discharged it again within ± 2.7V

• **Test 3.2:** we went further and we charge the supercapacitor until the voltage increase was almost zero so to reach the maximum limit of the supercapacitor, then we discharged and charged it again.

Parameters to Evaluate: behavior of the supercapacitor beyond its limits.

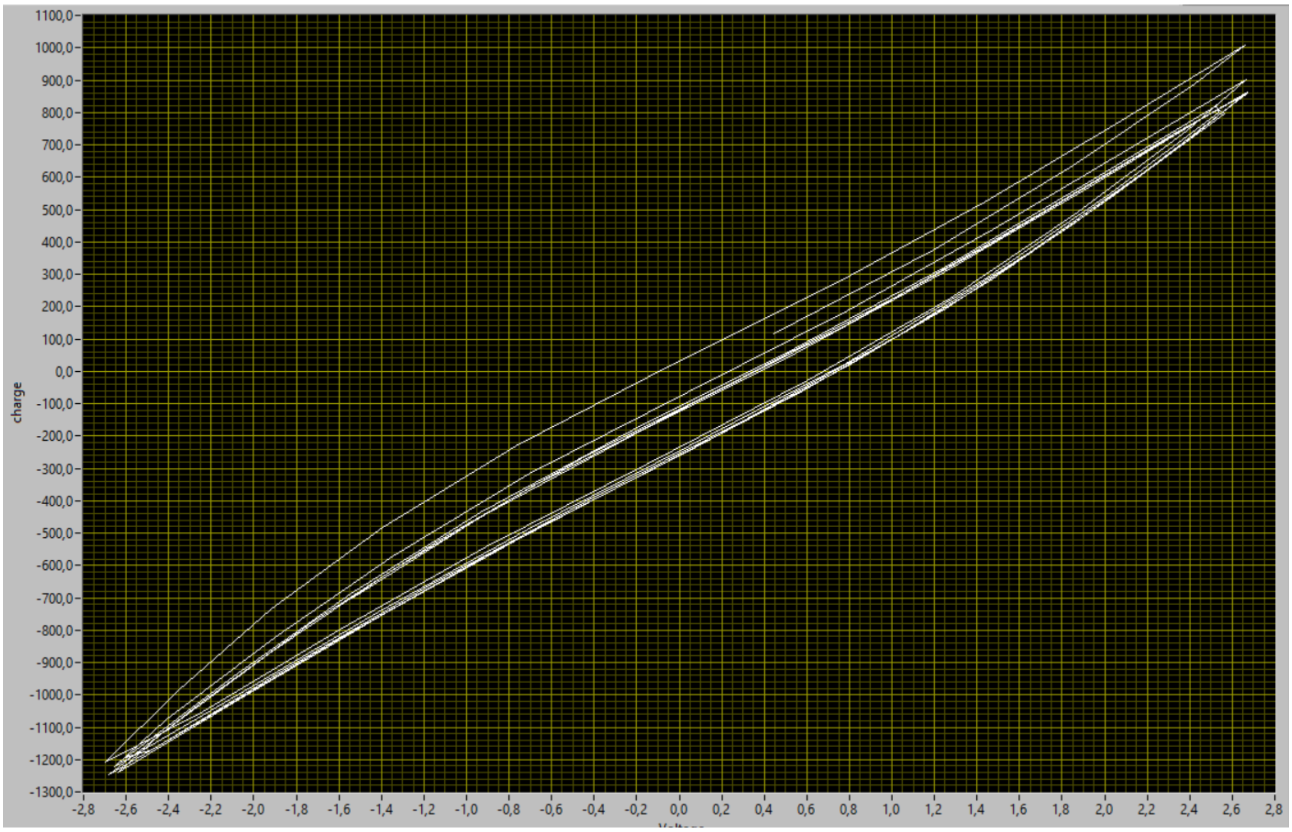
Test 3.1: as already mentioned, we first cycled the supercapacitor between ± 3V:



And this is what the result was. It's possible to see that the hysteresis cycle is maintained and does not show significant alterations respect to the other tests carried out; in the same way the slight asymmetry in the charge accumulated in charge and discharge is maintained.

