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TRABAJO FIN DE MASTER EN INGENIERÍA INDUSTRIAL

SANDWICH-LIKE ZnAl LDH-GRAPHENE-POLYPYRROLE COMPOSITES TOWARDS FLEXIBLE SUPERCAPACITORS

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Resumen

La necesidad de encontrar alternativas a la utilización de combustibles fósiles es una de las principales preocupaciones de los científicos. Los supercondensadores tienen la habilidad de almacenar grandes cantidades de electricidad y tiene un largo ciclo de vida, en comparación a las baterías. Este trabajo se concentrará en la fabricación de un innovador compuesto material basado en un sándwich estructura para conceder todas las propiedades de cada uno de los componentes al electrodo final. Uno de los objetivos de este trabajo consiste en la creación de un electrodo flexible, pues los sustratos que fueron utilizado son polietileno cubierto con un oxido de indio/estaño y algodón. Varias combinaciones del compuesto sándwich fueron examinadas y los mejores resultados fueron obtenidos con el deposito del LDH ZnAl (layered double hydroxide) como primera capa, el oxido de grafeno reducido (rGO) después, y con polipirrol en electro polimerización como ultima capa. Estos componentes fueron depositados en el PET/ITO primero, y luego en el algodón. El LDH esta depositado con un método potentiostato y el oxido de grafeno fuera deposito en drop-cast, antes de estar reducido con voltametría cíclica.

Varios parámetros como la cantidad de grafeno, la interfaz LDH/rGO o la reducción del GO fueron analizados en el PET/ITO sustrato y cuando se encontró la combinación perfecta, los experimentos muevan al algodón, donde el deposito del oxido de grafeno se realizo con filtración al vacío.

Los resultados mostraron que la mejor estructura sándwich basado en el sustrato PET/ITO es LDH/rGOx2/PPy, con una capacitancia del electrodo de 5,42 mF/cm^2. Los experimentos en el algodón mostraron una buena resistencia a las pruebas de flexión para el sándwich algodón/rGOx3/PPy, con una capacitancia del electrodo de 6,99 mF/cm^2 y una retención de 75% después 50 pruebas de flexión.

El futuro de este trabajo podría ser el analizo de los parámetros de los métodos de deposición para ver si una mejora capacitancia del electrodo seria lograda. También, la membrana de policarbonato utilizada par la filtración al vacío podría ser un nuevo sustrato flexible.

Abstract

The need to find alternatives to the fossil fuel usage is one of the primary concerns of the scientists. Supercapacitors have the ability to store large amount of electricity and have a long cycle-life, compared to batteries. This work will focus on the fabrication of a novel composite electrode material based on the sandwich type composite structure, in order to confer all the useful properties of the different components to the final electrode material. One of the objectives is to create a flexible electrode so the substrates used were polyethylene covered by an indium/tin oxide (PET/ITO) and cotton. Several combinations of the sandwich-type structure were tested, and the best results were obtained by depositing the layered double hydroxide ZnAl first, followed by the reduced graphene oxide, and finally depositing the polypyrrole by electropolymerization. These components were deposited first on PET/ITO and later, the experiments moved to the cotton substrate. The LDH was deposited by potentiostatic method and the graphene oxide was drop-casted before being reduced by cyclic voltammetry.

Various parameters such as the graphene oxide load, the LDH/rGO interface, the GO reduction were tested on the PET/ITO substrate and when the perfect combination was found, the experiments moved to the basic recycle fabric where the deposition of the graphene oxide was performed by vacuum filtration.

The result revealed that the best sandwich composite electrode material based on PET/ITO was LDH/rGOx2/PPy, reaching a specific capacitance of 5,42 mF/cm^2. The cotton experiments demonstrated the good bending stability of the cotton/rGOx3/PPy, achieving a specific capacitance of 6,99 mF/cm^2 with 75% retention after 50 bending cycles.

The perspectives of this work would be to change the electrodeposition parameters to see if a higher specific capacitance can be reached. Also, the polycarbonate membrane used for vacuum filtration could be a conceivable flexible substrate to explore.

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Abbreviations

EDLC:	electrochemical double-layer capacitor
PC:	pseudo capacitor
AC:	activated carbon
CDC:	carbon derived carbon
PPy:	polypyrrole
LDH:	layered double hydroxide
GO:	graphene oxide
rGO:	reduced graphene oxide
PET:	polyethylene
ITO:	indium/tin oxide
CV:	cyclic voltammetry
LSV:	linear sweep voltammetry

I) Introduction

1) The need for supercapacitors

The use and storage of renewable energy had always been a concern within the scientific community but as the concern grows over fossil fuel usage, with the global warming and all the environmental issues that implies, it becomes more than urgent to develop more efficient storage devices for renewable sources of energy. These systems can be based on several types of energy such as potential energy, pressure energy, thermal energy, chemical or electrical energy for example. The electricity is one of the most important sources of renewable energy and thus, numerous investigations were and are still conducted in order to improve the storage of electricity as well as its retrieving.
Currently, there are two different manners to store the electricity, directly and indirectly. The direct way of electricity storage is electrostatic. It consists of negative and positive electric charges on the plates of a capacitor stored by a non-faradaic electrical energy storage process. A capacitor is made of a dielectric sandwiched between two identical electrodes. On the opposite, the direct method used to store electricity in used for batteries. In such devices, faradaic oxidation and reduction of the electroactive reagents leads to their releasing of charges. These charges can perform electrical work when they flow between two electrodes with different potentials. Unlike capacitors, batteries are made of two different sorts of active materials that are captured in a conductive matrix as anodes and cathodes in order to carry the net cell reactions [1].

In the case of the batteries, the storage of electrochemical energy is synonym of charge and discharge processes which involves the inter-conversion of the chemical electrode-reagents which is irreversible. Therefore, storage batteries have a limited cycle-life which varies depending on the type of batterie. When it comes to capacitors, their cycle-life is almost unlimited because there are not any chemical changes involved in its process for storing energy. As a result, the cycle-life of a capacitor lies between 10^5 and 10^6 times. The main drawback of a capacitor according to *Shukla, Sampath and Vijayamohana* is the size of the device. Unless the capacitor is quite large, only small amount of charges can be stored, which leads to a low energy-density. Nonetheless, investigations proved that devices as charged electrode/solution interfaces contain double layers with a capacitance between 16 and $50\mu F.cm^{-2}$. When combining these properties with a large accessible surface-electrode-area achievable with high surface-area (1000-2000 m^2/g) carbon powders, felts and aerogels, even higher capacitances around 100 F/g can be reached. These investigations led to the creation and development of electrochemical supercapacitors, also called ultracapacitors [1]. The main advantage of a supercapacitor over a battery, is its ability to perform with large amounts of power and has a long cycle-life. Supercapacitors were made in order to reach greater energy densities while maintaining the high-power density of capacitors. To do so, high surface area electrode materials and thin electrolytic dielectrics are utilized in supercapacitors. Hence, their capacitance is several orders of magnitude larger than conventional capacitors [2].

2) The capacitance mechanism

The origin of the capacitance of supercapacitors is well explained in *Shukla, Sampath and Vijayamohana*'s article. The result of a contact between an electronic conductor and a solid or liquid ionic-conductor is an electrostatically achieved accumulation of charges on each side of the interface, leading to the creation of an electrical double-layer which is mostly a molecular dielectric. There are not any charge transfers across the interface and the current resulting of the process is a displacement current coming from the rearrangement of charges that can be described as a polarized electrode [1]. The charges can only be physically absorbed into the double layer without any electron transfer: this is the double layer capacitance, a non-faradaic process [3]. Additionally, an electron transfer producing oxidation changes in the electrostatic materials following Faraday's law also takes part in the charge storage of a supercapacitor [1]. Faradaic mechanism relies on reduction and/or oxidation reactions that take place at the electrode, leading to the generation of an electrical current. Redox probes as well as the application of a direct current are mandatory to promote the development of the electrochemical reactions. This faradaic process is called pseudo capacitance [3].

As a consequence, two different supercapacitors were developed and tested. The first one operates through the charging and discharging of the electrical double-layer at the interface [1].

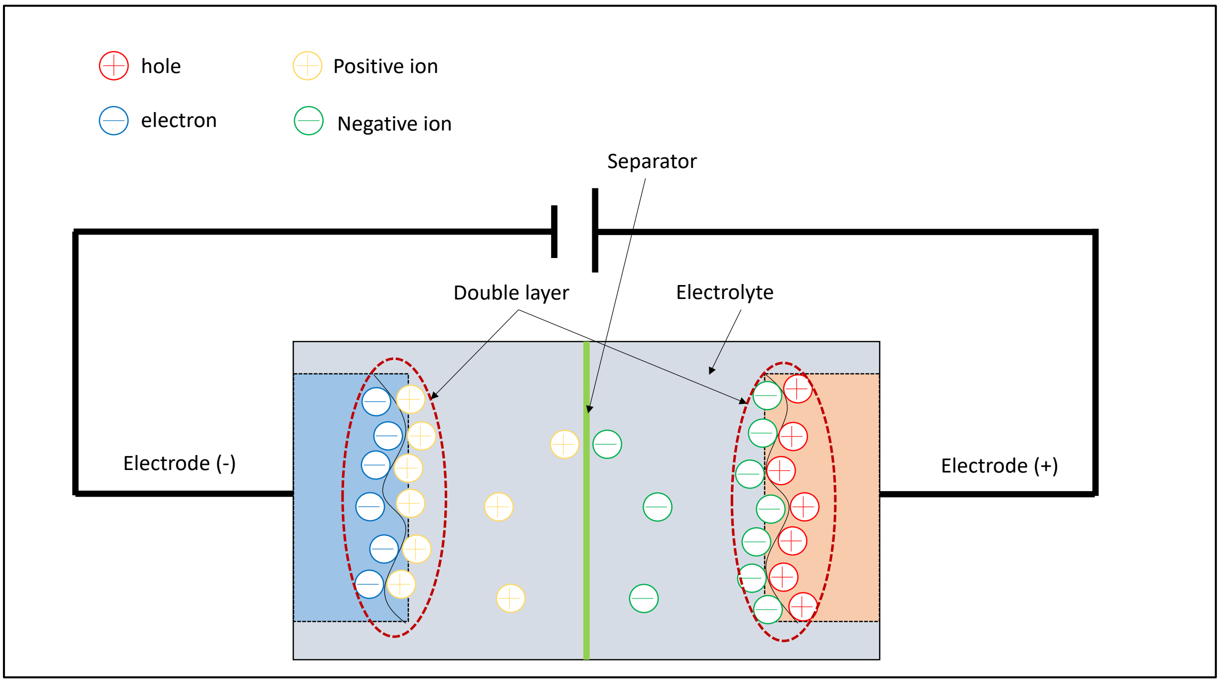


Figure 1: Schematic of an electrochemical double-layer capacitor [4]

The structure of an EDLCs is based on two carbon-based electrodes, an electrolyte and a separator. As it had been said before, the EDLCs store the charge non-faradaically so there is no transfer of charge between the electrode and the electrolyte. The process for storing the energy starts with the application of a voltage which leads to the accumulation of charges on the electrodes surface. The ions in the electrolyte solution then diffuse across the separator because of the natural attraction of charges of the opposite sign. These ions diffuse into the pores of the electrode of opposite charge.

The double layer of charge is possible thanks to the engineering of the electrodes which is made to avoid the recombination of the ions.
As a consequence of the creation of this double layer of charges on each electrode, the distance between them is reduced and the surface area is increased. Thus, the energy densities achieved by the device are greater than the conventional electrodes [6].

As for the second type of supercapacitor, the charge/discharge process takes place thanks to the transfer of electric charges between the different phases [1].

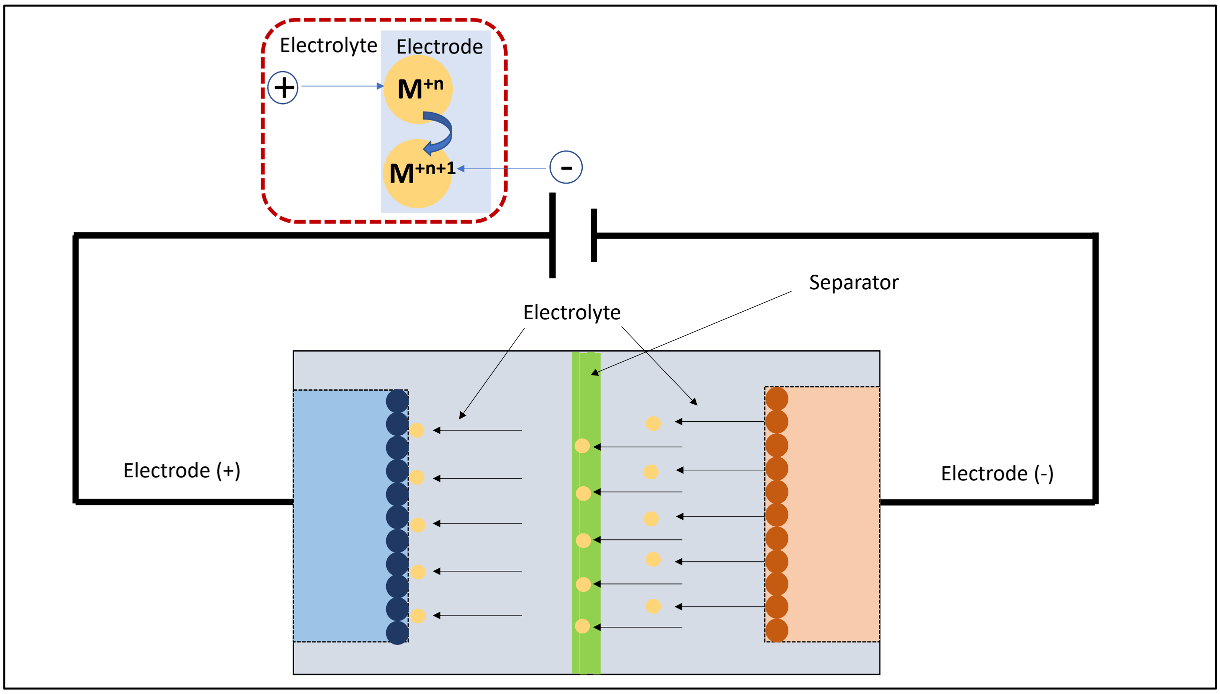


Figure 2: Schematic of a pseudo capacitor [5]

A pseudo capacitor is made of two electrodes separated by an electrolyte. The process behind a pseudo capacitor is chemical and displays charge transfer by means of oxidation/reduction reactions. As it had been previously said, pseudo capacitors use a faradaic mechanism which means that they store charge through the transfer of charge between electrode and electrolyte. Pseudo capacitors are known to achieve a greater capacitance and energy densities than electrochemical double-layer capacitors because of this faradaic process [6].

The capacitance mechanism is based on these two storage principles which contribute to the total capacitance.

3) Materials used for supercapacitors

As it can be seen on the schematics of the electrical double-layer capacitor and the pseudo capacitor, the main components of a supercapacitor are the electrodes, the electrolyte and the separator.

The materials used for these elements are not the same for an electrical double-layer capacitor or a pseudo capacitor.
The electrical double-layer capacitors use nanoporous carbon electrodes whereas pseudo capacitors use redox-active transition metals with several oxidation states materials or conducting polymers [7].

The basic electrolyte for supercapacitors is salt and solvent and plays a fundamental role in the electrical double layer formation for EDLCs and in the reversible redox reactions in the pseudo capacitors. The cell voltage mostly used nowadays is 2.5-2.8V. The parameters influencing the electrical double-layer and pseudo capacitance are numerous: the ion type and size, the ion concentration and solvent, the interaction between the electrolyte and the electrode materials, the potential window. The field of application for electrolytes is very vast and it was sketched as follows:

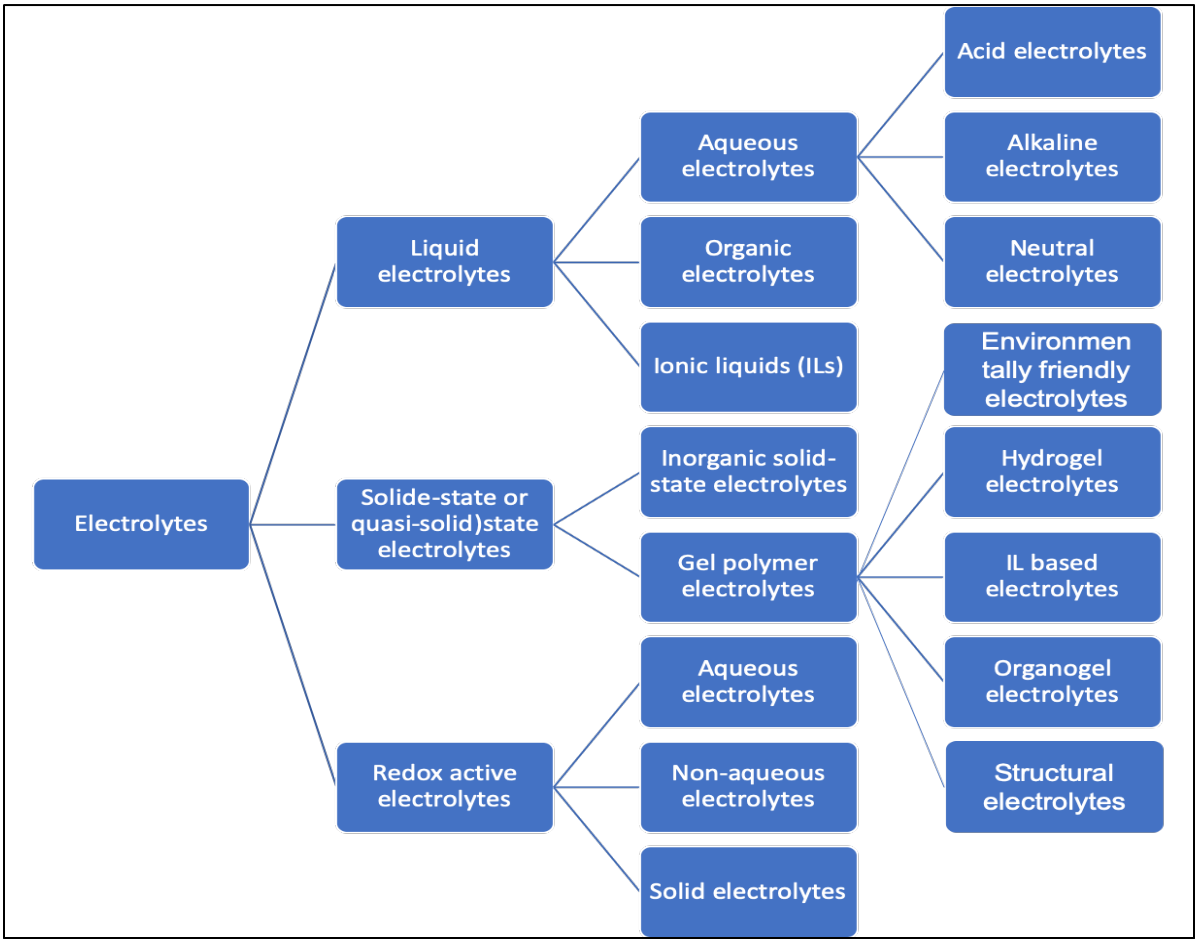


Figure 3: Organization chart of the electrolyte types [15]

a) Electrical double-layer capacitors (EDLC)

♦ *Carbon materials*

Numerous parameters must be taken into account when choosing the correct material for EDLCs and carbon is a perfect candidate since it offers a large panel of choice for the porous electrode. For example, the specific surface area, the pore volume and distribution as well as the particle size can be controlled.

According to *Lin and al.,* the carbon materials more investigated recently are activated carbons, carbide-derived carbons and graphene. In addition, carbon nanotubes, carbon onions can also be considered as potential materials for electrical double-layer capacitors.

Activated carbons (ACs) present a disordered structure obtained after physical or chemical activation of a charcoal or hydrochar for example.

