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Comparison of Printing Techniques for Textile PEDOT Electrodes: Electrical Characterization under Operating Conditions

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Abstract

The advances in material science and nanotechnology have led 3D printing to be the most versatile method for custom sensor fabrication.

3D printing is nowadays a rather common technique for production of custom objects for both scientific research and personal hobbies, making use of plastic filaments for structural printing. New and improved 3D printers allow the use of special made inks for specific analytes sensing, opening the way for countless applications in sensor manufacture.

This thesis studies the 3D printing of the PEDOT:PSS polymer as a base for textile applications.

Poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) is a semiconducting polymer that is flexible and compatible with many textile materials, being already widely used in organic optoelectronic devices.

PEDOT:PSS is able to be mixed with other reagents to create conductive ink that can be deposited and dried onto textile material, useful for different textile sensing applications. Two different inks were fabricated, analyzing their electrical and morphological properties when 3D printed onto two different, commercially available, gauze fabrics.

One of the fields in sensing with the most potential for wearable sensors applications is the monitoring of wounds. The healing process of an external injury is extremely vulnerable to foreign interference, such as proper sterilization of the wound and continuous change of the wound's dressing: monitoring a wound's status through sensors printed onto the gauze fabric may completely remove external influences, leading to a faster recovery.

The "Results" chapter contains the morphological and electrical properties of the two inks when 3D printed on either fabric. The inks were also analyzed in a wet environment, simulating that of a wound's.

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Introduction

Internet of Medical Things

Healthcare is and always has been one of the first sectors to benefit from the advancements in technology. No era in human history has ever been free of health challenges, requiring ever new methods to treat new and old diseases. The accidental discovery of penicillin in 1928 due to microbial biology, the development of Magnetic resonance imaging in 1977 thanks to the advancements in atomic theory, the invention of CRISPR-Cas9 in 2012 due to advancements in genetics, every major healthcare innovation requires new and improved scientific frameworks that challenge old ones.

Although medical technique and medicine philosophy have become more and more advanced, the world around them changes at a even speedier pace. These days, physicians have more advanced examination instruments and more effective treatments, which can be used to fight disease and protect people's health, while on the other hand the overpopulation crisis and the rise of new diseases puts the healthcare system worldwide under extreme stress. The recent pandemic of corona virus has just highlighted how vulnerable modern medical systems remain to major infectious diseases. The medical sector urgently needs to develop new ways to prevent and treat diseases and to improve the resilience of medical systems to public health crises.

The rise of Internet in the 1990s has been an epochal change for most human lives, being able to connect people across the world almost effortlessly, so it is no surprise how it has been integrated into the medical world.

In recent years, IoMT, or the Internet of Medical Things, has emerged as a hot technology field in the healthcare industry. IoMT encompasses a network of interconnected healthcare devices and systems that gather, analyze, and transmit health data. This enables remote patient monitoring, diagnosis, and treatment, revolutionizing the way healthcare is delivered. To understand the development of IoMT, it is necessary to trace back to the concept of Internet of Things (IoT). The IoT connects not only people but all theoretically connectible entities in this physical world, entities such as both people and objects. The IoT has made good progress in many fields, including smart transportation, smart cities, smart factories, smart homes, etc. In a smart city, for example, the citizens and the city managers, as well as the infrastructure and buildings of the city, are all on a common platform of the IoT. Every street light, every road camera, and every first aid station in the city is a node in the IoT, playing a role in data collection and realizing city functions. Similarly, the IoMT connects experts in different roles with various devices and objects in the medical scene, establishing an information platform where people-to-people, people-to-things, and things-to-things are all freely connected. The objects in the IoMT include traditional medical instruments and tools, such as medical examination instruments like CT machines and MRI machines, as well as hospital facilities and medical records. This interconnection between machines and medical per-

sonnel lightens the load that the healthcare system is under, providing quick and easy connections between specialists and administrative apparatuses for faster and efficient patient data analysis. At the foundation of the system lie the various sensors used to gather a patient's data, as new and improved sensing technologies allow medical staff to quickly and precisely gather information to treat illnesses.

Translating the body's physiology to analyzable data requires many new sensing technologies, which means advancements in materials and production techniques.[1]

Conjugated polymers: PEDOT:PSS

Polymers are a class of organic molecules composed of many repeated sub units, used in a plethora of applications, usually as a building block for flexible plastic applications: they possess no mobile charges, acting as electric insulators.