After the test carried out, we spent a period of 30 minutes to allow the supercapacitor to cool down in order to eliminate possible transient effects and then we carried out several charge and discharge cycles between ± 2.7V.

The result was the following;



What can be observed is that the major loop of the supercapacitor, when this is subjected to stress, changes and, in particular, the capacity of the supercapacitor to accumulate charge is reduced.

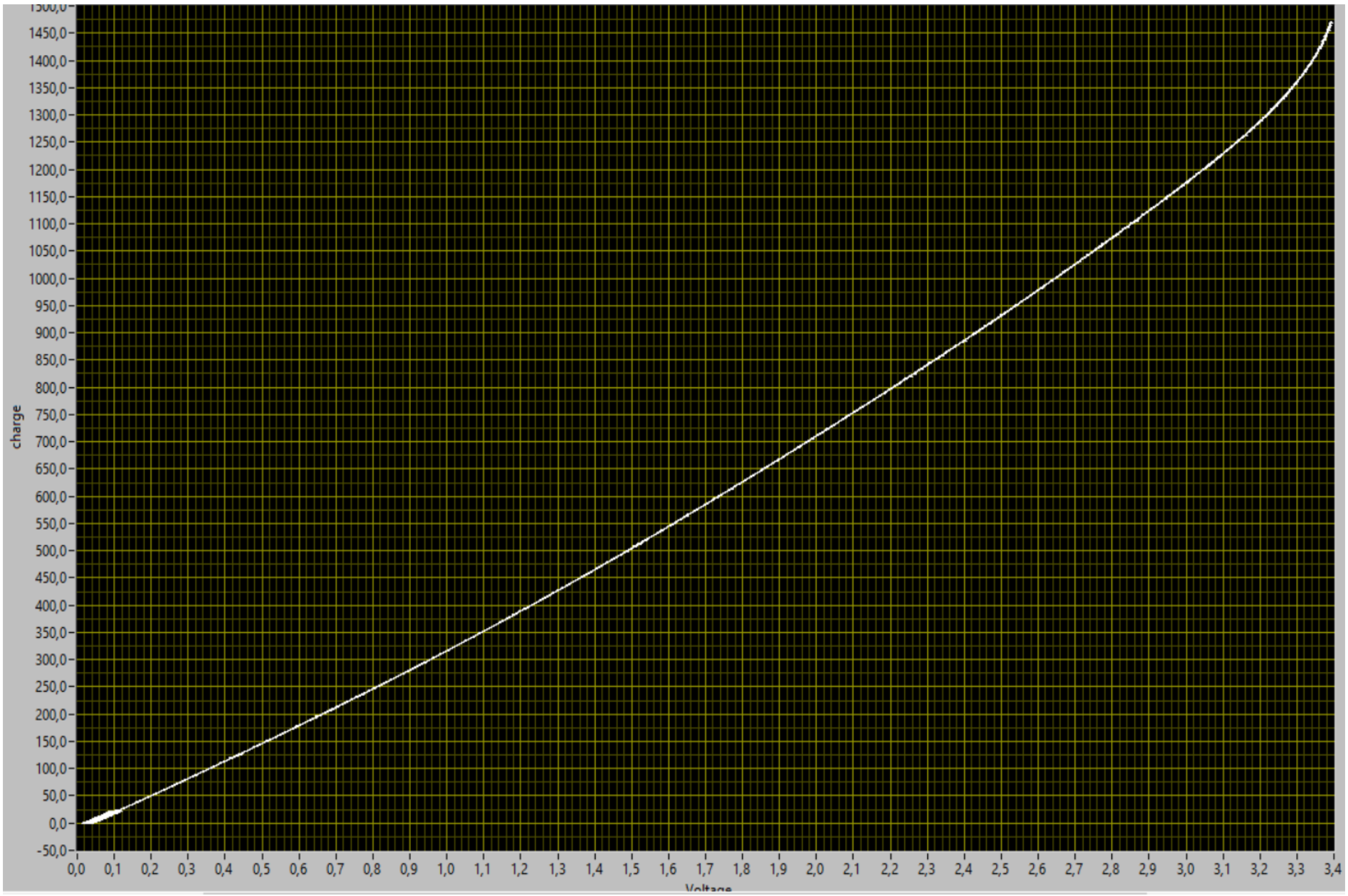
The explanation for this phenomenon, since the capacitor is still capable of functioning, can be related to the liquid electrolyte which, subjected to excessive tensions, could presents chemical alterations and is no longer able to transfer ions as before.