On one hand, in the case of a physical activation, steam or carbon dioxide are used as activation agents at high temperature under a mixed inert/oxide atmosphere. On the other hand, chemical activation takes place at high temperature, but the precursor carbon is mixed with alkalis, carbonates, chlorides, acids or similar reagents. The chemical activation is mainly performed at the laboratory scale and allows a certain control on the pore size distribution. Concerning the values reached for EDLCs using ACs, the maximum specific capacitance reached 60 $F.cm^{-2}$ in organic electrolyte and 80 $F.cm^{-2}$ were recently obtained in ionic liquid electrolyte [7].

Carbide derived carbons (CDCs) are described in *Lin and al.*'s article as microporous carbons (pore size smaller than 2nm) with a very narrow pore size distribution. They come from high temperature etching of metal carbides such as titanium carbide TiC, silicum carbide SiC or vanadium carbide VC, under chlorine atmosphere or vacuum deposition. This type of electrical double-layer capacitors can reached high values of energy densities but the main drawback remains in the cost of CDC materials, which is higher that ACs materials [7].

Recently, graphene and graphene-like carbons are more and more popular, but several problems come with the use of such a material because the graphene powders endure restacking of graphene layers and low electrode density. These two issues lead to the decrease of the surface area as well as the decrease of capacitance values. Nevertheless, the production of activated graphene with a large surface area can be performed by chemical activation with KOH for example. These activated graphene showed a capacitance of 160 $F.g^{-1}$ and 60 $F.cm^{-3}$ in acetonitrile-based non aqueous electrolyte. This capacitance can compete with activated carbons based EDLCs. Other types of two-dimensional carbons like reduced graphene oxide of exfoliated graphene flakes can be used as a carbon material for EDLCs [7].

As a conclusion of the carbon materials part, the strategies for preparing high-capacitances materials at the laboratory scale reside in the control of the porosity, the average pore size and the pore size distributions. Until now, the activated carbons are the best carbon material, for commercial EDLCs, due to economic matters [7].

b) Pseudo capacitors

♦ *Metal oxide pseudo capacitive materials*

The aim of changing the porous carbon materials into pseudo capacitive materials is to improve the capacitance of the supercapacitor. This idea started to be studied in the 1970s by Dr. Brian Evans Conway and other electrochemists when they observed fast reversible redox reactions could take place at or near the surface of an electrode material. The result of such reactions was a higher charge storage compared to the EDLC device.

Manganese dioxide is a good example of pseudo capacitive material displaying a low cost and being environmentally friendly. Indeed, the charge-transfer reactions that take place in MnO_2 are due to cation insertion in highly accessible sites located at the near-surface of the manganese oxide particles. However, MnO_2 displays a low electron conductivity which may hinder its practical applications.

Researches were conducted regarding pseudo capacitive materials' behavior in non-aqueous electrolytes in the purpose of improving the energy density of the supercapacitor. The intercalation pseudo capacitance had been a promising discovery in order to obtain high-rate charge storage devices [7].

Augustyn, Simon and Dunn describe this process as the intercalation of ions into the tunnels or layers or a redox-active material accompanied by a faradaic charge-transfer with no crystallographic phase changes [9].

In regard to the numerous metal oxides that can be used as pseudo capacitive materials, there are still several difficulties when it comes to practical applications. Indeed, thicker electrode (100+ μm) with a low fraction of conductive additives are synonym of reduced rate performances, lower cycle stability and faster self-discharge rates when compared to EDLCs [7]. This phenomenon is even more present at high temperatures.

However, the idea of using intercalation pseudo capacitive materials in non-aqueous electrolytes seems promising in order to create cost-effective and high-performance pseudo capacitors [7].

- *Conductive polymers*

As a faradaic process, the pseudo capacitance of conductive polymers is established thanks to reversible redox reactions. Nowadays, four different conductive polymers are mostly used as pseudo capacitive materials: polyaniline (PANI), polypyrrole (PPy), polythiophene (PT) and poly(3,4-ethylenedioxythiophene) (PEDOT). Some tests were realized in aqueous and organic electrolytes and the specific capacitance reached lies between 100 $F.g^{-1}$ and 600 $F.g^{-1}$. Of course, these values depend on several properties such as the electrolyte composition, the morphology of the polymer used, the presence and distribution of conductive additives or the electrode potential range [7].

- Polyaniline

Polyaniline is a conductive polymer used for supercapacitors and batteries. It is one of the best candidates when it comes to pseudo capacitive materials because of its high electroactivity, its excellent stability and high specific capacitance (400-500 $F.g^{-1}$ in acidic medium). This polymer is easily processed but requires a proton to be charged and discharged. As a result, only a protic solvent, acidic solution or a protic ionic liquid can be used [10]. Studies on rechargeable batteries were conducted and polyaniline has been reported to have a capacity range lying from 40 to 270 $mAh.g^{-1}$ [11]. This polymer has the most variable specific capacitance achievable, due to its morphology, the amount and type of binders and additives, the thickness of the electrode. Researches also showed that the electrodeposition of polyaniline leads to higher specific capacitance than chemical formation of polyaniline. The stability of polyaniline can be improved through the formation of poly(n-methyl aniline).

The higher stability of this polymer is due to the fact that the proton exchange sites are blocked by the methyl groups as *Snook and al.* explained in their article. As a result, chemical degradation is avoided [10].

- Polypyrrole

Polypyrrole has been in the center of a lot of researches recently because its flexibility in electrochemical processing is better than most conducting polymers. However, polypyrrole can only be used as a cathode material because it cannot be n-doped. The capacitance of polypyrrole lies between 400 and 500 F.cm$^{-3.}$ This high value of capacitance is due to the high density of this polymer, but this high density also affects the access to the interior sites of the polymer for dopant ions. As a result, the capacitance per gram is reduced, and particularly for thick coatings on electrodes.

Since it can only be doped with negative charges, the single-charged anions usually used as dopants can be Cl^-, ClO_4^- and SO_3^- for example. Some investigations showed that using multiple-charged anions as dopants leads to the crosslinking of the polymer. These anions could be SO_4^- for example [10]. *Suematsu and al*. investigated the use of multiple dopants such as anions with two or three negative charges in order to study the ion selectivity and diffusivity of the polymer. They showed that the resulting polymer films have microporous structures. This type of structure is considered as an advantage for supercapacitor materials because it enhances their capacity and diffusivity [12]. In their work, they quoted the capacitance per unit volume, but it appears to be lower (100-200 F.cm^{-3}) than typical denser polypyrrole layers. Another way to improve the charge storage properties of a polypyrrole based pseudo capacitor would be to combine it with polyimide. The role of this high molecular weight dopant would be to protect the PPy from oxidation degradation. The thermal stability and mechanical properties of the polyimide are excellent, but this polymer is often considered as an insulative material and thus, it could mean poor performances [10].

- Thiophene-based conducting polymers

Thiophene-based conducting polymers can be n-doped but the mass specific capacitance and the conductivity are usually lower than for the p-doped thiophene-based conducting polymers. As a consequence, the n-doped form is only used as an anode material. The n-doping of polythiophene happens at low potentials, below -2,0V vs Ag/Ag^+. Also, its oxygen, conductivity and water stability are low compared to the p-doped form. Therefore, it is easily oxidized back to neutral form and has a low-cycle life. These difficulties can be overcome by creating substituted thiophene derivatives as *Snook and al*. explained in their article. One of these derivatives is the poly(3,4-ethylenedioxythiophene) also called PEDOT. This is a highly conductive polymer that can be either n or p-doped. Its potential range is 1,4V but its large molecular weight of the monomer unit combined to its low doping level lead to a small specific capacitance around 90 F.g^{-1}. The following table shows the conductivities of the conducting polymers mentioned here [10].

Polymer	Conductivity (S.cm^{-1})	Reference
Polyaniline	0.1-5	[10]
Polypyrrole	150-200	[14]
PEDOT	300-550	[13]
Polythiophene	300-400	[10]

Table 1: Conductivity of several conducting polymers [10]

This polymer has highly useful properties such as the fact that it is electron rich, which results in a low oxidation potential and a wide potential window over which the capacitance is high (1.2-1.5V wide). PEDOT also has a high surface area and appeared to present some good film-forming properties as well as an ability to be rapidly switched with a minimum of side reactions. All of these properties convey to a long cycle-life [10].

c) Electrolytes

♦ *Liquid electrolytes*

- Aqueous electrolytes

As the Fig.3 shows, there are numerous categories for electrolytes. Among the liquid electrolytes lies the aqueous, organic electrolytes and ionic liquids. The aqueous electrolytes are usually not the first choice when it comes to commercial supercapacitors because of their narrow voltage windows. As a result, the organic electrolytes are preferred for the most part of the supercapacitors. Nevertheless, aqueous electrolytes are highly used in research and development area since aqueous electrolytes are inexpensive and can be easily handed in the laboratory, under simple conditions. On the contrary, when organic electrolytes and ionic liquids, the purification procedure must be performed under strictly controlled atmosphere to avoid moisture.

Aqueous electrode can be divided into three categories as acid, alkaline and neutral solutions. As examples for each category, sulfuric acid H_2SO_4, potassium hydroxide KOH and sodium sulfate Na_2SO_4 can be presented.

Acid electrolytes for electrical double-layer capacitors

Most of the researches conducted on EDLCs in acid and neutral electrolytes showed that the device achieves a higher specific capacitance in an acid electrolyte than in a neutral one. It appears that the specific capacitance would increase with an increasing electrolyte conductivity. These specific capacitances lie between 100 and 300 F.g^{-1}, and this is generally higher than the specific capacitance achieved in the organic electrolytes [15].

Acid electrolytes for pseudo capacitors

Some investigations showed that in the case of carbon-based electrode materials, the pseudo capacitance was contributing besides the electrical double-layer capacitance in the aqueous H_2SO_4 electrolyte.

The main disadvantage of a pseudo capacitor in aqueous electrolytes is its short cycle-life because of the degradation of electrode material.

Metal oxides and conductive polymers, as pseudo capacitive materials, can also be used in aqueous electrolyte but they are not stable in acidic aqueous electrolyte because they are sensible to the pH and the type of the electrolyte [15].

Alkaline electrolytes for electrical double-layer capacitors

Generally speaking, the specific capacitance and energy density is approximately the same whether the EDLC is in an aqueous KOH electrolyte of aqueous H_2SO_4 electrolyte. Many researches had been done for the improvement of supercapacitor energy densities using base electrolytes by increasing the capacitance and/or widening the operating voltage window.

Alkaline electrolytes for pseudo capacitors

It is well-known that several metal oxides have high theoretical capacitances and that the capacitance process for pseudo capacitive electrodes materials involves the insertion/extraction of electrolyte ions from the electrode material. *Feng and al.* studied a metal oxide Co_3O_4 nanofilm and they reached a high specific capacitance of 1400 $F.g^{-1}$, in the 2M KOH electrolyte.

In this alkaline electrolyte, the electrolyte concentration has a significant impact on the specific capacitance. The use of a concentrate electrolyte leads to the appearance of corrosion at the electrode substrate surface and this could end with the electrode material peeling off from the substrate. Also, in alkaline electrolyte, the electrode materials tend to dissolve, thus decreasing the capacitive performances after a long-term charging-discharging cycling [15].

Neutral electrolytes for EDLCs

The results of the comparison between neutral, KOH and H_2SO_4 electrolyte showed that the specific capacitance was the lowest in the case of a neutral electrolyte, probably because of the lower ionic conductivities.

Nevertheless, for carbon-based supercapacitors, the use of a neutral electrolyte could signify larger operating windows compared to acidic and alkaline electrolytes.

Researchers showed an outstanding cycle-life with 10 000 charging-discharging cycles at a voltage of 1,6V in a Na_2SO_4 electrolyte.

Neutral electrolytes for pseudo capacitors

Numerous neutral electrolytes factors have an influence on the supercapacitor's performances, such as pH, type of cation and anion species, additives, solution temperature for example.
Moreover, the scan rate of cyclic voltammetry or charging/discharging current density could also be influencing the specific capacitance values, since the cation intercalation/deintercalation was involved in MnO_2 -based electrode materials.
In regard of the cycling stability of MnO_2 electrode under temperature changes, it has been found that such electrode materials would undergo structural change at high temperatures during the charging-discharging process and this is affecting the cycling stability [15].

- Organic electrolytes

Organic electrolyte-based supercapacitors are at the center of numerous studies for the commercial market thanks to their high operation potential window in the range of 2,5 to 2,8V. Organic electrolytes can be used with cheaper materials. However, like every type of electrolytes, they display some issues such like a higher cost than aqueous electrolyte-based supercapacitors, a smaller capacitance, a lower conductivity and concerns about toxicity [15].

Organic electrolytes for electrical double-layer capacitors

As *Zhong and al*. say in their article, the specific capacitance of an electrical double-layer capacitor depends on the surface area and the pore size/size distribution of the carbon material.
It is known that pores in carbon materials with very small particle help increasing the specific surface area, but the accessibility of electrolyte ions suffers from it. Indeed, large organic ions access with small pores is limited and thus, the specific capacitance is harmed.
Consequently, the low conductivity of this organic electrolyte limits the maximum power density. In addition, trace amounts of water in organic electrolytes induce self-discharge mechanism [15].

Organic electrolytes for pseudo capacitors

This type of electrolyte is used with pseudo capacitive materials such as metal oxides for example. The ion intercalation/deintercalation can be facilitated by including Li ions to the organic electrolytes used for pseudo capacitors. $LiClO_4$ and $LiPF_6$ are usually used [15].

- Ionic liquids

Ionic liquids can be described as salts only composed of ions with low melting point (below 100°C). The usual composition of ionic liquids is a large asymmetric organic cation and an inorganic or organic anion. ILs variety is virtually unlimited and it is very attractive for supercapacitors because the composition of the electrolyte can easily be optimized to fulfill precise requirements like operating cell voltage, working temperature range for example.

The ionic liquids used in the literature are mostly based on imidazolium, pyrrolidinium, ammonium, sulfonium and phosphonium cations.
However, several disadvantages come with the use of ionic liquids. Indeed, they display high viscosity, low ionic conductivity and high cost.

♦ *Solid-state or quasi-solid-state electrolytes*

The use of solid-state electrolytes simplifies the packaging, the fabrication process of supercapacitors and the liquid-leakage free. The main type of solid-state electrolyte studied for supercapacitors is currently based on polymer electrolytes. There are three types of polymer electrolytes which are dry polymer electrolytes, gel polymer electrolytes (GPE) and polyelectrolyte.

- Gel polymer electrolytes (GPE)

A gel polymer electrolyte is made of a polymer matrix called host polymer and a liquid electrolyte which can be either an aqueous electrolyte or an organic solvent containing conducting salt or an ionic liquid.
The polymer used as a matrix can be poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), potassium polyacrylate (PAAK), poly(ethyl oxide) (PEO), pol-(methyl methacrylate) (PMMA), poly(ether ether ketone) (PEEK) and many others.

Hydrogel polymer electrolytes for carbon-based electrodes

The design of the electrode/electrolyte is highly important with this type of electrolyte because, the supercapacitor could undergo poor rate capabilities in relation to the limited ion diffusion rate, or large interfacial resistance at the electrode/electrolyte interface.
The challenge lives in the association of the electrode/hydrogel electrolyte interface with the electrode material and the hydrogel electrolyte. As a consequence, electrodes materials with several structures such as carbon nanotubes grown on carbon cloths, activated carbon cloths, 3D graphene network or even graphene/porous carbon aerogels were studied with PVA-based hydrogel electrolytes. This type of structures can ease the infiltration of a hydrogel electrolyte into the porous electrode [15].

Hydrogel polymer electrolytes for pseudo capacitors

For neutral PVA-based hydrogel electrolytes, examples of pseudo capacitive electrode materials could be MnO_2 or V_2O_5 for example. In comparison to aqueous electrolytes, the electrochemical stability of hydrogels is greatly improved.

Added to PVA, poly(acrylate)- and poly(acrylic acid)-based hydrogels are polymers that can be used for hydrogels in supercapacitors. Concerning the thermal stability of hydrogel electrolytes, scientists found a way to improve it by creating a phosphosilicate gel to serve as an electrolyte with MnO_2-CNT composite as a positive electrode. The operating temperature range varies from -30°C to 100°C according to *Zhong and al*.

Organogel electrolytes

The organogel electrolytes result from a gel polymer electrolyte based on organic solvents called plasticizers. The polymer hosts used for organogel electrolytes are PEO, PMMA, polyvinylpyrrolidone (PVP), PEEK and copolymers. The plasticizers typically used in organogel electrolytes are polycarbonate PC, ethylene carbonate EC, dimethyl carbonate DMC or their mixture. With the use of this type of organogel electrolytes, the cell voltage is up to 2,5-3V, which is a significant improvement compared to hydrogel electrolyte-based supercapacitors. The consequence of this high cell voltage is a high energy density that is up to 18-25 W.h.kg^{-1} [15].

IL-based solid-state electrolytes

Ionic liquids are also called ionogels and are made by incorporation of ionic liquids into polymer hosts. The nature of the IL, the nature of the host polymer and their interaction influence the properties of the ionogel. And when ionic liquids are considered as a solvent, the selection of a suitable host polymer must be crucial in order to fulfill high supercapacitors performances of the IL-based gel polymer electrolyte. Nowadays, several host polymers are being studied for ionogel electrolytes such as PVA, PEO, PMMA, poly(ethylene glycol) diacrylate, and PVDF-HFP [15].

Environmentally friendly gel polymer electrolytes

Environmentally friendly material coming from renewable source can be corn starch, chitosan and biodegradable materials as poly(epsilon-caprolactone) can be a polymer host for solid-state electrolytes. Nonetheless, the low mechanical properties of natural polymers are a real issue for this application. In order to improve these properties, scientists developed blended materials like a blend of chitosan and starch, a blend of chitosan and polyethylene glycol PEG for example.

Structural electrolytes

This type of gel polymer can be applied for solid-state supercapacitors in vibration devices like electric vehicles for example. An ionic liquids-epoxy resin composites were prepared by *Shiroshova and al.* and they concluded that several properties were dependent on the weight ratio between the IL and the epoxy resin, such as the morphology, the ionic conductivity and mechanical properties as well [15].

- Inorganic solid-state electrolytes

This type of electrolytes does not receive as much attention as the others because it is not bendable and has a very low flexibility. Their advantage lies in the fact that they are mechanically highly resistant and thermally stable.

♦ *Redox-active electrolytes*

The Faradaic reactions occur in the electrolyte so they can bring extra capacitance to the supercapacitor. The pseudo capacitance is brought by the pseudo capacitive electrode materials but also by the reduction/oxidation of the redox mediator in the electrolyte.

- Redox-active aqueous electrolytes

Redox-active aqueous electrolytes for carbon-based supercapacitors

The main example could be an iodine/iodine redox pair, which had been used by researchers as redox-active aqueous electrolyte for carbon-based supercapacitors. This type of device could be able to reach outstanding values of capacitances like 1840 $F.g^{-1}$ but this type of value had only been witnessed at the positive electrode in a very narrow potential range [15].

Redox-active aqueous electrolytes for pseudo capacitive electrodes

There is a wide choice within the redox-active electrolytes such as KI and HQ for example. It appears that with the addition of a redox mediator to the electrolyte, the specific capacitance could be increased and thus, the energy and power densities as well. However, the cycling stability of redox-active aqueous electrolytes and especially during the initial cycles, was worse than the cycling stability of conventional aqueous electrolytes without redox mediators.

- Redox-active non-aqueous electrolytes

The goal of using redox-active non aqueous electrolytes is to reach higher cell voltage, hence, a higher energy density. Among these electrolytes, some are organic electrolytes, and some can be IL-based electrolytes [15].

- Redox-active solid electrolytes

The use of redox-mediators was tested in solid-state or quasi-solid-state electrolyte-based supercapacitors and it showed enhanced performances. The electrolytes were iodides, organic redox mediators (hydroquinone, p-benzenediol), mixture of redox additives, etc. The polymer hosts studied in majority were GPE with PVA or PEO. The conclusion was that these GPEs displayed a higher specific capacitance than the GPEs without redox mediators [15].

d) Separators

As it can be seen on Schem. 1 and 2, the two electrodes of a supercapacitors are separated by a separator whose role is to prevents any electrical contact between electrodes. This separator is damped in the electrolyte. In order to allow the ionic charge transfer of the device, it is mandatory for the separator to be ion permeable.