Conjugated polymers are a subclass of polymers, possessing particular properties that makes them rather useful for multiple purposes. Conjugated polymers are artificially synthesized polymers containing single and double bonds, whose presence creates delocalized π electrons in the main polymer chain. When multiple polymer chains aggregate the delocalized π electrons overlap; charge can be transferred along the main chain of the delocalized π electron system, resulting in electrical conductivity.

Being organic molecules, conjugated polymers can be tuned through synthetic chemistry, and their biological properties can be controlled using a variety of strategies: they can be engineered on various forms, such as ionically and electronically conducting inks or hydrogels. Because of their conductive properties, conjugated polymers are heavily used in the creation of organic electronic materials.

Organic electronic materials are the organic analogous of inorganic semiconductors such as silicon, sharing similar conductive properties. A semiconductor is formed by a repeating crystal matrix held together by covalent bonds between atoms, while organic materials do not have a precise repeating pattern, often being macroscopic clumps of material held together by Van der Waals interactions.

This difference in structure generates important properties of organic electronic materials:

- **Facile chemical modification:** organic molecules have been used in every aspect of industrial applications, generating countless way to modify a given organic compound to one's specifications.
- **Low temperature processing:** due to the relatively low intensity of the Van der Waals interaction, the bonds in an organic electronic material are easier to break for processing compared to an inorganic semiconductor's covalent bonds.
- **Oxide-free interface:** in order to interact with an electrolyte inorganic semiconductors need to have broken covalent bonds in contact with the medium, which

generates oxidation on the surface layer of the material, which hinders the material's conductivity. In organic materials this doesn't happen due to the absence of broken covalent bonds.

- **Flexibility:** due to the Wan der Walls interaction the material is not being constrained by the need of a repeating lattice, giving it a higher flexibility than traditional semiconductors.
- **Ionic conduction:** due to the presence of spaces between clumps of material, inorganic electronic materials are capable of being ionic conductors when properly doped. Ionic conductors are materials with highly mobile ions that, moving around, transport charge while the material stays electronically insulating[2].

PEDOT:PSS is an organic electronic material made by a blend of the PEDOT polymer and the PSS molecule.

Deriving from $(C_4H_2S)_n$ polythiophene, 3,4-ethylenedioxythiophene (PEDOT) is a conjugated polymer that shows great electron conductivity.

Polystyrene sulfonate $(CH_2CHC_6H_4SO_3Na)_n$ (PSS) is a sulfonated derivatives of polystyrene with high ionic mobility: when doping PEDOT with PSS, ions can flow thanks to the conductivity of PSS while electrons flow comfortably due to the PEDOT polymer.

PEDOT:PSS is typically synthesized in the aqueous phase through the oxidative polymerization of ethylenedioxy-thiophene in the presence of PSS, and the resultant PEDOT:PSS particles in water are composed of a PEDOT-rich core and PSS-rich shells[3].

Changing the concentrations of either PEDOT or PSS or determines which is the dominant charge transport phenomenon in the material, while rearranging the polymer microstructure changes conductivity aswell by affecting how easily the charges can flow from one portion to another. A scheme of PEDOT:PSS's structure is shown in Fig[1].

Ionic conductivity is of great importance for interfaces between biological processes and electronic interfaces: the human body is made of organs, tissues, and cells regulated by the movement of ions and charged organic molecules. Although interfaceable with human physiology, in a material ionic conductivity alone is difficult to integrate with electronics, which requires electron transport to achieve reliable communication with digital interfaces. Therefore organic electronic materials, supporting the transport of both ions and electrons, allow for the direct translation of biological information into electronic read-out, leading to the creation of the research field known as "Organic bioelectronics" [4][5] [2].