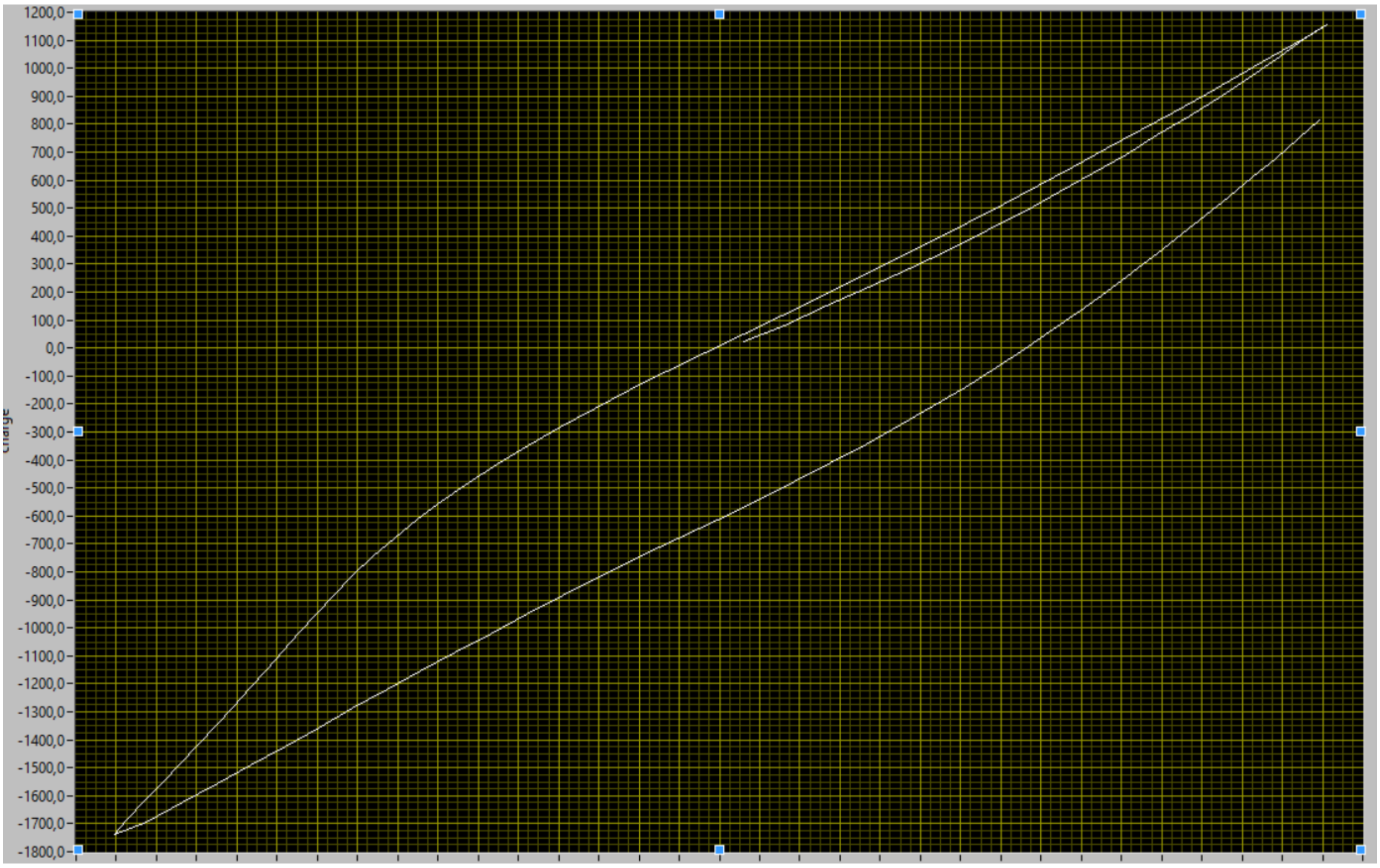
Note: we did more tests with cycles higher than ± 3 V; in this cases the major loop is lowered again and therefore it can be concluded that the consequence due to the operation of the supercapacitor beyond its limits is a reduction in the ability to accumulate charge.