The separator must also by highly electrical resistant, highly ionic conductive, and have a low thickness. The usual materials used for the separator can be a mixture of polymer and paper when the electrolyte is organic. Ceramic or glass fiber separators are also separators' material but only when the electrolyte is aqueous.

4) The approach of hybridizing for improving capacitance

Theoretically, the energy density is enhanced by 20-30 W.h.kg^{-1} in comparison to a basic supercapacitor. The materials used for a hybrid supercapacitor are a mixture between redox and EDLC materials such as graphene or graphite, metal oxides, conducting polymers and activated carbon. The storage mechanism of a hybrid supercapacitor results from the association of the storage principle of EDLCs and pseudo capacitors.

With this method, the limiting properties of EDLC does not appear in the pseudo capacitor and in return, the limiting properties of pseudo capacitors does not stand in the electrical double-layer capacitors. A pseudo capacitor has a poor cyclic stability but the combination of this device with an electrical double-layer capacitor allows to overcome this limiting property.

There are two types of hybrid supercapacitors: the symmetric one and the asymmetric one. When two similar electrodes are assembled in a hybrid supercapacitor, the device is called a symmetric hybrid supercapacitor. On the supercapacitor's market, symmetric hybrid supercapacitors are made of binary electrodes of acetyl carbonate inside organic electrolyte and the operational potential reached is up to 2,7V. In the case of an asymmetric hybrid supercapacitor, two dissimilar electrodes are joined together and the most used materials are acetyl carbonate AC electrode and manganese oxide along with AC-$Ni(OH)_2$. The commercial hybrid supercapacitors are all asymmetric and those displaying conducting polymer electrodes are the main concern within the scientific world [17].

The storage and the release of charges in an asymmetric hybrid supercapacitor relies on the redox reactions undergone by the conducting polymer. The oxidation, representing the doping part displays the transfer of the ions to the polymer and during the reduction, or dedoping, the ions are transferred back to the solution. This phenomenon happens in the bulk volume of the polymer matrix whereas it takes place at the interface when carbon electrodes are used.

It has been proved that the use of conducting polymers leads to higher specific capacitances. The following table shows different types of hybrid supercapacitor electrode materials.

Electrode	Electrolyte	Specific capacitance (F.g^{-1})
Carbon/rGO	Na_2SO_4	175-430
RuO_2/MWCNT	H_2SO_4	169.4 mF.cm^{-1}
MnO_2/MWCNT	Na_2SO_4	141
MnO_2/CNTA	Na_2SO_4	144
rGO/MnO_2	Na_2SO_4	60
PAN/Carbon nanofibers	KOH	134
PANI/MWCNT	H_2SO_4	360
PPy/MWCNT	H_2SO_4	200
PANI nanotubes/Ti nanotubes	H_2SO_4	740

MWCNT = Multiwalled carbon nanotubes / CNTA = Carbon nanotube arrays / PAN = Polyacrylonitrile

Table 2: Different hybrid supercapacitor materials [17]

a) Hybrid supercapacitors components

The first electrodes composing a hybrid supercapacitor is a supercapacitor electrode and the second one is a battery electrode. Three methods can be applied in order to reach higher capacitance values.

- Using an electrode material with higher capacitive properties
- Variation of the electrolytes
- Development of hybrid capacitors

The family of hybrid capacitors can be categorized as carbon/metal oxide composite electrode, redox asymmetric electrodes and battery-capacitor electrode. The first class of hybrid capacitors is made of composite electrodes with incorporated carbon and either conducting polymers or metal oxides. As a result, the storage of charges is physical and chemical. The carbon materials represent the electrical double-layer capacitor part, thus supplying a capacitive double layer and a greater surface area. On the other hand, metal oxides and conducting polymers display the behavior of a pseudo capacitor.
Then, redox asymmetric electrode hybrid capacitors are made of two materials with redox properties and finally, the last family of hybrid supercapacitors features battery type material electrode and supercapacitor electrode.

◆ *Asymmetric and symmetric hybrid systems*

The aim of creating asymmetric hybrid capacitor devices is to improve the energy and power density of electrochemical capacitors. With the use of an asymmetric device comes a long-term cycling stability. Also, the reversible non-faradaic negative electrode combined to the high capacitive positive electrode accomplish high energy and power density.
Usually, the typical asymmetric hybrid device is composed of activate carbon acting as a negative electrode and conducting polymer as a positive electrode. The performance is limited because of the conducting polymer, which has the behavior of a pseudo capacitor.

When comparing symmetric and asymmetric hybrid capacitors, the main difference lies in the material used because in the case of a symmetric device, the electrodes comes from the same material that is itself in the hybrid form. As an example, a symmetric hybrid capacitor can be made of PANI-PANI but with a different mass concentration of PANI in each electrode.

On the opposite, the electrodes composing an asymmetric hybrid capacitor come from different materials. In such a device, the supercapacitor’s behavior is inherent to the electrodes’ operational voltages that is different for each electrode. An example of an asymmetric system can be Mn-Ni-Co (MNCO) ternary oxide along with carbon black. This device displayed excellent performances due to large surface area available for faradaic reactions and rapid ion transfer [17].

♦ *Hybrid systems containing battery type electrode*

This system allows to pair a supercapacitor electrode to a battery type electrode. The improved energy density comes from the supercapacitor electrode while the power density improvement comes from the battery electrode. The electrode undergoing the electrical double-layer capacitance procedure is the supercapacitor electrode and the other electrode, undergoing faradaic redox reactions during charging and discharging is the battery type electrode.

It exists different type of supercapacitor materials such as porous carbon, graphene, oxide compounds, conducting polymers and intercalated lithium compounds. One of the systems which attracts most interests is the combination of supercapacitor with Li-ion storage systems because Li-ion has the highest energy density [17]. This energy lies from 120 to 200 W.h.kg.$^{-1}$ and supercapacitors have the highest power density ranging from 2 to 5 kW.kg^{-1}. Creating hybrid supercapacitor leads to the combination of these parameters, thus, enhancing the performances of the device. The company called Telcordia created this combinational device and called it nonaqueous asymmetric hybrid. They use activated carbon and lithium intercalated devices.

The material used as the anode is Li4Ti5O12 because of its high-power capability and outstanding cycle life, in a highly conductive acetonitrile-based electrolyte. Activated carbon acts as double-layer capacitive (positive) electrode, and when coupled with the anode, the device has charge storage of a battery at the negative electrode and charge storage behavior of a supercapacitor at the positive electrode.

Other materials can be used for this type of systems instead of activated carbon, such as $LiCoO_2$ or $LiMn_2O_4$ [17].

♦ *Hybrid systems formed by coupling of EDLC and pseudo capacitive materials*

When conducting polymers are coated with carbon, the cycling stability becomes outstanding and it leads to a better energy and power density. One of the advantages of using carbon materials is that the pseudo capacitive conducting polymers get more stable. Also, these conducting polymers serve the improvement of the energy density.

Some examples of conducting polymers can be PANI or PPy (polypyrrole) and they are coated on carbon materials, assuming a retention of 95% and a capacitance of 85% in aqueous electrolyte after 10 000 cycles, according to *Liu and al.* [18].

In the same article, it has been proved that the cycling stability can be improved by depositing a thin carbonaceous shell on the conducting polymer surface.

♦ *Hybrid systems formed by various electrode materials*

Carbon materials, inorganic materials and conducting polymers are hybrid components materials. Within the carbon-based category are activated carbon, carbon nanotubes CNTs, carbon aerogels and graphene. Manganese oxide and lithium-based materials are the inorganic materials used for hybrid devices and within the conducting polymers are found PEDOT, PANI, PPy etc. One example of an asymmetric hybrid capacitor with activated carbon as one electrode is AC-MnO_2 with aqueous electrolyte. This device in K_2SO_4 electrolyte has an energy of 17 $W.h.kg^{-1}$ and a power of 2 $kW.\ kg^{-1}$, at a potential range of 0-1,8V. The cost of a supercapacitor is a very important parameter since it is made to be commercialized. The low-cost supercapacitor is made of carbon nanofibers CNF coupled with MnO_2 with a core-shell design, offering therefore a high conductivity thanks to the effective electrical connection between the core-CNF and the shell- MnO_2. Reduced graphene oxide is also used as the negative electrode when $Co(OH)_2$ or $Ni(OH)_2$ is the positive electrode. These examples of hybrid capacitors were tested and the $Ni(OH)_2$-rGO devices showed a specific energy around 30 $W.h.kg^{-1}$ with a power density of less than 1 $kW.kg^{-1}$ [17].

The studies concerning the association of different electrode systems to create hybrid devices are still very recent and thus, the possibilities of development are extraordinary. The materials that draw the attention the most currently are graphene-based or activated carbon-based but metal oxides only or metal molybdates for example are also becoming interesting.

The specificities of a hybrid capacitor vary from one type of device to another. The hybrid systems composed of electrical double-layer capacitor and pseudo capacitor, whether symmetric or asymmetric, offer a specific capacitance in the between 100 and 800 $F.g^{-1}$. If the application of the hybrid capacitor requires low-medium power, this device is well suited.

When it comes to combining a battery-type electrode with a supercapacitor electrode, the specific capacitance reached lies between 100 and 1000 $F.g^{-1}$, and therefore can be used for needs of medium to high power applications.

b) Electrolytes materials for hybrid capacitors

The electrolytes used for hybrid capacitors are either aqueous electrolytes, organic electrolytes or ionic liquids.

Within the aqueous electrolytes can be found the usual H_2SO_4, KOH, KCl, which are the most commonly used because they are highly available and low cost. As it has been said before, the nature of the electrolyte has an influence on the specific capacitance of the device. An aqueous electrolyte helps enhancing the capacitance but on the other hand, it limits the voltage window, which is only 1,2V.

As examples of organic electrolytes, acetonitrile and propylene carbonate can be mentioned and the main advantage lies in their extended operating voltage window. Indeed, compare to the aqueous electrolytes' window, the operating voltage window of organic electrolytes is higher, of the scale of 0-2,7V. As a result, the energy density achieved by the device is higher in an organic electrolyte than in an aqueous electrolyte [17].

The most commonly used organic electrolyte is acetonitrile, because of its lower ionic resistivity but this type of electrolytes also have limitations such as its toxicity and flammable properties.

When it comes to the ionic liquids as electrolytes for hybrid capacitors, it must be mentioned that they are non-toxic, inflammable and have a wide operating voltage window of 5V.

The concept of ionic liquid electrolytes is based on a liquid form of solvent-free molten salts at room temperature. The main disadvantage of using ionic liquid electrolytes is that their ionic conductivity is not as good as the aqueous and organic electrolytes ionic conductivity.

c) Separator materials for hybrid capacitors

The separator is an important part of the supercapacitor because an inferior quality separator leads to additional resistance and therefore impedes the cell performance. Some examples of separators' material are glass, paper, ceramics and polymers. This last material is widely used because of its low cost, porous nature and flexibility.

The separator based on polymer materials are made of polypropylene, polypropylene-carbonate, polyvinylidene difluoride, polyethylene and polyamide. Other researches showed that graphene oxide had also been used as a separator.

The advantages of using polymer-based separators is their low-cost, simple process, accessibility as well as their high mechanical and chemical resistance [17].

5) The electrodeposition method to improve the specific capacitance

Now that the different materials used to create a supercapacitor are known, it is time to take an interest in the deposition of these materials. Several techniques exist in order to deposit or generate the different materials for supercapacitors. For supercapacitors electrodes, the different materials must be deposited as thin films on the substrate [20]. Therefore, the chemical fabrication of conducting polymers for example cannot be used in this case because it produces powdery materials [21].

The electrodeposition is widely used in the case of supercapacitors because this process can be easily adapted for this type of devices. The electrodeposition consists of the materials deposition onto a conducting surface from a solution containing ionic species such as salts. Electrodeposition can be used for simple purposes like the application of thin films on a surface to change the external aspect or for corrosion protection and is also used for more complicated application such as supercapacitors [19].

As the interest for electrochemical supercapacitors grows, the advantages and drawbacks of such a device are discovered. While a high-power density, a long cycling life are some great advantages of using supercapacitors, there are some issues remaining in the low energy density and the high production cost.

One of the solutions that has been found to try to overcome these disadvantages is the electrodeposition. Indeed, this process is relatively simple and cost-effective. It can be applied to various types of materials like conducting polymers and metal oxides.

For example, researches conducted in 2018 studied the electrodeposition of manganese dioxide on carbon cloth for supercapacitors electrodes [20]. The standard three-electrode setup was used with Ag/AgCl as the reference electrode and a platinum wire as a counter electrode, in Na_2SO_4 solution.

The electrodeposition process occurs through different chemical reactions that are easily explained by *Shanthi and al*. in their article. The first step is the water electrolysis happening on the surface of the carbon cloth electrode thus producing hydroxide ions OH^-. These ions will then be able to bond with the manganese ions Mn^{2+} and as a result, the manganese dioxide MnO_2 is deposited on the electrode surface. This process is fast, simple and low cost, which are three of the most important advantages for the commercialization of supercapacitors.

Later after the electrodeposition, the power density of the device was tested by cyclic voltammetry and the specific capacitance achieved was 483 $F.g^{-1}$. It also has been proved that this specific capacitance can vary depending on the scan rate of the cyclic voltammetry test.

The power density and the energy density values obtained were about 330 $kW.kg^{-1}$ and 22 $W.kg^{-1}$ respectively, which is higher than for carbon-based electrode according to the article. Another advantage of using the electrodeposition for supercapacitors is that the process can be applied on flexible substrates [20].

In their article on conducting-polymer-based supercapacitor devices and electrodes, *Snook and al*. explained that the highest specific capacitance of polyaniline was achieved with electrodeposited polyaniline, rather than with chemically formed polyaniline [10]. In the same article, Snook and Best tried to associate two conducting polymers that are PEDOT and polypyrrole, by electrodeposition of a mixed monomer solution. The specific capacitance reached was the same as for electrodeposited polypyrrole on its own, but this combination brought a higher ionic transport and an improved morphology of the polymers [10].

Among the material that can be electrodeposited for supercapacitor application are found ruthenium oxide (RuO_x), manganese oxide-based fibers, polyaniline-based fibers and polypyrrole-based fibers. *Mohd Abdha and al.* created composite electrodes based on transition metal oxide and electrodeposition was used for four of them: RuO_x/GNFs (graphitic nanofibers), MnO_2/CFP (carbon fiber paper), $Mn0_2$/CFS (carbon fiber-sheet) and ZnO/MnO_2 NFs. In the same article, they performed electrodeposition on conducting polymer-based and transition metal oxide/conducting polymer-based composite electrodes.

As it has been said before, polypyrrole PPy and poly(3,4-ethylenedioxythiophene) PEDOT has both very good candidates to undergo an electrodeposition process. For instance, nanowires of polypyrrole can be combined with carbon nanofibers (NPPy/CNFs). A composite electrode designed as a sandwich ad also been tested: PPy-CNFs/MS/PPy-CNFs (MS= melamine sponge), and it appears that this electrode showed a higher capacitance than the previous composite electrode (148,4 and 189,9 $F.g^{-1}$ respectively).

A third type of electrode was tested, and it was based on polypyrrole, reduced graphene oxide and carbon fibers: PPy-rGO/modified carbon bundle fiber.

The scientists concluded that the electrodeposition allows to increase the contact area with the electrolyte and thus, improves the supercapacitive performances of the electrode [22].

6) The need for flexibility for supercapacitors

Traditional rigid supercapacitors use a silicon substrate as their foundation and therefore, the supercapacitor's applications are limited by the rigidity and the production of such a device is expensive. On the opposite, flexible supercapacitors can be created from cheaper substrate such as polycarbonate or cotton for example [23]. The development of flexible supercapacitors allows major advances for electronic applications since the strong consumer market demand for portable, thin and flexible devices grows every day [30].

The recent high popularity of these wearable and flexible electronic sensors forced the research to tend to use flexible substrates for supercapacitors [24]. Throughout the concept of conductive fabric, the physical and mechanical properties of a textile such as the flexibility can be achieved.

The production of such device can be done thanks to different methods but in order to choose the suited one, several criteria must be taken into account. Indeed, for supercapacitors, the specific area and the porosity of the substrate are very important properties that can be achieved while coating the textile substrate. Nevertheless, the porosity can also be seen as a disadvantage because it leads to discontinuity on the surface of the textile after the coating meaning a less homogenous smooth surface. As a result, the electrical conductivity is decreasing. [25]

The advantages of a flexible sold-state supercapacitors over a traditional supercapacitor lie in their small size, low weight, ease of handling, excellent reliability and their wider range of operating temperatures [29].

At first, the scientists investigated on liquid-based supercapacitors with aqueous solutions, organic solutions or ionic liquids as electrolytes. Nevertheless, these devices had important drawbacks limiting their application. Indeed, the packaging materials and techniques required were very expensive because they had to ensure to avoid any leakage of electrolytes. The packaging was also the cause of a second drawback because it makes the fabrication of small and flexible supercapacitors using liquid electrolytes very difficult. This is the reason why flexible solid-state supercapacitors were invented [29].

Flexible supercapacitors are often called flexible solid-state supercapacitors because they are usually made of flexible electrodes, solid-state electrolyte and a separator, all of this in a flexible packaging material. The interest of the scientists has been focused in the first place on carbon-based flexible electrode material because of their good electrical conductivity, excellent cycling stability, high power density and outstanding mechanical properties. The type of electrolytes used for flexible solid-state supercapacitors are mostly gel polymer electrolytes due to their high ionic conductivity [29].

7) Substrates used for flexible supercapacitors

Metal foils were tested as possible flexible substrates, but the main disadvantage was their easy corrosion in aqueous electrolytes, so the lifetime of the device was very low.

In addition, the total weight of the device would definitely be increased by the use of metallic compounds and it impedes on the specific power and energy densities. This is why the researches tended to study non-metal material as flexible electrodes for supercapacitors.

a) Flexible carbon electrodes

Among all the carbon materials, the nanoscale ones are the most attractive when it comes to build flexible electrodes for supercapacitors. They can be zero-dimensional like carbon particles, one-dimensional like carbon nanotubes or nanofibers or two-dimensional like graphene. Some of them stand out of the crowd because of their good mechanical properties, electrical conductivity and extremely large surface area such as carbon nanotubes (CNTs), graphene, and their composites.

The concept of creating a flexible electrode is based on the coating of these carbon materials on the flexible, porous and light-weight substrate. As an example, studies showed that paper could be an efficient substrate for flexible electrode. Indeed, the paper can bind strongly with CNTs thanks to the capillary effect. This supercapacitor had been tested and the specific capacitance achieved was of 200 $F.g^{-1}$.

Another type of substrate is graphene-paper and for these investigations, the multilayer graphene was deposited on the cellulose paper, resulting with a specific capacitance of 2,3 $mF.cm^{-2}$.

Porous cotton is also a good candidate as a substrate for a flexible carbon electrode, as well as synthetic sponges based on polymers. The comparison between paper and cotton or synthetic sponges shows that the last two substrates lead to a higher surface area than paper substrates.

Additionally, cotton and synthetic sponge substrates are more stretchable and compressible than paper [29].

b) Flexible composite electrode

Metal oxides and conducting polymers are able to achieve a better specific capacitance than carbon materials and therefore, several pseudo capacitive materials can be used as flexible electrode materials. Manganese dioxide MnO_2, NiCoO4, polyaniline PANI and polypyrrole PPy are used to enhance the energy density of flexible electrodes. Nonetheless, the major drawback of metal oxides is their low conductivity, of 10^{-5} to 10^{-6} $S.cm^{-1}$ for MnO_2 for example, and the disadvantage of conducting polymers is their poor cycling stability. In order to overcome these problems, scientists investigated combining the pseudo capacitive materials with highly conducting materials. This combination allows the good conductivity of the composite electrode and helps improving the capacitance and stability of the electrode [29].

c) Sponge substrate

The sponges find on the market are made of polyester fibers and they display a hierarchical macroporous network structure as well as a high absorbance to liquid media with high internal surface area.

Also, a homogeneous continuous coating of the substrate is possible thanks to the junction free network structure and the access of the electrolyte to the surface of the active electrolyte is facilitate by the high absorbance of the structure.

Several types of sponges had been investigated throughout various researches such as CNT sponges that showed good performance due to the robust sponge structure able to maintain the conductive network and surface area under cyclic compression. This carbonaceous sponge was also mixed with Fe_3O_4 in order to improve the energy density.

Other investigations were run on the synthesis of a sponge-structured graphene-MnO_2 hybrid supercapacitor. The graphene oxide GO was in a nanosheet shape and the substrate was dipped into the GO nanosheet solution before being dipped into hydroiodic acid in order to reduce the graphene oxide. Then, also using a dipping technique, the MnO_2 was deposited on the conductive sponge. After the test, it has been discovered than coating the rGO-coated sponge with MnO_2 increased the specific capacitance by 3 or 4. But the suited amount of MnO_2 must be found because the specific capacitance decreases with increasing mass loading of this dioxide.

d) Textile substrate

The mechanical properties of textile substrates such as flexibility, lightweight and high stretchability are perfect for their use as flexible substrate for supercapacitors' electrodes. Also, the 3D open-pores structure of textile helps the coating of the substrate, leading to a high areal mass loading of the active materials and therefore, in a high areal power and energy density.
Activated carbon can be coated on cotton or polyester microfibers in order to create flexible electrodes and the symmetric supercapacitor built with these materials showed a retention of 92% over 10 000 cycles. Other experiments including graphene sheet to the electrode were conducted and a porous hybrid graphene-CNT layer was deposited on carbon cloth textile. The role of the carbon nanotubes is to prevent the restacking of the graphene sheet after being reduced.
In order to increase the energy density of the supercapacitor, MnO_2 can be deposited on the CNT-textile composite electrode. The drawback of the MnO_2/CNT/textile flexible electrode supercapacitor is its poor cyclic performance with a 20% capacitance loss after 200 cycles and 40% loss after 10 000 cycles.
There are two manners of creating a supercapacitor based on textile: the substrate can either be coated with thin film layers or the fibers can be modified.

II) Objectives

The objectives of this work are numerous, but the main purpose is to create low-cost sustainable active materials with improved properties by simple methods.
The first objective is to create novel electrode materials to use for supercapacitors making. These materials must display improved capacities properties compared to the materials currently used. The improvement of the capacitive properties can be initiated by building a composite sandwich type electrode containing elements that will contribute to the enhancement of the surface area, to the electrical double-layer capacitance as well as the pseudo capacitance. An improve surface area leads to a higher capacitance and thus, a better ability to store electricity.
The aim here is to build the electrode by using simple electrodeposition methods at the surface of the substrate. Therefore, the building of the electrode will be fast and applicable in large scale.

Then, the new supercapacitor must be made with sustainable substrate such as cotton. Nanocarbon materials obtained by chemical oxidation will also be used as deposited layers onto the substrate, to form the composite sandwich type electrode. This method must also be applicable at large scale.

A third objective is to confer flexibility to the electrode by using a flexible substrate. This flexible substrate must show high cycling stability and bending resistance. The cotton is one of the best substrates here because it combines flexibility and sustainability.

A lot of researches had been performed before on sustainable electrodes for supercapacitors and flexible electrodes for supercapacitors and in this project, the combination of these two properties is studied in order to improve the application field of supercapacitors keeping in mind that the fossil fuel usage must be replaced by the use of renewable energy.

III) Workplan

A sandwich composite on flexible substrate will be fabricated for this work. Several materials will be used such as layered double hydroxide (LDH) ZnAl, polypyrrole, graphene oxide and they will be deposited on different substrate that are polyethylene covered with an indium/tin oxide layer and cotton.

The schematics of the ZnAl LDH is showed below:

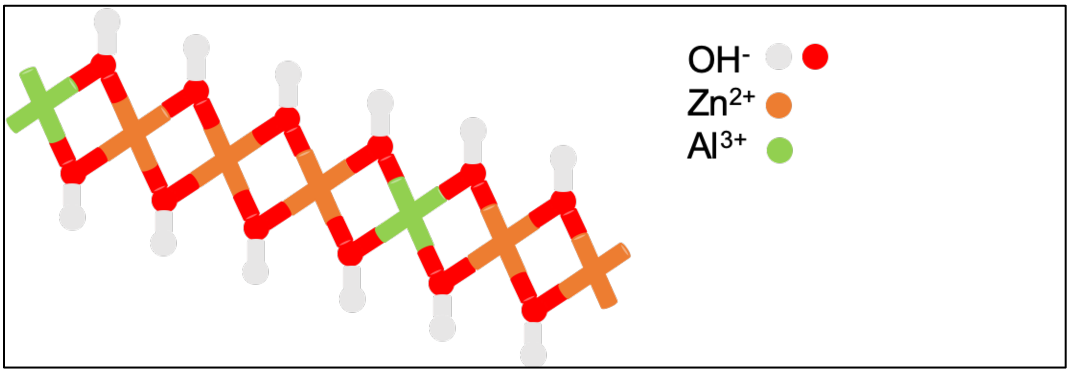


Figure 4: Schematic of the ZnAL LDH [31]

The first investigations will concern the variation of the structure of the sandwich composite. Different combination of ZnAl LDH, polypyrrole and reduced graphene oxide on the PET/ITO substrate were tested such as:

- LDH/rGO/PPy
- LDH/rGO
- LDH/PPy
- PPy/LDH/rGO
- PPy

The goal of these test is to determine the importance of each component and to understand how they interact with each other, depending on their position in the sandwich composite.

Once the structure of the sandwich composite is known, several parameters will vary in order to find the best ones to build the electrode.

Within these parameters is the amount of reduced graphene oxide, adjusted by the number of layers deposited on the substrate. The type of reduction applied on the graphene oxide is also a varying parameter because it can be chemical, realized by potentiostatic method or by cyclic voltammetry.

The interface between the PET/ITO substrate and the next layer will also be studied by depositing another layer of graphene oxide or not.

The next step will be to adapt the previous results onto the cotton substrate. First, the activation of the cotton will be tested in order to check if the specific capacitance achieved is higher on an activated cotton or on a non-activated cotton (also called treated and non-treated). As for the PET/ITO substrate, the number of layers of graphene oxide will be also investigated. Then, the investigations will move from sterile cotton to basic commercial recycled fabric to test the influence of the amount of GO on this new substrate. At the end of these experiments, the best structure of the electrode with the suitable amount of each of the materials should be known and thus, leads to the best specific capacitance achieved.

IV) Materials and methods

In this part will be presented the reagents used and how there had been used (directly, purified, etc.). The different substrate will also be presented and the methodology to obtain the sandwiches to be employed as electrode materials for supercapacitors as well.

1) Polyethylene covered with indium/tin oxide layer PET/ITO

This section is about the first experiments that had been conducted concerning the designing of a new flexible electrode for supercapacitors. PET covered with ITO layer is a flexible substrate which can be used for supercapacitors thanks to the conductive behaviour of the ITO.

a) Cleaning process

The cleaning step of the experiment is essential so that the deposition of the different components gives the best results. For polyethylene covered with ITO layer, the cleaning process is fast and easy since tape is protecting ITO until its use. It consists in washing the sample with ethanol on paper and dry it with paper as well. The substrate should be used directly after the cleaning in order to avoid impurities to deposit on the substrate and influence the results.

b) Preparation of the solutions

There are three different solutions needed for the experiments on PET/ITO: the graphene oxide solution, the polypyrrole solution and the layered double hydroxides solution.

- *Graphene oxide solution*

The concentration of this solution is 0,1mg/mL and was prepared from a 2mg/mL solution. The stability performances of the GO solution are not perfectly known. Therefore, the solution undergoes ultrasounds for 15min after its preparation.

- *Layered double hydroxide solution*

As it has been said in the introduction, the LDH solution is based on zinc nitrate $Zn(NO_3)_2$ and aluminum nitrate $Al(NO_3)_3$. The concentration of $Zn(NO_3)_2$ in the LDH solution is equal to 12,5mg/mL and the concentration of $Al(NO_3)_3$ is equal to 7,5mg/mL. According to literature, the pH of the solution must be between 3 and 4. The initial solution was too basic, so its pH was decreased to 3 thanks to a nitric acid solution.

- *Polypyrrole solution*

The preparation of this solution relies on the polymerization of the monomer pyrrole. For this polymerization, sodium p-toluenosulfonate 95% was used, as well as sodium lauryl sulfate and pyrrole. The concentration of sodium p-toluenosulfate is 0,05M, the concentration of sodium lauryl sulfate is 20mg/mL and the pyrrole concentration is 0,1M.

c) Methods of deposition of the different components

The majority of the components are deposited by electrochemical methods. Nevertheless, the graphene oxide solution was drop casting in this work, but spin casting would be preferred.
For all of these methods, the counter electrode is a platinum electrode, the reference electrode is an Ag/AgCl electrode, and the composite electrode studied is the working electrode. The three-electrode cell setup is the most common electrochemical cell setup used in electrochemistry [32].

- *Potentiostatic method*

First, the potentiostatic method can be used to deposit the LDH solution for example, or to reduce the graphene oxide.
The principle of the potentiostatic method is to control the voltage difference between the working electrode and the reference electrode. The potentiostat measures the current flow between the working electrode and the counter electrode.

- *Cyclic voltammetry*

Then, cyclic voltammetry can be used to deposit the polypyrrole or to reduce the graphene oxide.
Cyclic voltammetry is an electrochemical technique performed by cycling the potential of a working electrode and measuring the resulting current. During a reduction process, the potential is scanned negatively.
The potential extremum is also called the switching potential and is reached when the voltage is sufficient enough to have caused an oxidation or a reduction. The cycle can be repeated, and the can rate can vary [33].

d) Parameters of the deposition

♦ *LDH ZnAl deposition: potentiostatic method*

Before running the potentiostatic method to deposit the LDH ZnAl layer, a liner sweep voltammetry (LSV) was realized, in order to find the correct deposition potential.
During LSV, the voltage implemented by the user is scanned from the lower to the higher potential [34]. The deposition potential found thanks to the linear sweep voltammetry is -1,65V for the LDH ZnAl.

As a result, for the deposition of the LDH, the potential is set to -1,65V and the deposition time is set to 100 seconds. Setting -1,6V as the deposition potential was tried but the curve did not show a sharp peak representing the nucleation because this potential was probably too high.

♦ *Graphene oxide deposition: drop-casting*

Several trials were conducted before finding the correct concentration of the graphene oxide solution and the correct volume of solution to drop-cast on the samples. The drying method also had to be adjusted.
The parameters that suit the best the deposition method of graphene oxide is as followed: the concentration is 0,1mg/mL, the volume drop-casted is 40μL and the samples are dried at 50°C in an oven during 30min. The 40μL of solution are drop-casted in two steps. 20μL of the GO solution is drop-casted twice in order to optimize the homogeneity of the GO layer.
When several layers are drop-casted on one sample, they are dried during 30min at 50°C between each layer.

♦ *Polypyrrole deposition: cyclic voltammetry*

To grow polypyrole on the samples, the electrochemical method used is cyclic voltammetry with the following parameters: the potential varies from 0 to 1V at a scan rate of 50mV/s during 40 crossings (20 cycles). The potential window is on the positive side because the deposition of polypyrrole must be an oxidation.

♦ *Graphene oxide reduction: potentiostatic method, cyclic voltammetry, chemical method*

Three methods were tested to reduce graphene oxide, in order to know which of them gives the best results.
One of them is the potentiostatic method with a deposition potential equal to -1,4V and the deposition lasts 300 seconds.
When the deposition is performed by cyclic voltammetry, the potential varies from 0 to -1,5V. The potential window this time is negative, in order for the reduction to happen. The deposition lasts during 20 crossings (10 cycles).

The solution used to reduce the graphene oxide is a sodium nitrate solution at a concentration of 0,5M.

2) Cotton substrate

a) Cleaning and activation of the cotton

The cleaning process of the cotton samples was performed on the basic commercial fabric. Indeed, further in this work, both sterile cotton and basic commercial fabrics will be used but the sterile cotton did not require the cleaning process.

The process for cleaning the cotton consists in washing subsequently in acetone, ethanol and distilled water by using ultrasounds for 10min, for each washing. Then, the samples were dried at 60°C for 2h in the oven.
The activation process took place for both sterile cotton and basic commercial fabrics. It consists in boiling the substrate in NaOH 4M (for 1g of cotton) for 30min using ultrasounds and drying the samples at 80°C overnight in the oven.
The final step of the activation process is to neutralize NaOH with HCl 2M under ultrasounds for 30min. Then, the sample is washed with distilled water several times and dried at 110°C in the oven for 2h.

b) Filtration process

The aim of the filtration process is to deposit the graphene oxide on the cotton by forcing the solution to go through the cotton and the membrane thanks to the vacuum. During the cotton experiments, two types of cotton were used: sterile cotton and basic commercial fabrics. The filtration of the basic commercial fabrics requires to filter half of the graphene oxide solution on one side of the sample and half of the solution on the other side of the cotton, in order for the sample to be homogeneously coated.
The graphene oxide solution prepared for the filtration is made of 200µL of graphene and completed up to 5mL with distilled water. Before filtrating the solution through the cotton, the graphene oxide solution must be ultrasonicated for 15min to homogenize it.
The membrane used in this filtration is made of polycarbonate and is placed under the cotton sample. Before starting filtrating the graphene oxide solution, distilled water is filtrating through the sample in order to improve its wettability.
When more than one layer of GO is deposited on the cotton, the sample is dried between each layer.

c) Reduction process

Following the filtration process, the graphene oxide must be reduced. The sample is drowned in the reduction solution made of 10mg of ascorbic acid in 10mL of water. This vitamin C solution is left with the sample on a hot plate at 80°C for several hours.

d) Electrodeposition of polypyrrole

The parameters of the electrodeposition of polypyrrole were changed for this part and the number of crossings raised to 60 crossings (30 cycles). The scan rate remains 50mV/s and the potential window lies from 0 to 1V.

Also, before depositing the polypyrrole, the sample is left in the PPy solution for 10 min in order to improve the wettability and therefore, improve the deposition process.

V) Characterization methods

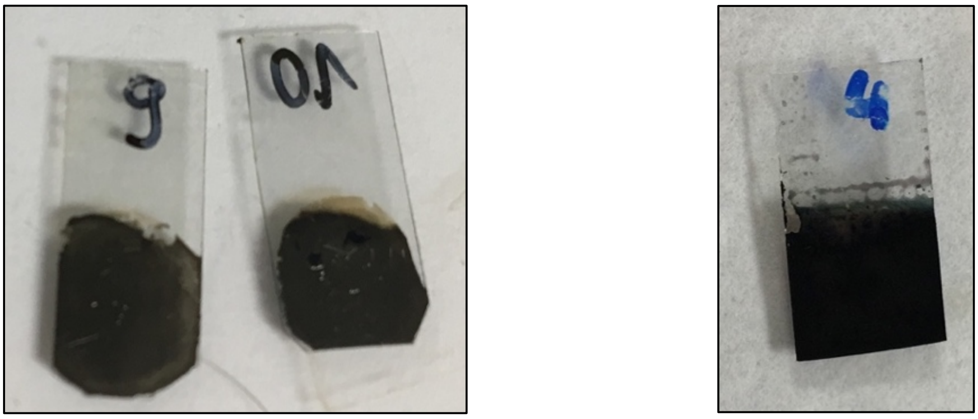
1) Visual inspection

The first characterization method is the simpler one: visual aspect. Indeed, the visual inspection of the materials help to know if the deposition method is well suited in this type of experiments. First, the deposition of the graphene oxide by drop-casting is followed by the reduction of the GO and upon reduction, this material is supposed to become black.

Picture 1: Pictures of a samples covered by reduced graphene oxide (left) and graphene oxide (right)

On the first picture, it can be clearly seen that the graphene oxide layer is black once it is reduced. To compare with the second picture, the aspect of the graphene layer before the reduction is between grey and brown.

The visual inspection also allows to check the continuity and the homogeneity of the layers. If the material displays a continuous and homogeneous layer, it can be concluded that the deposition is appropriate for this type of process.



Picture 2: Pictures of a PET/ITO substrate covered by LDH, rGO and PPy

On the picture on the left, it is witnessed that the aspect of the material is not homogeneous nor continuous. The right picture shows a perfectly homogeneous and continuous layer; Whether the problem comes from the deposition of the graphene layer at the beginning or had been altered during the fabrication process, it clearly shows that the visual aspect of the electrode help having an idea on the performances of the final device.

2) Electrochemical methods

The investigation of the conductivity of the graphene oxide upon reduction can be performed by electrodeposition. Indeed, the polypyrrole is electropolymerized onto the reduced graphene oxide layer because it needs a conductive substrate and the quality of this step depends on the quality of the reduced graphene oxide layer underneath. Therefore, the curve of the electropolymerization can indicate the quality of the device. As an example, the following graphs represent two different electropolymerizations.

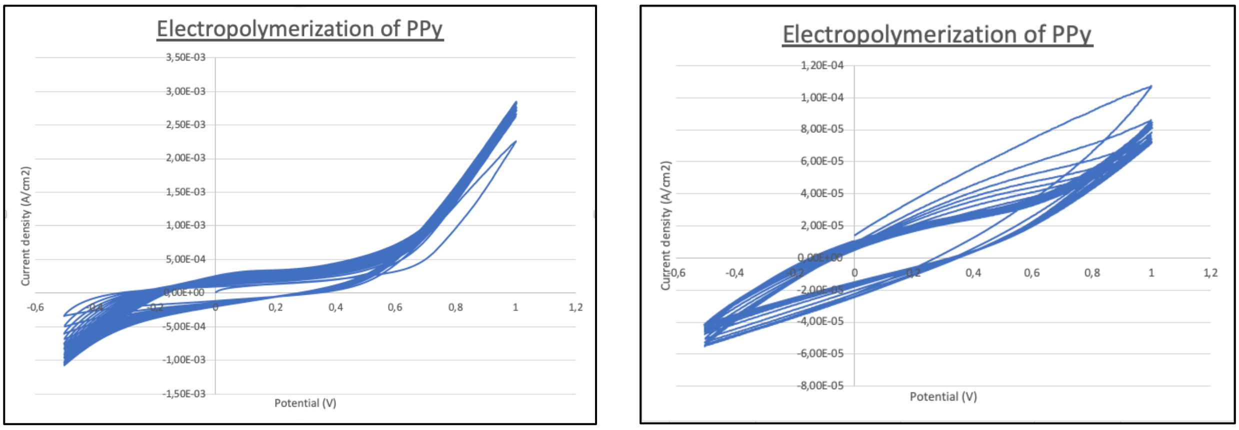


Figure 5: Graphs of the electropolymerization of LDH/rGOx2/PPy (left) and rGOx6/LDH/rGOx2/PPy

The graph on the left testifies of a good electropolymerization because current density reached is around 2,8.10^{-3} A/cm^2 whereas the current density reached on the graph on the right is around 1,1.10^{-4} A/cm^2.

3) Cyclic voltammetry to characterize the electrode material

The characterization of the electrode material is performed by cyclic voltammetry. The capacitance of the composite electrode is measured thanks to this cyclic voltammetry test. For this test, the potential window lies from -0,2V to 0,6V and last during 4 crossings (2 cycles). The solution used for the cyclic voltammetry test is a solution of sodium sulphate at a concentration of 0,5M. The scan rate of the process is 50mV/s. This test gives the current as a function of the potential and from this graph can be calculated the specific capacitance by using the integral of the cyclic voltammetry curve.

A dimensional analysis can help to understand how the specific capacitance is calculated from the value of the integral.

The SI unit of the capacitance is the Farad $(\mathcal{F})$ but since the samples do not have the same surface, it is mandatory to work with the specific capacitance in $\mathcal{F}/cm^2$.
The integral of the curve is the area under the curve so the unit of this value is $A \times V \times cm^{-2}$ with $A \times cm^{-2}$, the unit of the current density and V, the unit of the potential applied.
This value must be divided by the potential window (V) and the scan rate (V/s). Nevertheless, it must be taken into account that the electrode undergoes two cycles so the value of the integral must also be divided by 2.

$$\boxed{\frac{\mathcal{F}}{cm^2} = (\frac{A \times V}{cm^2}) \times \frac{1}{2 \times V \times \frac{V}{s}}}$$

Equation 1: Expression of the dimensional analysis of the specific capacitance

4) Flexibility characterization method

The cotton is more flexible than PET/ITO so it has been decided to run bending test on this substrates in order to evaluate the bending cyclability of the electrode.
The test consists of bending the sample fifty times at 180°, and perform a cyclic voltammetry test each five bending cycles. It is very important to bend the sample with the same process each time. To explain how this test had been performed, here is the scheme of the bending process.
The static part is maintained with a plier while another plier bends the moving part. Between each cyclic voltammetry test and the next series of bending, the samples are flushed with water and quickly dried with air.