This reduction is also permanent and therefore, if we need operation in anomalous conditions and above the limits, we will have to take it into account.

Test 3.2: in this case before carrying out the charging and discharging cycle, we charged the supercapacitor up to its voltage limit.

After doing this test, we discharged it completely, we waited 30 minutes to cancel any transient effects, and then we charge our device with a cycle of ± 3V to compare it with the initial cycle we did in test 3.1





As we can notice, the capacity of accumulate charge now decrease a lot and the difference between the two cycles is 300 C.

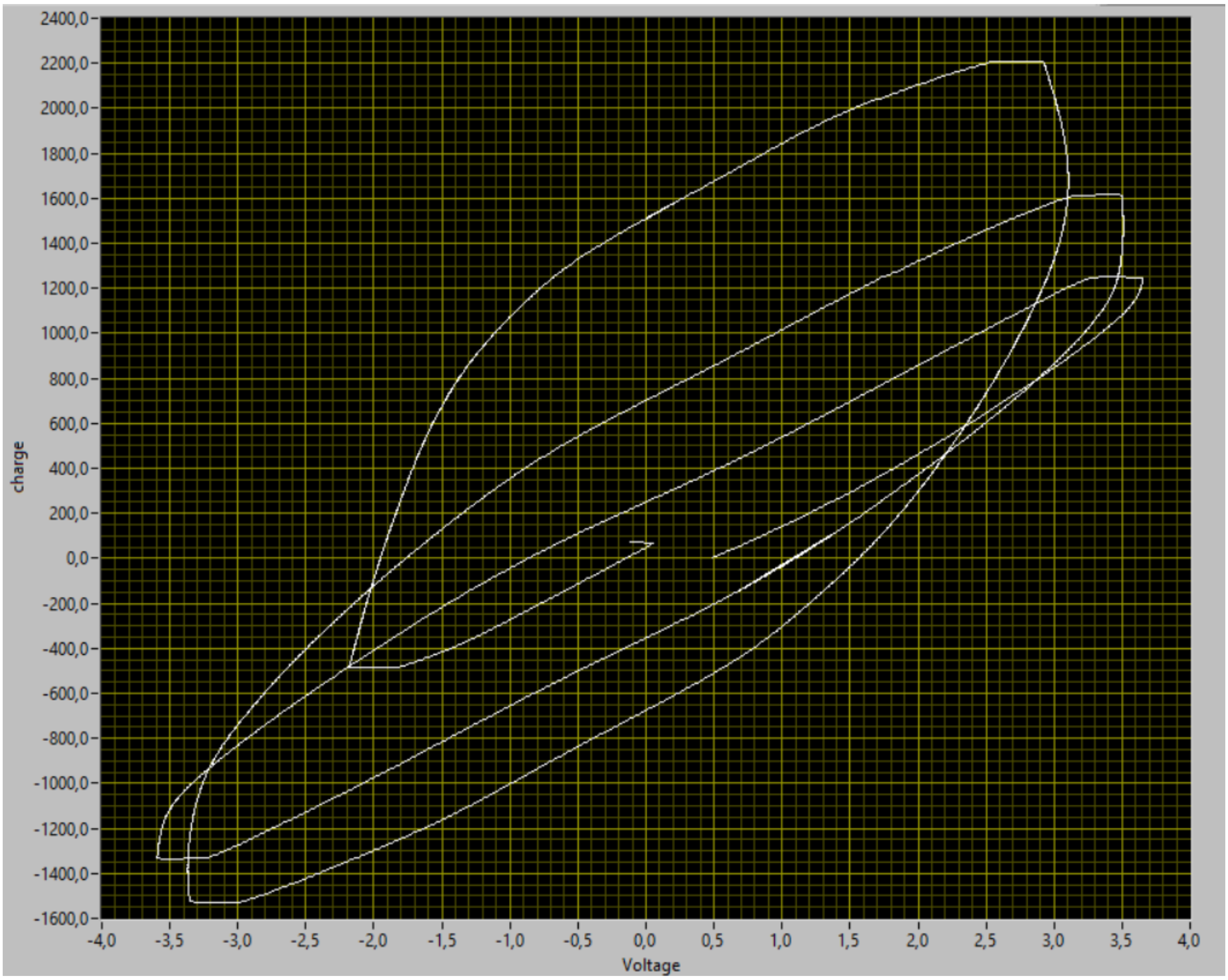
This second test confirms what we have already seen and reinforces the hypothesis according to which greater stresses follow greater losses in the capacity of charge accumulation.