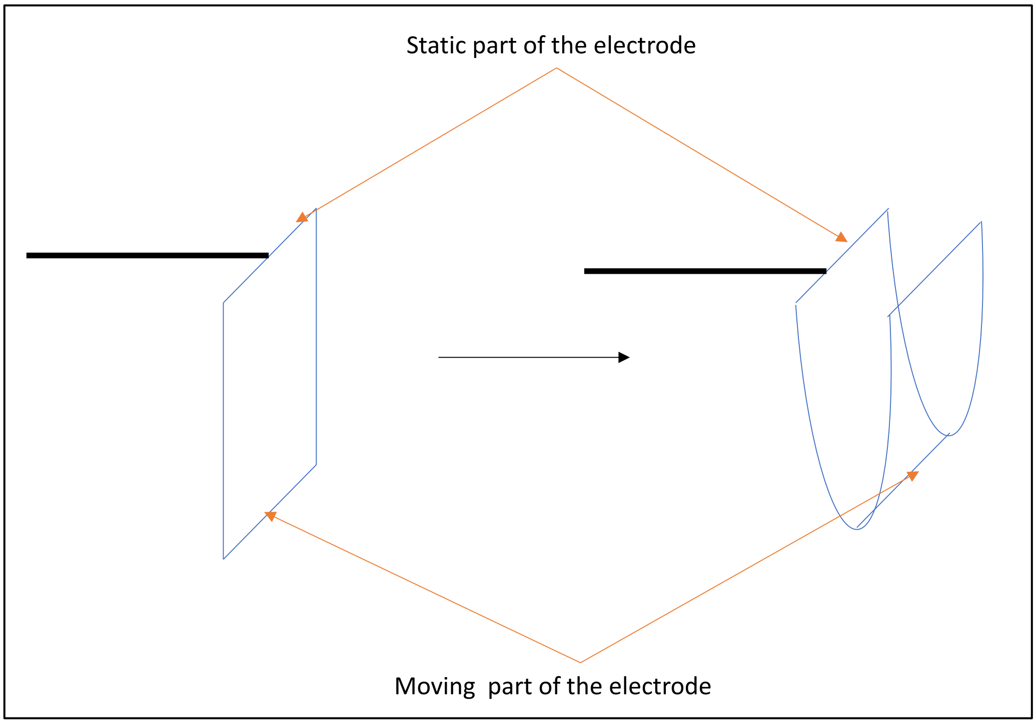


Figure 6: Bending test process for the cotton samples

5) Scanning electron microscopy

The obtained films were characterized in terms of morphological characteristics by scanning electron microscopy working at 20kV. Scanning electron microscopy is a characterization technique utilized order to study the topography, the morphology and the composition of the surface of a solid material. Micrometer and millimeter measures can be achieved thanks to this technique, whose principle relies on electron-sample various interactions when the focused beam of high-energy electrons hits the surface of the material.

A tungsten filament of a field emission gun produces the beam of electrons and this beam is then accelerated going through a high voltage. The lenses that can be seen of the schematic diagram form a system in which the beam passes through in order to create a thin beam of electrons. Then, the surface of the solid material is scanned thanks to the scan coils part of the microscope. The angle between the incident beam and the surface is very important to control because it influences the local electron flux. This angle is set by different lenses and magnetic coils.

Several types of electrons interact with the solid surface: the high-energy electrons are reflected by elastic scattering when the secondary electrons are emitted by inelastic scattering. To these two types of electrons are added the emission of electromagnetic radiations and each one of them are collected by a different detector. The samples analyzed by scanning electron microscopy must be conductive.

Here is the schematic diagram of a scanning electron microscope.

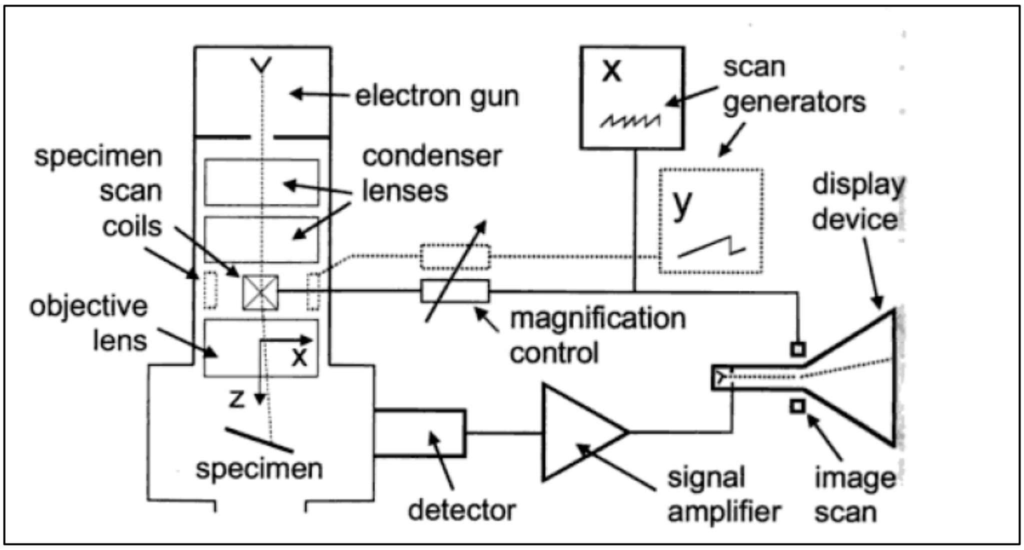


Figure 7: Schematic diagram of the scanning electron microscope [35]

In the present work, following an electrodeposition experiment, the morphology of the deposit was observed using SEM technique in order to check the presence of various components and their morphology characteristics.

VI) Results

1) Experiments on PET/ITO

a) Sandwich composite structure

In the first set of samples, the components were deposited on the substrate PET/ITO. In order to find which type of sandwich gives the best results, the order of the layers changed from one sample to the next one.

- Sample 1: PET/ITO/LDH/rGO/PPy
- Sample 2: PET/ITO/LDH/rGO
- Sample 3: PET/ITO/LDH/PPy
- Sample 4: PET/ITO/PPy/LDH/rGO
- Sample 5: PET/ITO/PPy

In this part, two samples LDH/RGO/PPy were made: the first one underwent a linear sweep voltammetry procedure before the deposition of the LDH layer, and the second one did not.
As a result, the first sample had a potential deposition of LDH ZnAl of -1,6V whereas the second sample LDH/rGO/PPy had a potential deposition of -1,65V. The graphs coming from these two types of deposition clearly showed the influence of the potential deposition.

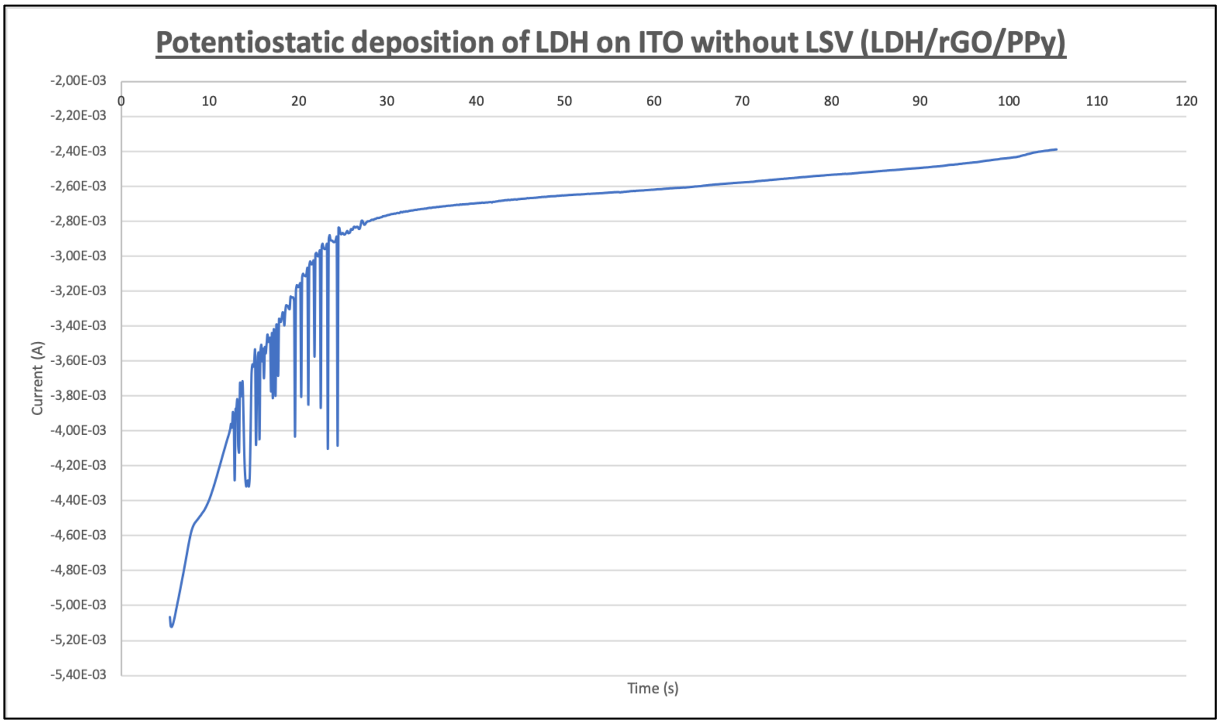


Figure 8: Graph of the potentiostatic deposition of LDH on the sample LDH/RGO/PPy without a scanning sweep voltammetry

This graph shows peaks at the beginning of the deposition corresponding to the nucleation.

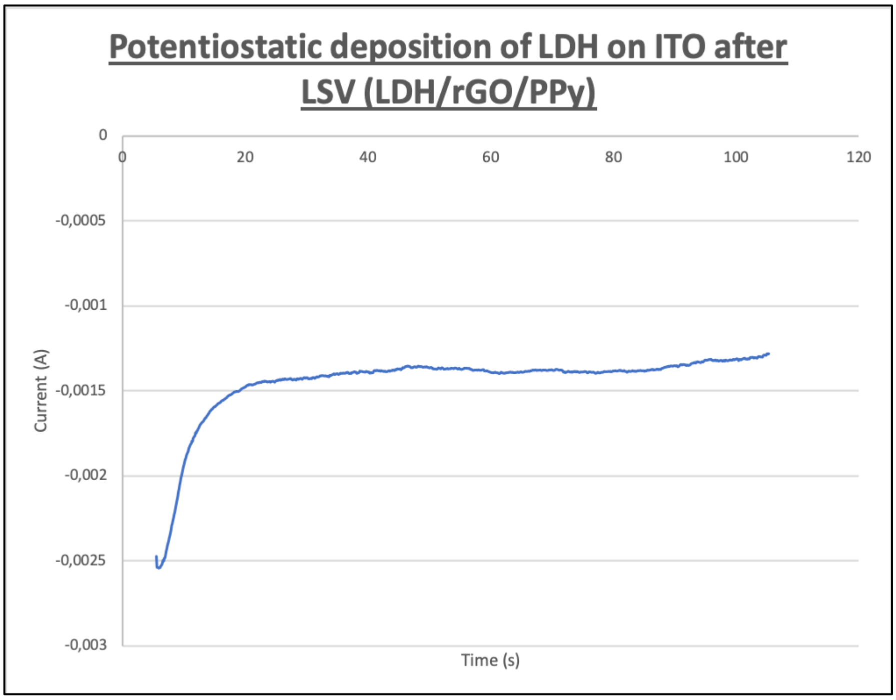


Figure 9: Graph of the potentiostatic deposition of LDH of the sample LDH/rGO/PPy after scanning sweep voltammetry

In this graph, the nucleation peaks do not appear, which means that it already happened during the linear sweep voltammetry which was realized in the LDH solution.

During the LSV, a thin layer of LDH was already deposited so during the potentiostatic deposition, the rest of the LDH was deposited on this thin layer.

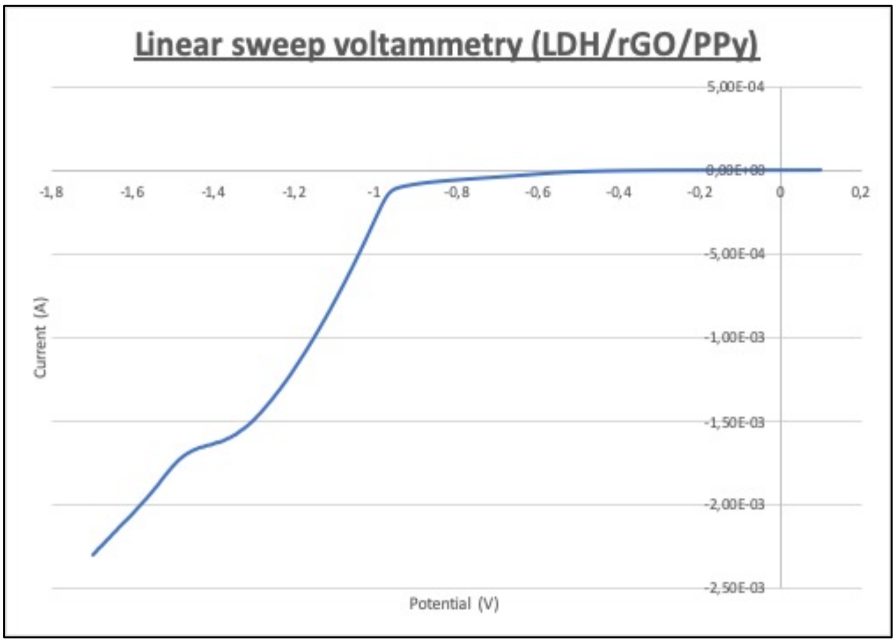


Figure 10: Graph of the linear sweep voltammetry on the sample LDH/rGO/PPy

The nucleation process appears on this graph, although it is less sharp than on figure 2, because less LDH ZnAl was deposited.
The best comparison between the samples comes with the cyclic voltammetry testing which is performed at the end of all the depositions. In order to compare the samples correctly, the CV test graph needs to represent the current density as a function of the potential. The original graphs coming from the CV test represent the current (A) as a function of the potential (V) but the area of the sample covered by all the layers is not the same for every sample. That is why the current density must be used to compare the sample conductive performances.

Although, the sample LDH/PPy was declared unusable because the polypyrrole deposition performed directly on the layer double hydroxide layer did not give suitable results. This sample will therefore no longer be part of the comparisons.

Here is the graph comparing the conductive performance of the sample LDH/rGO/PPy (with linear sweep voltammetry), the sample LDH/rGO, the sample PPy/LDH/rGO and the sample PPy only on top of the substrate.

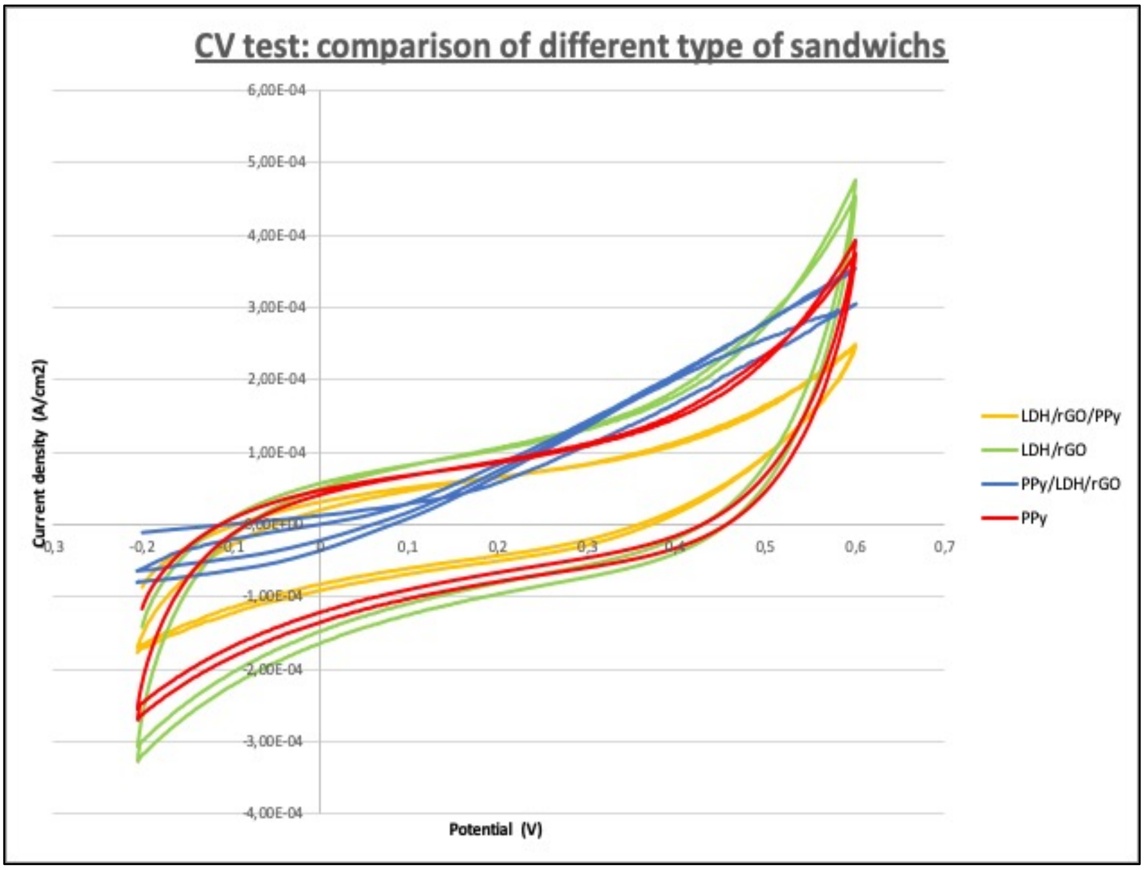


Figure 11: Graph of the CV tests for the samples in current density

The interpretation of this graph tells that the sample made of LDH/rGO on top of the substrate is the best type of sandwich because the current density is higher than any other. Nevertheless, this sample does not contain polypyrrole, which can spoil the cycling stability.

The blue curve representing the sample PPy/LDH/rGO current density as a function of the potential does not show the shape expected. Either one of the deposition steps went wrong or the layers cannot bond together because they are not deposited in the correct order.

When the red and the yellow curve are compared to each other, it appears that polypyrrole alone has better conductive capacities than the LDH/rGO/PPy sandwich electrode.

This can be easily explained because on one hand, the ITO film is highly conductive whereas on the other hand, the LDH and the reduced graphene oxide are only semi-conductive. Even if they increase the surface area, they decrease the capacitance. That is why a compromise must be found between the surface area and the capacitance.

The graphs of the electrodeposition of PPy on the samples LDH/rGO/PPy and PPy only prove this theory.

The LDH/rGO/PPy sandwich reaches a current density of 0,25mA/cm^2 whereas the PPy sample reaches a current density of 0,40mA/cm^2.