The test was interrupted at the end of the second charging cycle because the supercapacitor was heating up a lot and therefore, for safety reasons, we considered it right to conclude here since what interested us was to evaluate the reduction in the ability to accumulate charges.

4th Test: stress test with maximum cycle: this test aims to test the maximum limits of the supercapacitor to understand the absolute limits of this device.

Test conditions: the supercapacitor is charged until the voltage variation is practically nil (and therefore the capacitor has reached its limit). The charging and discharging phases are carried out with a current of 10 A, which is the maximum current available to us.

Parameters to Evaluate: behavior of the supercapacitor to its maximum limits.



Conclusions: from the graph obtained it can be observed that already after a cycle between ± 3.7 V the supercapacitor shows evident alterations in the behavior. These alterations result in a lower saturation in voltage and, after the third cycle, slight deformations on the physical level (slight enlargement) and a huge increase in temperature.

For this reason, after the third cycle we concluded the test considering that this was the maximum limit of cycles (in a practical application in fact, if this object was placed in a bench of supercapacitors, such heat would create problems for other nearby devices risking to compromise the operation of the entire bank.

Conclusions: In the case of a charge above the limits we had seen that the reaction of the supercapacitor was to reduce its ability to accumulate charge;

Reaching the upper limits we also see a saturation in voltage, so we can adfirm thath the supercapacitor is still able to accumulate charges but the entire structure is not able to do that.

Regarding the damage that we observed the explanation could be an internal damage of the supercapacitor which involves the chemical and the electrical part; by heating everything above the expected limits, one can think that the supercapacitor reaches its limits much more quickly and with more accelerated dynamics.

To better understand these phenomena, however, we need a more in-depth analysis that goes beyond these preliminary tests.

Conclusions

As a result of the work carried out, we can divide the conclusions into a part related to the Howland pump and one relating to the supercapacitors.

With regard to the Howland pump we can conclude that:

- Starting from simple and economical components, we have built a voltage / current converter that allows us to work with any type of load.
- We have built a device that, although not totally innovative from the point of view of the operating principle, is positioned in a category of voltage / current converters outside the standards that, starting from low voltages, can produce high currents.
- The designed device presents measures with a harmonic distortion content of 2% and an amount of noise below   in any operating condition.

Regarding the supercondensators we can say that:

- Supercapacitors, pushed to the limits of their operating zone, behave in an atypical manner assuming a non linear behaviour and that we can compare this behavior with an hysteresis cycle;
- The supercapacitor, subjected to step currents, has a resistance of 22 mΩ. this resistance can't be classified as continuous internal resistance because it responds to a transitory situation that is precisely the current step and not to a regime situation.
- Once the ± 3V is exceeded, the supercapacitor has permanent damage to its structure, which modifies its capacity to accumulate charge and, in the case of extreme cycles, which completely redefine the voltage limits; we can't precisely define which of the components is damaged but we can think that both the dielectric and the electrolyte suffer permanent damage.
- The supercapacitor has a voltage limit which is reached well before the limit in charge; in fact, it can be seen from the graphs obtained that, when the saturation occurs in voltage, the supercapacitor is still able to accumulate charge; however, it is not possible to study the limits of this accumulation because the capacitor breaks and therefore we are in the presence of technological limits.

  We can however suppose to find ourselves in what, in the field of electromagnetism, is called Rayleigh zone, and which represents the part of the hysteresis cycle still far from saturation and this can make us think that, beyond the technological limits, there are still many things to evaluate in the behavior of these devices and that they can accumulate still a lot of charges.

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