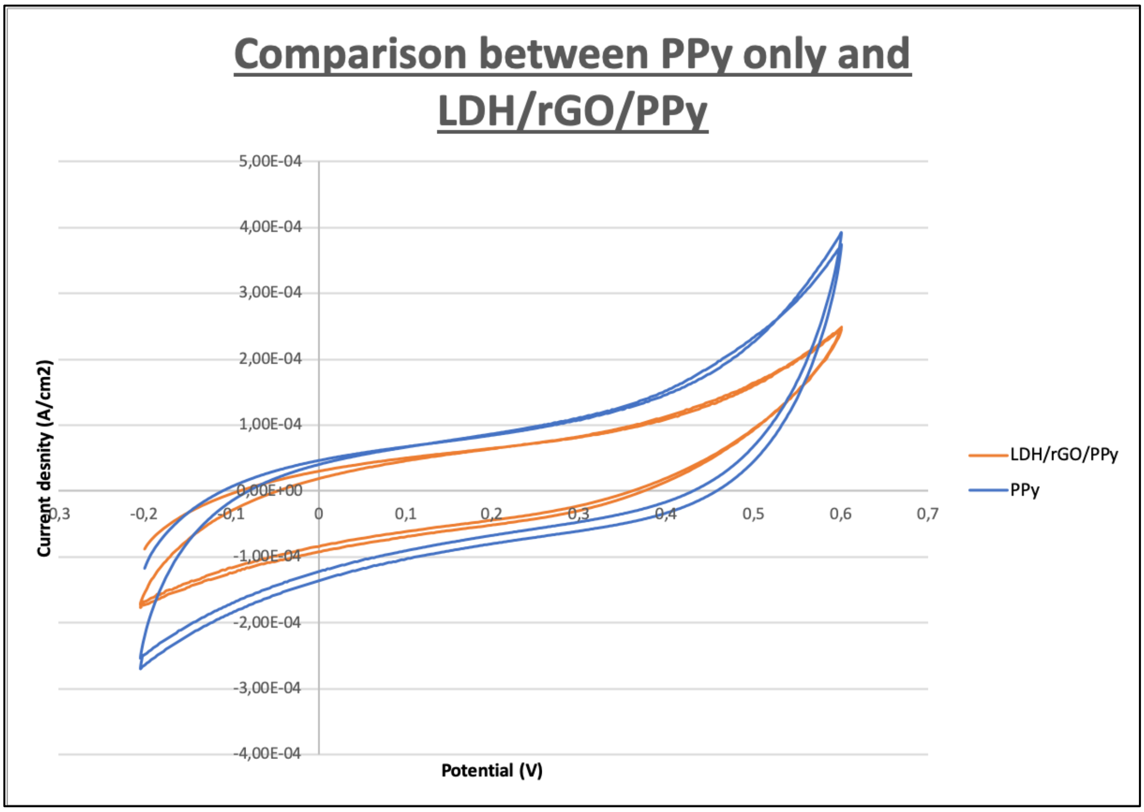


Figure 12: Graph of the CV tests for the samples LDH/rGO/PPy and PPy only– current density

To conclude on these five first samples, the sandwich LDH/rGO/PPy seems to have the best conductive performances so the next step is to find a way to improve its performances by working on the reduced graphene oxide layer.

b) Improvement of the reduced graphene oxide layer

The next two samples were made in order to test the theory according to which adding a second layer of graphene oxide on top of the other one would increase the current density.
The first sample here has two layers of graphene oxide between the LDH and the PPy layers and the second sample has three layers of GO.

As it was explained in the experimental part, the sample was dried in the oven between each layer of graphene oxide.

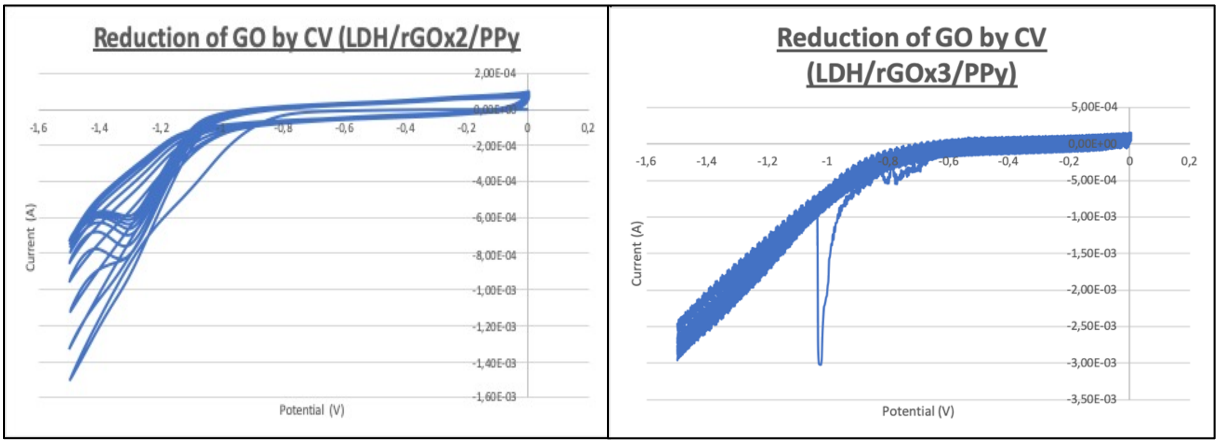


Figure 13: Graphs of the reduction of the graphene oxide for samples LDH/rGOx2/PPy and LDH/rGOx3/PPy

Even if the area of the sample is not taken into account here, it clearly appears that reduction is not working as expected on the sample covered by three layers of graphene oxide. The one-layer of GO sample graph will also be compared to these two graphs, for a better understanding of the thickness influence of the rGO layer in the reduction process.

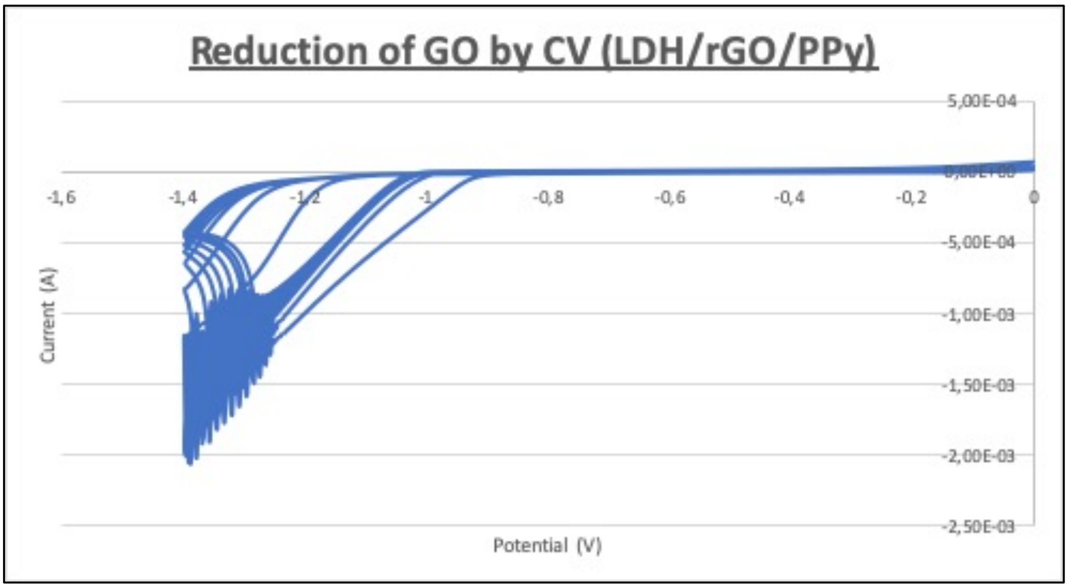


Figure 14: Graph of the reduction of the graphene oxide for sample LDG/rGOx1/PPy

The graph for the sample with one layer of GO has the same shape as the graph for the sample with two layers of GO.

The only information that can be kept from these three graphs is that drop-casting three layers of graphene oxide leads to a thickness of GO that cannot be properly reduced (without changing the parameters of the reduction). On the surface, the material will be reduced but the graphene oxide below the surface might not be reduced as it should. As a result, the conductive properties of the electrode are threatened.

Once that the three-layers of GO option is put apart, there is still a decision to make between one or two layers of graphene oxide between the LDH layer and the PPy.

This information can be found by comparing the cyclic voltammetry test results of the samples covered by one and two layers of graphene oxide, taking the current density into account.

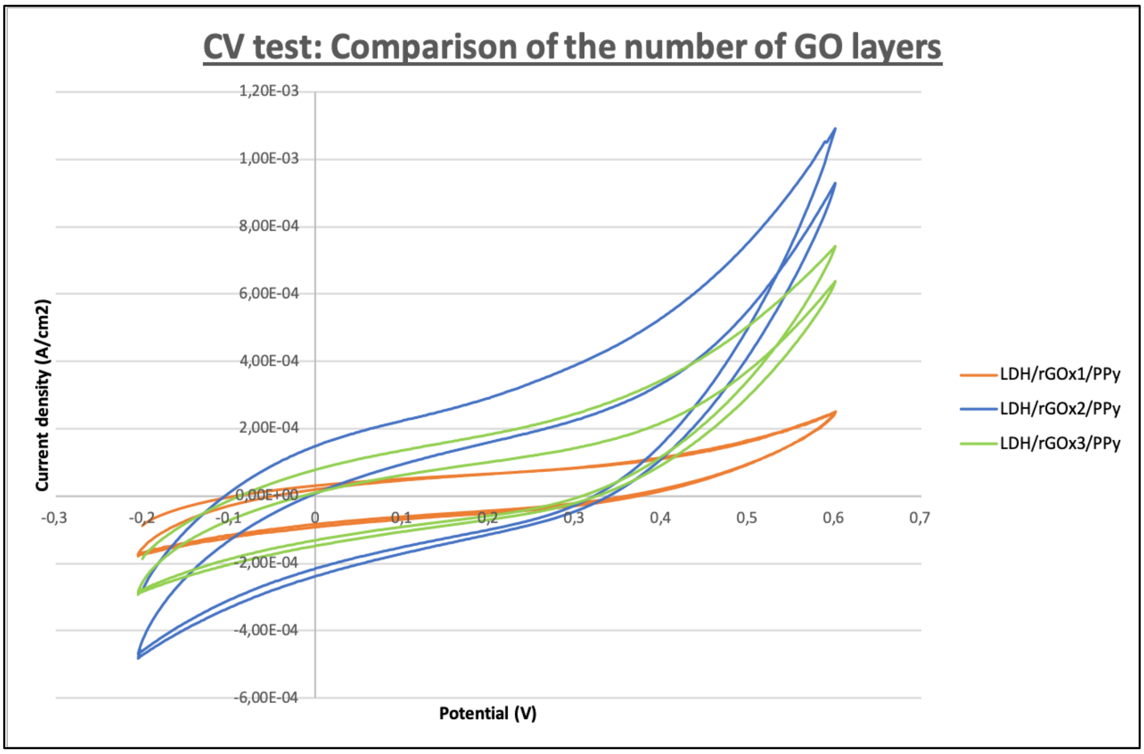


Figure 15: Graph of the reduction of the graphene oxide for sample 1-layer, 2-layers and 3-layers of GO

This comparison between the sample with one layer of GO and the sample with two layers of GO shows that the reduction is better with two layers graphene oxide. The values obtained are given in the following table.

	Integral (A*V/cm^2)	Specific capacitance (mF/cm^2)
LDH/rGOx1/PPy	1,53E-4	1,91
LDH/rGOx2/PPy	4,34E-4	5,42
LDH/rGOx3/PPy	2,62E-4	3,28

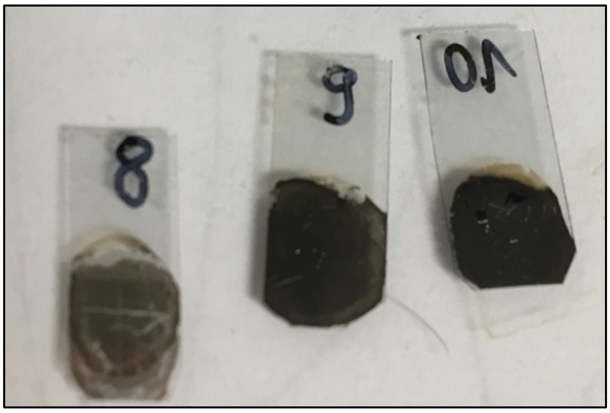
Table 3: Specific capacitance values for the different amount of reduced graphene oxide

Indeed, one layer of GO is not enough to cover all the LDH below, so when the reduction happens, this LDH layer is etched and thus, the current density is relatively low. On the opposite, when two layers of GO are drop-casted on the sample, the LDH is homogeneously coated and as a result, the reduction does not have an impact on the LDH layer. The values strengthen this idea because the highest specific capacitance is achieved for the sample made with two layers of reduced graphene oxide.

The next idea to improve the interfaces of the samples was to drop-cast a GO layer between the PET/ITO and the LDH ZnAl.

c) Improvement of the ITO/LDH interface

For this part, three samples were tested with different amount of GO between the ITO and the LDH layer. The first sample has two layers of graphene oxide between the substrate and the LDH because the previous results showed that two layers lead to better results than one layer. So even if the GO layer studied before was located between the LDH and the polypyrrole, the same theory can be applied between the substrate and the layer double hydroxide.
The second sample has four layers of GO between the substrate and the LDH and the last one has six layers of GO. For all of these samples, two layers of GO are deposited between the LDH and the PPy.
Once the graphene oxide had been deposited on the substrate, it is reduced thanks to cyclic voltammetry. The aspect of the sample before and after the reduction is expected to change since the reduction makes the layer of graphene oxide darker. This can clearly be seen on the following picture.



<u>Picture 3</u>: Picture of the three samples being tested for the GO layer between the substrate and the LDH

In this picture, the sample labelled 8 has two layers of reduced graphene oxide between the substrate and the LDH. The sample labelled 9 has four layers and the sample labelled 10 has six layer of reduced graphene oxide.
When more graphene oxide is deposited on the substrate, the darker the sample get because the thicker is the graphene oxide layer in total.
In order to see the influence of the presence of reduced graphene oxide between ITO and LDH, the cyclic voltammetry tests on the 3 samples were run and compared and the specific capacitance was calculated.

	Integral (A*V/cm^2)	Specific capacitance (mF/cm^2)
ITO/rGOx2/LDH/rGOx2/PPy	2,03E-4	2,53
ITO/rGOx4/LDH/rGOx2/PPy	7,59E-4	0,949
ITO/rGOx6/LDH/rGOx2/PPy	1,62E-4	0,202

Table 4: Specific capacitance values for the different amount of reduced graphene oxide before LDH

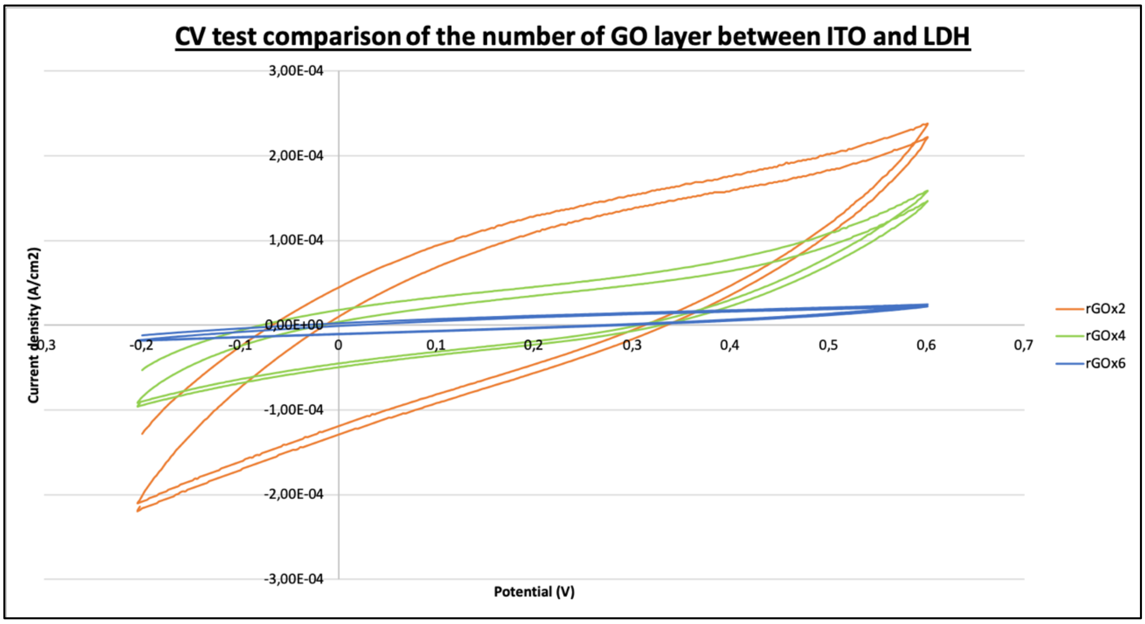


Figure 16: Graph of the CV test of samples with 2, 4 or 6 layers of GO between the substrate (ITO) and the LDH

The comparison between these curves clearly shows that as the quantity of graphene oxide increases, the conductive performances of the composite electrode decreases. The issue now, is to know if this new layer between ITO and LDH is useful in order to improve the capacitance of the supercapacitor. Hence, these three samples were compared to the sample LDH/rGOx2/PPy, which has revealed until now to be the best sandwich type of composite for the electrode.

The values show the same conclusion because the specific capacitance is lower with the last set of three samples, when reduced graphene oxide is deposited between the substrate and the layered double hydroxide.

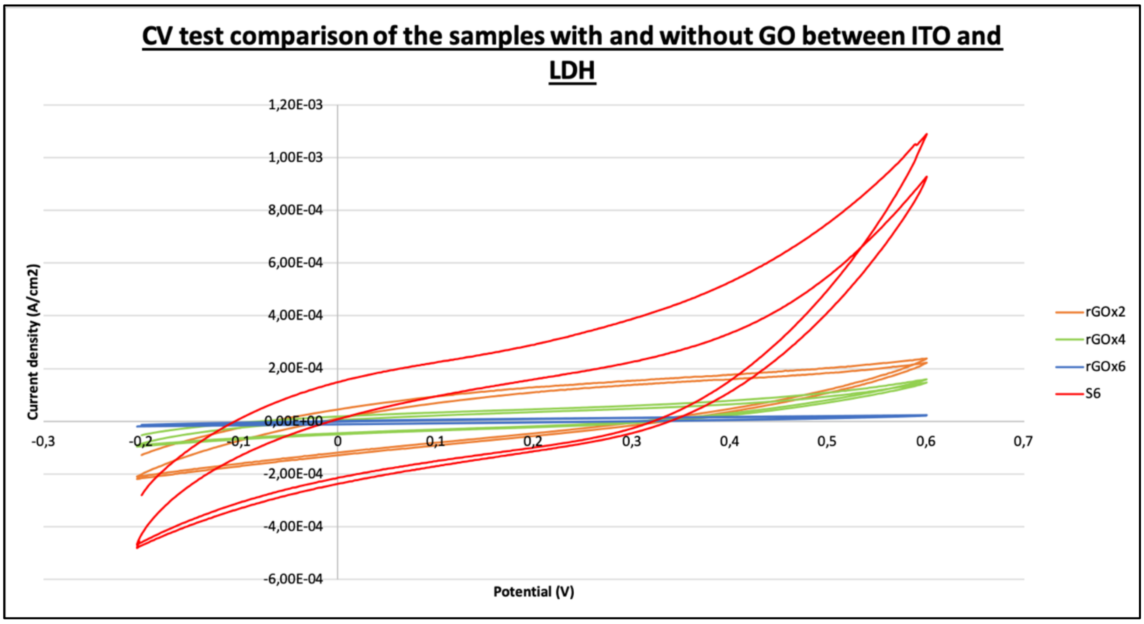


Figure 17: Graph of the CV test of samples LDH/rGOx2/PPy, and 2, 4 or 6 layers of GO between the substrate and the LDH

The red curve represents the CV test of the LDH/rGOx2/PPy sample.
This comparison shows that adding graphene oxide between PET/ITO and the LDH layer is not useful and even reduces the current density, thus, decreases the conductive properties of the electrode.
So, the decision was made to keep with the sample LDH/rGOx2/PPy without adding GO between ITO and LDH.
Another mean to improve the interface would be to change the reduction process of the GO layer between LDH and PPy and try this new process on a GO layer between ITO and LDH.

d) Reduction of the graphene oxide

Two different reduction process were tested, in addition to the cyclic voltammetry reduction that was usually performed.

- Potentiostatic reduction at -1,4V for 300 seconds
- Chemical reduction by diving the sample in vitamin C and leaving it dried at 60°C for 12h, as it was explained in the method part concerning the cotton experiments.

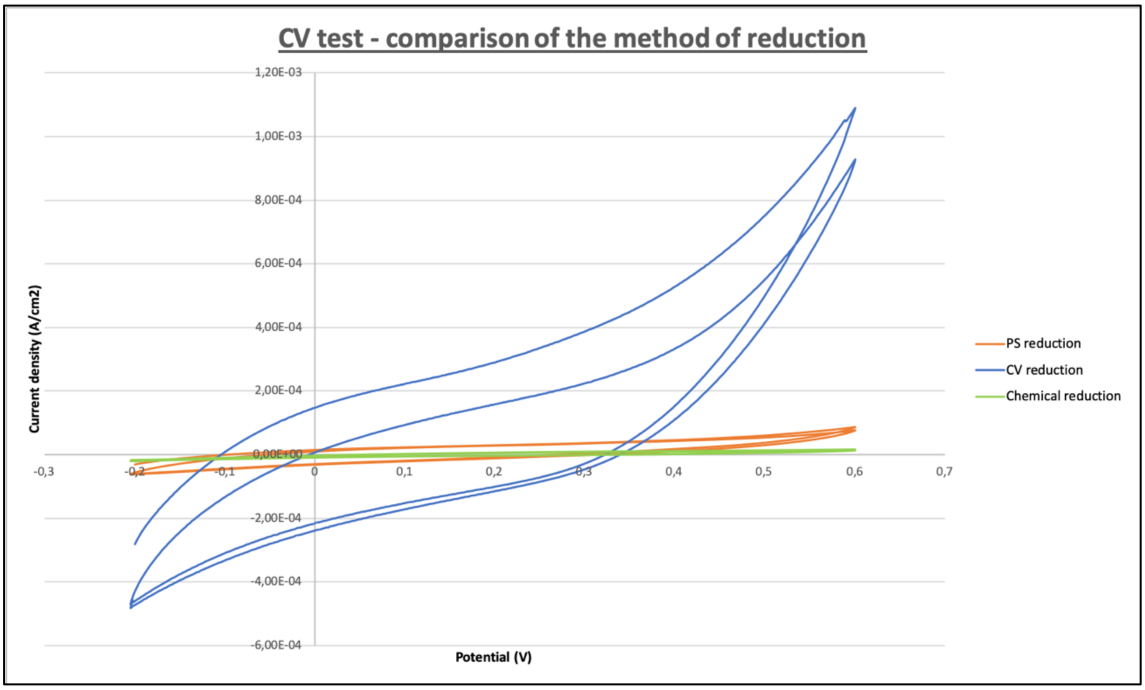
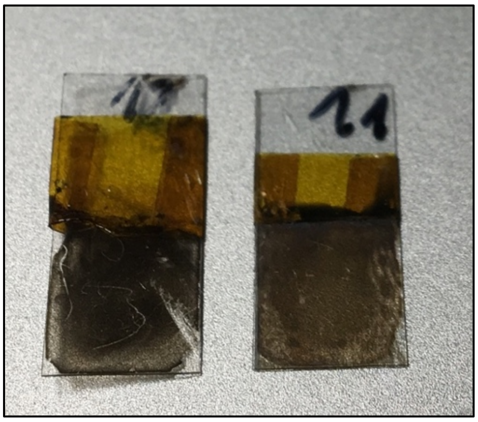


Figure 18: Graph of the CV test of samples with CV reduction, chemical reduction or PS reduction

These curves show that the new potentiostatic method for graphene oxide reduction did not work on the sample. After having analyzed the graphs from every step of the sample with potentiostatic method for reduction, it appears that the failing of the reduction process had an impact on the polypyrrole deposition and as a result, on the conductive performances of the electrode. According to the aspect of a sample surface after reduction, the chemical process did not work either for the reduction of graphene oxide. Indeed, the color of the sample should be darker after the reduction but in the case of a chemical reduction, the color did not change.

The aspect of the sample gives also a hint on the quality of the reduction. When the reduction takes place, the sample goes from grey to almost black. The following picture shows the aspect of the samples after a potentiostatic reduction and after a chemical reduction.



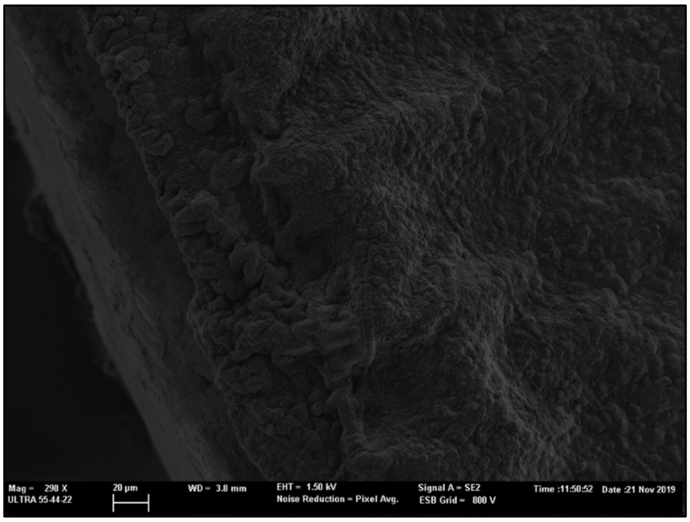
Picture 4: Picture of the two samples after a different process of reduction

The sample on the left underwent the chemical reduction whereas the sample on the right underwent a potentiostatic reduction. After the reduction, both of the sample were covered by a layer of polypyrrole and were run through a cyclic voltammetry test. It can clearly be seen that the surface is not homogeneous and does not present the aspect that was expected. Indeed, the composite electrode must be a homogenous black layer. These types of reduction with these parameters are not an optimal process for this case.

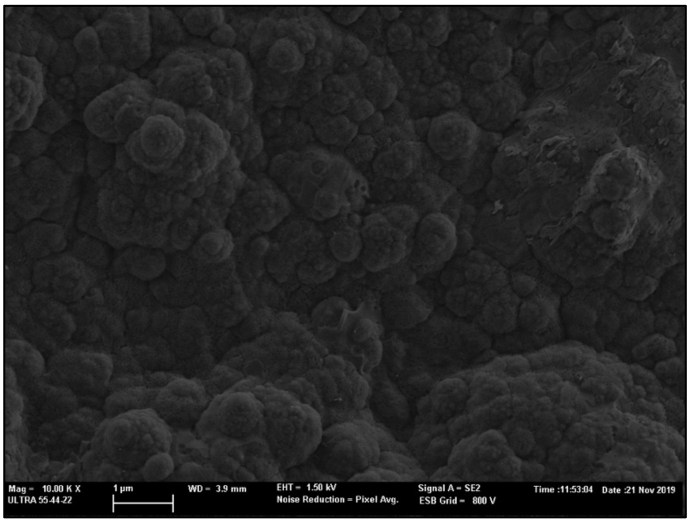
As a conclusion concerning the PET/ITO experiments, the best sandwich composite electrode material appears to be LDH/rGOx2/PPy with a cyclic voltammetry reduction of the graphene oxide, which displayed the highest specific capacitance of 5,42 mF/cm^2.

e) Scanning electron microscope observations

The following pictures are images of two samples with PET/ITO substrate: LDH/rGOx2/PPy and PPy only. They were taken at an increasing magnification.

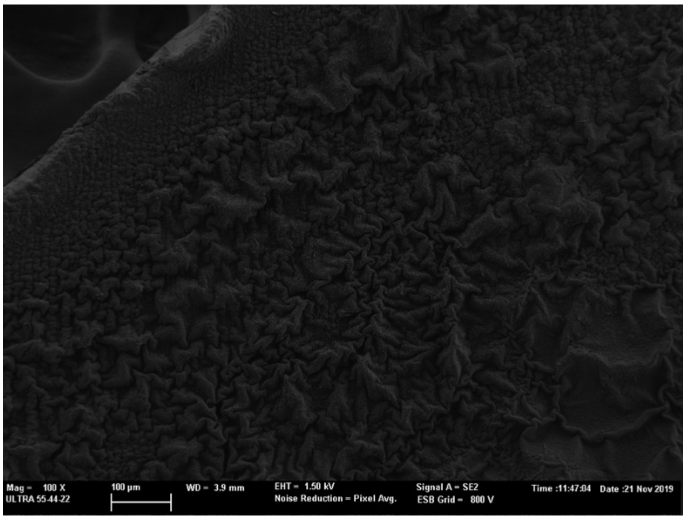


<u>Picture 5</u>: SEM image of PPy on PET/ITO substrate: Mag = 298X

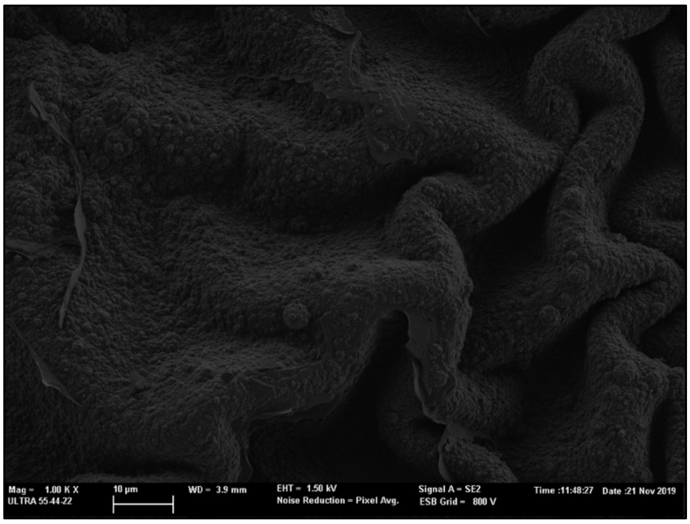


<u>Picture 6</u>: SEM image of PPy on PET/ITO substrate: Mag = 10,000 K X

The second image clearly shows the polypyrrole as a shape of cauliflower, on the surface of the PET/ITO substrate. This can only be seen at a very high magnification of 10,000 KX.

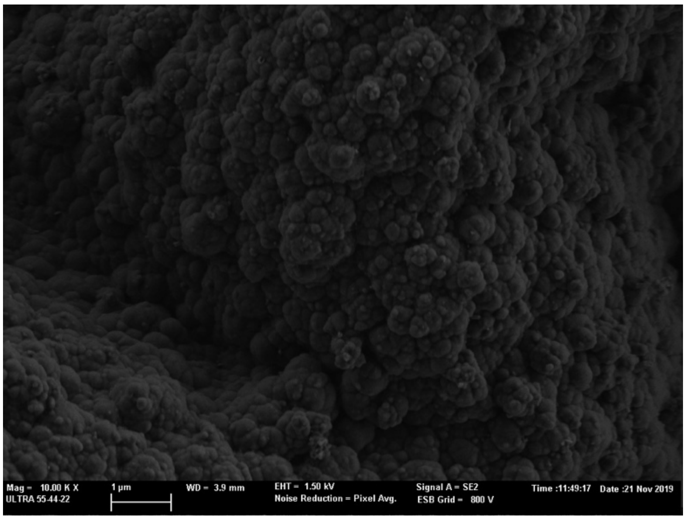


<u>Picture 7</u>: SEM image of LDH/rGOx2/PPy on PET/ITO substrate: Mag = 100 X



<u>Picture 8</u>: SEM image of LDH/rGOx2/PPy on PET/ITO substrate: Mag = 1,00 K X

On the second image here, at a magnification of 1,00 K X, the vertical walls that can be seen are made of LDH, the first layer to be coated onto the PET/ITO substrate.



<u>Picture 9</u>: SEM image of LDH/rGOx2/PPy on PET/ITO substrate: Mag = 10,000 K X

On this last picture of the sample LDH/rGOx2/PPy, the magnification is ten times the magnification of the previous image where the LDH can be seen. In this one, the cauliflower shape of the polypyrrole is observed.

2) Cotton experiments

a) Treated and non-treated sterile cotton

The aim of the first experiments run with cotton was to compare treated and non-treated sterile cotton to know which one give the best capacitance. The process to treat the cotton was explained in the experimental part, this treatment is the activation of the cotton.

Both treated and non-treated cotton were covered by graphene oxide thanks to vacuum filtration and the polypyrrole was then deposited on the samples. The cyclic voltammetry test was finally performed to evaluate the capacitance of both samples.

Figure 19: Graph of the CV test comparison between treated and non-treated cotton

This graph shows that the total area within the curve is higher for the treated cotton than for the non-treated cotton. Despite the fact that the maximum current density value is higher for the non-treated cotton, it can be concluded than the treated cotton has a better capacitance than the non-treated one.

b) The influence of the number of graphene oxide layers

From this point, the investigations were led in order to discover how the amount of graphene oxide affects the conductive performances of the electrode.

Starting with two treated cotton samples, one of them was covered with one layer of graphene oxide and the other one with two layers of graphene oxide. They both underwent reduction in vitamin C followed by the electrodeposition of polypyrrole and went finally though the cyclic voltammetry test.

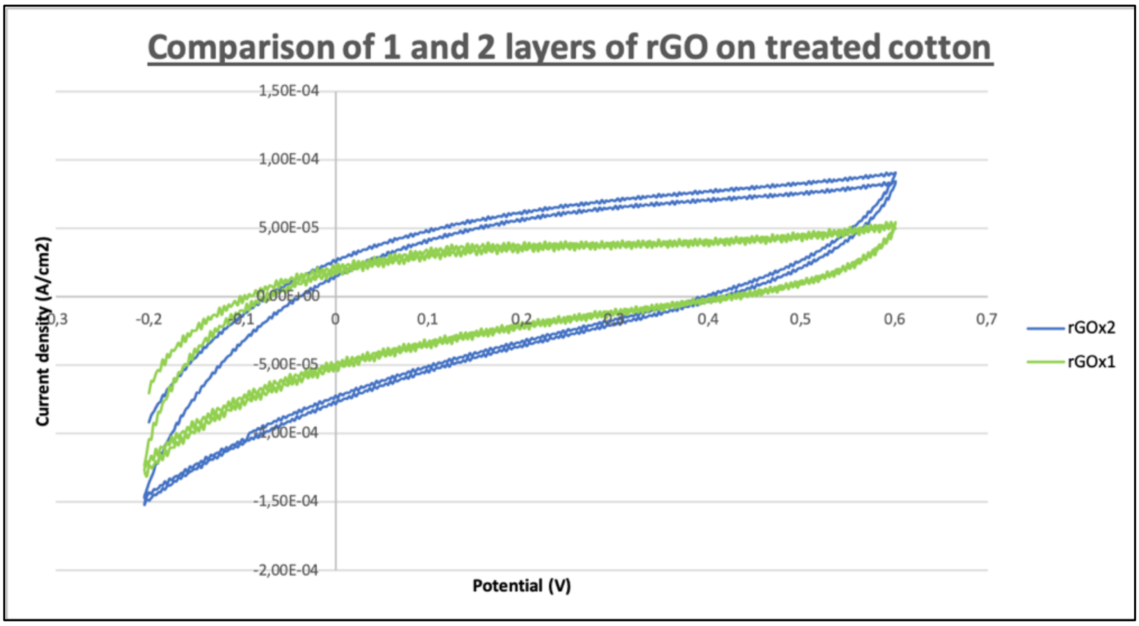


Figure 20: Graph of the CV test comparison between treated cotton with one and two layers of GO

On this graph, it can be seen clearly that the two-layers of GO sample has a better capacitance than the one-layer of GO sample. The area within the curve is higher for the blue curve than for the green one, which indicates that as the amount of graphene oxide increased, the conductive performances increased as well.

c) Experiments on basic commercial recyclable fabric

At this point of the investigations, the substrate was changed to basic commercial fabric. Since the previous experiments showed that a higher amount of graphene oxide resulted in a better capacitance, it has been decided to deposit three layers of graphene oxide on the cotton sample.

As it was explained earlier, within the 5mL of graphene oxide solution deposited on the sample, 2,5mL are deposited on one side of the cotton sample and 2,5mL on the other side. Between the several filtration steps, the samples were dried at 80°C during 5min.

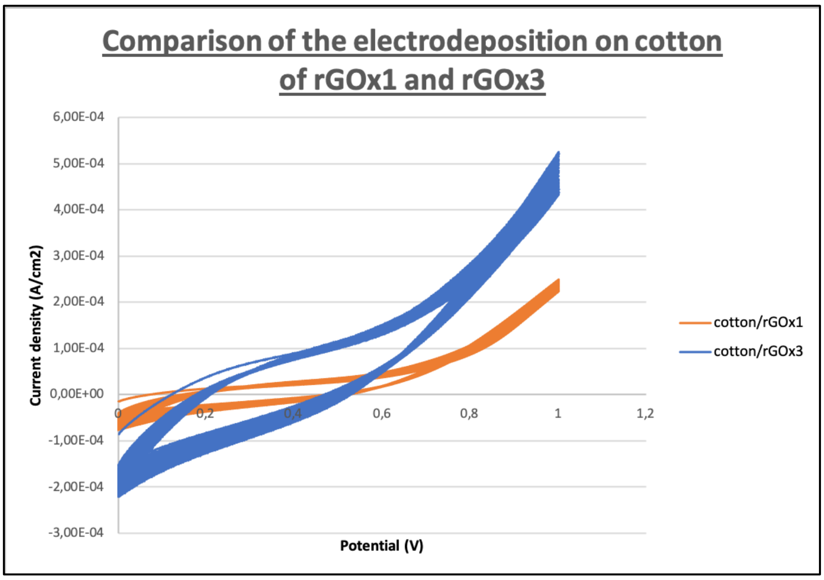


Figure 21: Graph of the electrodeposition comparison between cotton with one and three layers of GO

The electrodeposition of polypyrrole on the cotton revealed that the polymer bonds better to the cotton one the three-layer-GO cotton than on the one-layer-GO cotton. The CV test performed afterwards revealed the same conclusions.

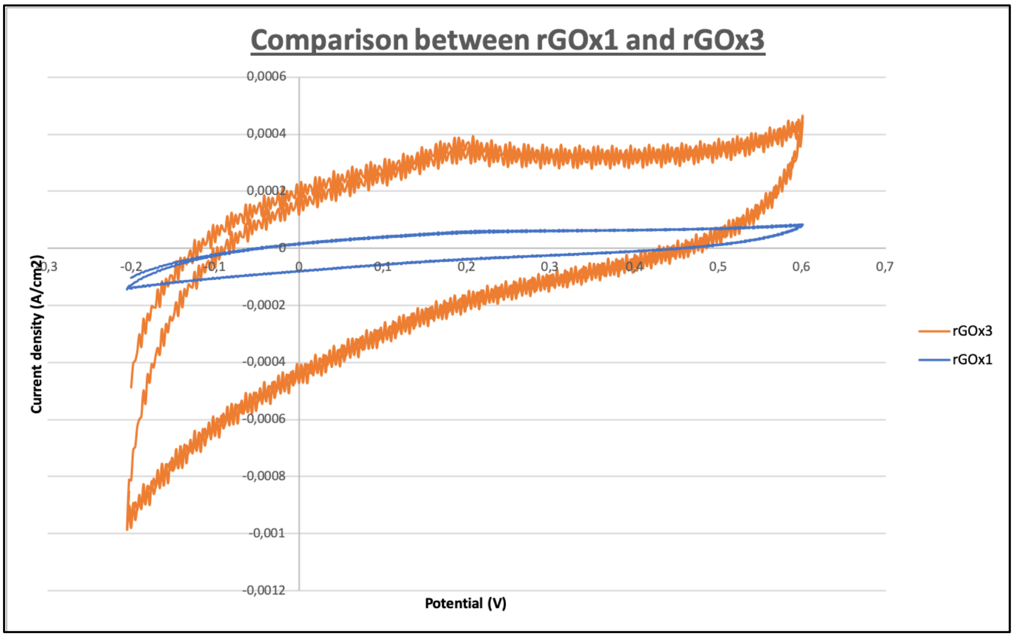


Figure 22: Graph of the CV comparison between cotton with one and three layers of GO

This graph shows that the capacitance of a three-layers-GO electrode is higher than the capacitance of the one-layer-GO electrode.

Indeed, the area within the curve corresponding to three layers of graphene oxide electrode is more important than the area of the one layer of graphene oxide electrode.

Therefore, the electrode made of cotton/rGOx3/PPy will be used to perform bending tests in order to insure the cyclability of the electrode.

The bending test process has been explained in the experimental part and the aim of these experiments is to evaluate the cyclability of the electrode when it undergoes several repeated bending cycles.

Fifty bending cycles were performed, and a cyclic voltammetry test was run every five bending cycles to follow the evolution of the capacitance.

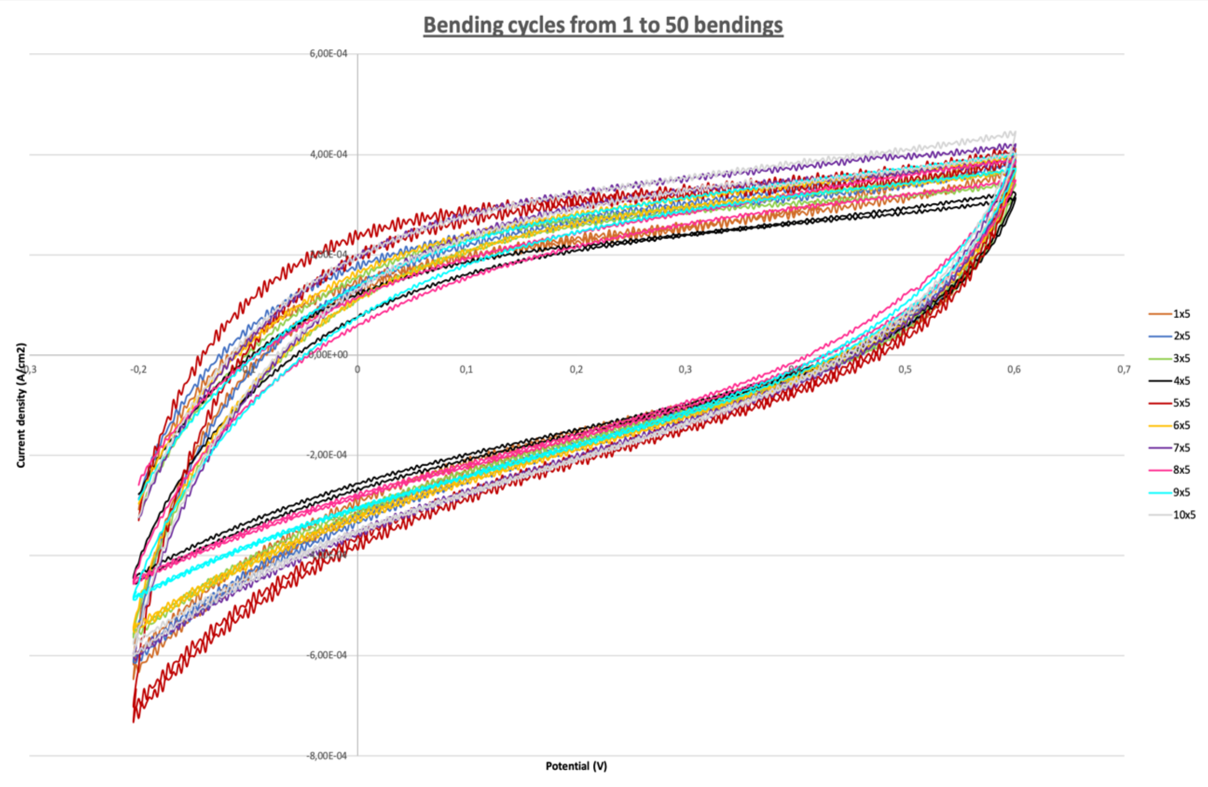


Figure 23: Graph of the CV test with bending cycles

It appears that fifty bending cycles do not have an important influence on the conductive performances of the electrode.

The specific capacitance of the electrode had been calculated for each series of bending cycles in order to quantitatively evaluate the cyclability.

The next step consists of plotting the specific capacitance as a function of the number of bending cycles to see how the bending operation has an influence on the specific capacitance of the electrode. The graph below shows that the specific capacitance is quite stable when the number of bending cycles increases. It testifies a good cycling stability against bending cycles.

Due to experimental errors, some values had not been taken into account for the plotting of the graph. Indeed, these values were too different from the others to consider that the bending cycles were responsible of these variations. One of the reasons why some values are very different from the others might be the contact between the screw of the equipment and the electrode. Indeed, if the contact is not made the same way for each measurement, it might have an impact on the results.

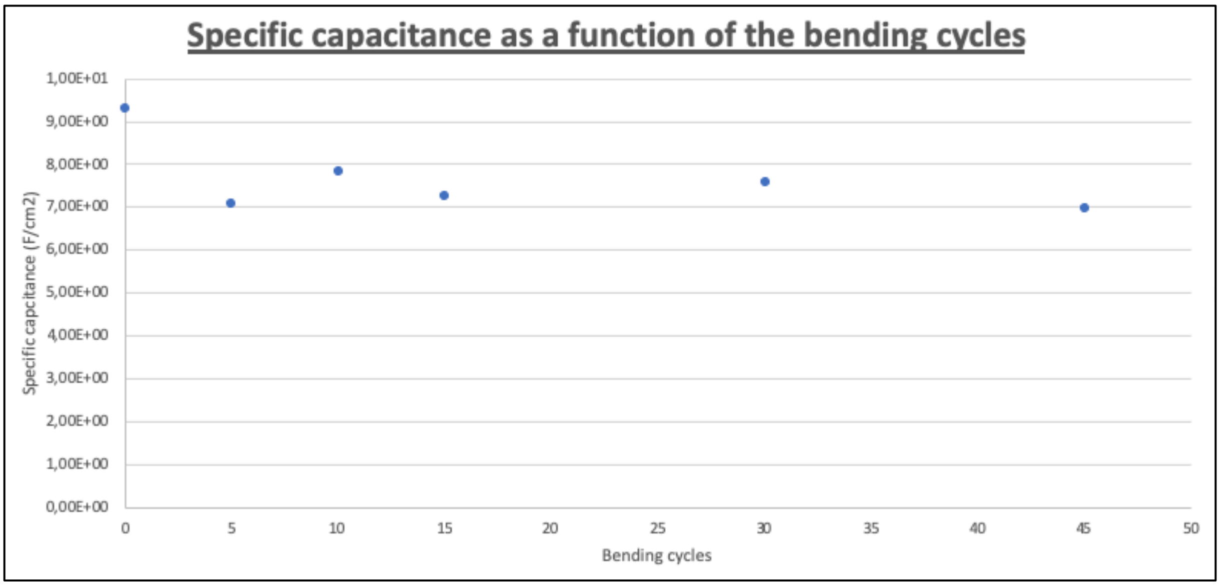
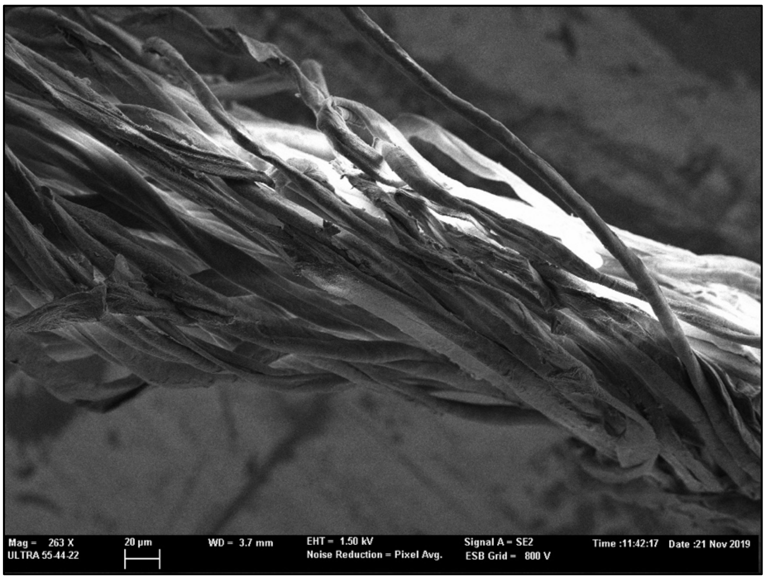


Figure 24: Graph of the specific capacitance as a function of the bending cycles

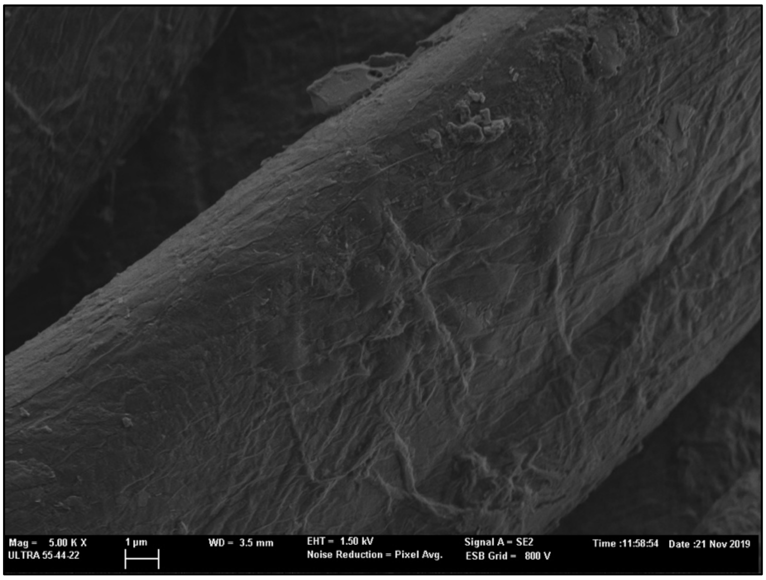
To conclude on the cotton experiments, the results showed that the best electrode material was made of cotton/rGOx3/PPy. This combination of the component showed a satisfying bending stability with a retention of 75% after 50 bending cycles. The specific capacitance achieved by this device was equal to 6,99 mF/cm^2.

d) Scanning electron microscope observations

The samples observed with the SEM were made of cotton coated with one and two layers of reduced graphene oxide.

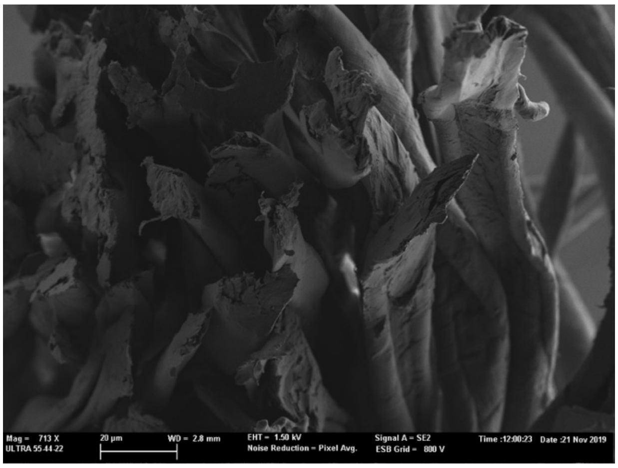


Picture 10: SEM image of rGOx1 on cotton substrate: Mag = 263 X

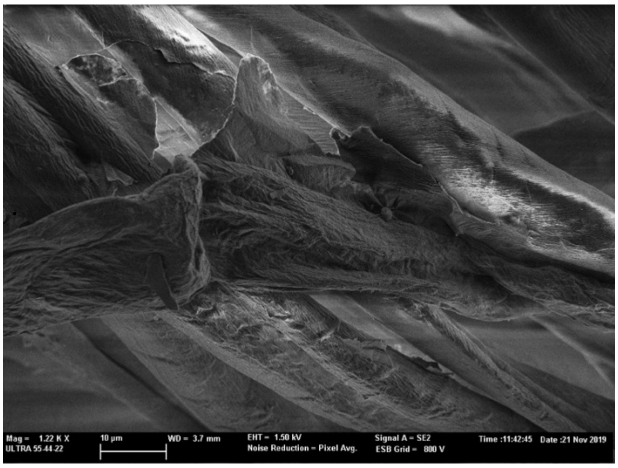


Picture 11: SEM image of rGOx1 on cotton substrate: Mag = 5,00 K X

Both of these images clearly show that the cotton wire is well coated with the graphene oxide material. To compare the influence of the amount of GO, these images must be compared to the following, showing the cotton coated with two layers of graphene oxide.



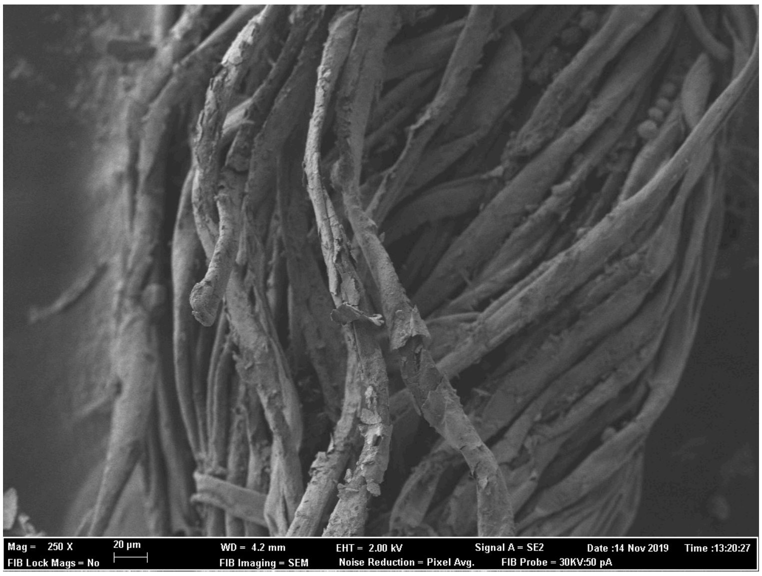
Picture 12: SEM image of rGOx2 on cotton substrate: Mag = 713 X



Picture 13: SEM image of rGOx2 on cotton substrate: Mag = 1,22 K X

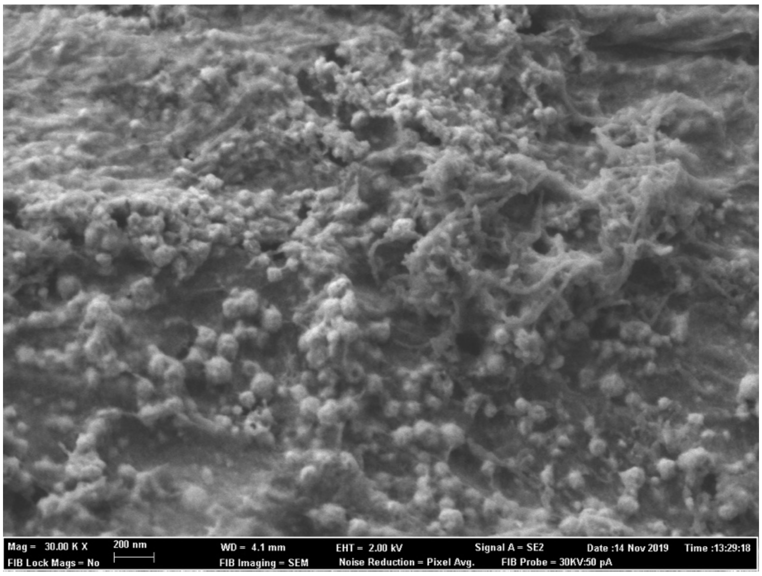
When comparing the images 12 and 13 with the images 10 and 11, it can be observed that the cotton wire is well coated with the graphene oxide material. Indeed, the graphene oxide sheets are crumpled and agglomerated but it can also be seen that when the cotton is coated with two layers, the coverage of the cotton is improved, compared to the cotton covered with only one layer of reduced graphene oxide.

The next scanning electron microscopy observation was on the sample based on cotton substrate, covered with reduced graphene oxide and polypyrrole.



<u>Picture 14</u>: SEM image of PPy and rGO on cotton substrate: Mag = 250 X

This image shows a thicker deposit, which is polypyrrole, coated on the reduced graphene oxide onto the cotton wire.



<u>Picture 15</u>: SEM image of PPy and rGO on cotton substrate: Mag =30,00 K X

On this last image, the globules of polypyrrole on top while the sheets of reduced graphene oxide are below.

VII) Conclusion

The main objective of this project was to create a new flexible electrode material for supercapacitor applications in order to help the researches on the storage of renewable energy. A supercapacitor device is made of two electrodes, one separator and the electrolyte. However, since the project focuses on the fabrication of a new electrode material, the device was simulated by using only one electrode and the separator and electrolyte were not analyzed.

The method used to elaborate the new electrode consisted first in finding the most suitable sandwich type composite based on the four components that are the flexible substrate, the graphene oxide upon reduction, the layered double hydroxide ZnAl and the conducting polymer, polypyrrole. One criterion here was to use simple deposition methods at the surface of the flexible substrate so the LDH was deposited by potentiostatic method while the polypyrrole was deposited by electropolymerization and the graphene oxide was drop-casted.

When the sandwich type composite was found, the next experiments focused on the most efficient amount of reduced graphene oxide in order to improve the properties of the supercapacitor. Drop-casting two layers of GO and reduce them by cyclic voltammetry has revealed to be perfectly fitted for this composite. The reduction process for the graphene oxide was then studied and three methods were possible: the chemical reduction, the potentiostatic method of the cyclic voltammetry and the last one had revealed to be the most adequate choice. The interface between the ZnAl LDH and the PET/ITO substrate was also investigated by depositing reduced graphene oxide between the two components, but a higher specific capacitance was achieved without this rGO underneath the LDH. The highest specific capacitance was reached by the sample made of LDH/rGOx2/PPy on the PET/ITO substrate with 5,42 mF/cm^2. The scanning electron microscope images showed that the LDH was forming vertical walls and the polypyrrole had a cauliflower shape.

When the sandwich type was set on the PET/ITO substrate with the correct amount of each of the materials, the investigations moved on to the sustainable and recycled material: the cotton. The first experiments were run on sterile cotton and the need of activating the substrate was revealed. The loading of the graphene oxide had been tested again because the deposition of this material was performed by vacuum filtration and was then reduced chemically in vitamin C. After that, basic commercial recycled fabric was used to test the resistance of the electrode to bending cycles. The samples showed a retention of 75% after 50 bending cycles and achieved a specific capacitance of 6,99 mF/cm^2, with a sample made of cotton/rGOx3/PPy. The scanning electron microscope images showed crumpled and agglomerated graphene oxide sheets and a better coverage of the cotton wire with a higher amount of GO. The polypyrrole is shaped as globules onto the graphene oxide sheets.

The perspectives of this project could be the variation of the deposition parameters, with another scan rate, number of cycles and potential window. The electrolyte in which the CV tests were performed could also be changed to see its influence on the specific capacitance. The vacuum filtration used to deposit the graphene oxide on the cotton substrate needed a polycarbonate membrane. This material could also be investigated as a substrate since it is highly flexible.

VIII) Budget

1) Labor costs

	Cost per hour (€/h)
Engineer	30
Technician	16,15

Table 5: Labor costs

2) Depreciation of machinery equipment

	Cost per hour (€/h)
Potentiostat	5,05
SEM	45,5
Vacuum pump	1,5
Oven	1,8

Table 6: Depreciation and machinery equipment costs

3) Raw materials

	Cost per gram (€/g)	Weight (g)	Final price (€)
Substrates			
PTE/ITO			50€
Sterile cotton			15€
Cotton fabric			10€
Reactive agents			
$Zn(NO_3)_2$	0,079	1,2	0,095
$Al(NO_3)_3$	0,137	1	0,137
Polypyrrole	26,2	2,22	58,2
Graphene oxide	34,25	23	787,75

Table 7: Raw material costs

4) Fabrication costs

	Cost per hour (€/h)	Number of hours (h)	Final price (€)
Potentiostat	5,05	96	484,8
Vacuum pump	1,5	45	67,5
Oven	1,8	240	432

Table 8: Fabrication costs (equipment)

	Number of hours (h)	Cost per hour (€/h)	Final price (€)
Engineer hours	120	30	3600
Technician hours	0	16,15	0

Table 9: Fabrication costs (labor)

5) Characterization cost

	Cost per hour (€/h)	Number of hours (h)	Final price (€)
Potentiostat	5,05	20	101
SEM	45,5	15	682,50

Table 10: Characterization costs (equipment)

	Number of hours (h)	Cost per hour (€/h)	Final price (€)
Engineer hours	230	30	6900
Technician hours	15	16,15	242,25

Table 11: Characterization costs (labour)

6) Total cost

Total cost = 13 431 €, trece mil cuatro cientos y uno euro

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