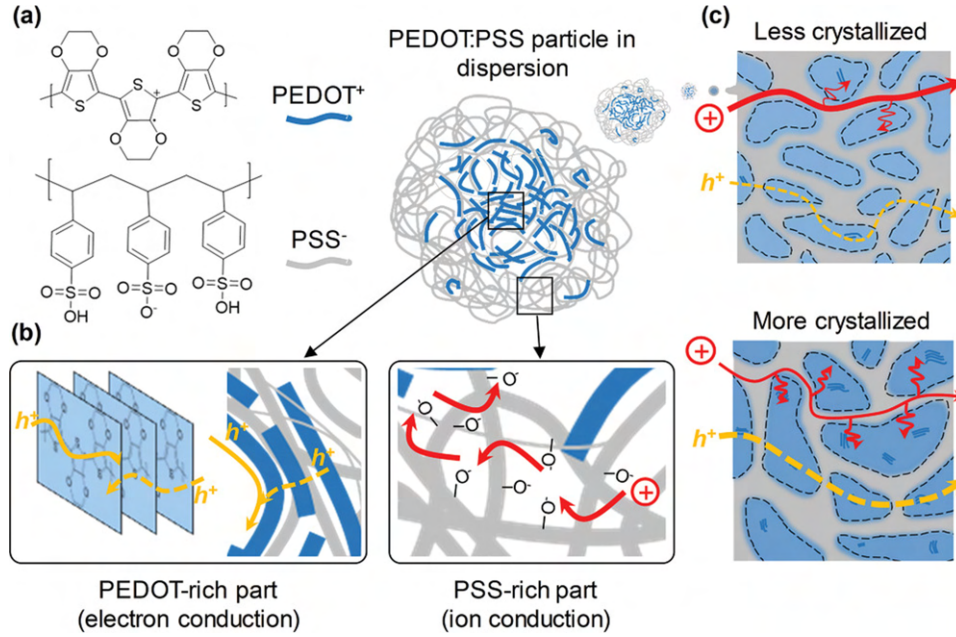


Figure 1: PEDOT:PSS structural formula and 3D view. The PEDOT (blue) acts as an electron conductor, while the PSS (grey) enables ionic conduction [3].

Organic bioelectronics and wearable sensors

The emerging field of organic bioelectronics bridges the world of organic electronic material-based devices with the predominantly ionic world of biology. This connection goes both ways: a biochemical reaction may change the doping state of an organic material generating an electronic read-out; on the other hand an electronic signal from a device may stimulate a biological process. These materials translate biological parameters into electronic readouts, allowing for precise sensing of key health parameters.

Tracking key health indicators such as body temperature, pulse rate, respiration rate, blood pressure, electrocardiogram (ECG), and glucose level can greatly increase the efficiency of diagnosis and disease treatment. Long-term and continuous monitoring of vital signs is particularly important in early diagnosis of diseases, management of chronic diseases such as diabetes, asthma, hypertension, and severe obesity, and timely response to life-threatening situations such as seizure and cardiac arrest.

The development of wearable sensors allows medical institutions to monitor these parameters without the need of constant specialist care, as the sensors themselves store the data, which is then transferred at once to the necessary infrastructure: this way medical personnel can monitor many patients at once without the need to follow each personally. Many types of wearable sensors have been developed in the years, here some are listed:

- **Piezoresistive** sensors: Piezoresistive sensors are based on the change of electrical properties of the material when subjected to mechanical deformation. A piezoresistive sensor is often named as a resistive strain sensor or simply strain gauge. The piezoresistive effect has been exploited for the detection of changes in physical properties in the body, widely used due to many advantages such as cheap device design, high sensitivity and simple readout circuits. One common application of piezoresistive sensors is in monitoring a patient's blood pressure[6].
- **Capacitive** sensors: As an alternative approach to piezoresistive sensing technology, capacitive-based sensors offer advantages such as higher linearity and fast response time, which are important parameters when sensors are intended to be used in real-life scenarios. The change in device capacitance with the applied external force/pressure can be measured either using a passive capacitor or through modifying the response curve of an active component, such as using field-effect transistors (FET). Capacitive sensors have been widely used in the medical context, such as for muscle contraction detection or reading the skin's bioelectrical signals[7].
- **Invasive** biochemical sensors (BCS): Invasive biochemical sensors use interstitial fluids (ISF) from the skin to assess key vital parameter, usually they necessitate microneedles to penetrate the epidermal/dermal tissues and ensure the transport of the ISF to biomarkers' receptors on the wearable BCS. One example of these sensors are the commonly commercially available glucose sensors.
- **Non invasive** biochemical sensors: non-invasive wearable BCS can use sweat to detect different parameters concentration. In contrast to ISF, sweat is produced on the skin naturally without invasive methods. From sweat, the wearable BCS can quantify various biomarkers. In literature, several human biomarkers are detected into sweat such as sodium, chlorine, potassium, lactate, calcium, glucose, ammonia, ethanol, urea, cortisol and various neuropeptides.[8]

Tracking of environmental conditions such as ambient temperature, ultraviolet radiation, humidity level, and concentration of harmful gases can provide valuable information for the prediction, management, and treatment of chronic diseases[9]. In addition, one of such chronic diseases that is still difficult to analyze and treat is the treatment of chronic wounds.

Wound healing

Acute wound healing involves a complex series of events including cell division, neovascularization, synthesis of new extracellular matrix and the formation and remodelling of the scar tissue. In acute wounds, these processes involve the overlapping phases of

haemostasis (the process to stop the bleeding), inflammation, proliferation of the new cells and remodeling. Alterations in one or more of the four healing phases could account for the impaired healing observed in chronic wounds: growth factors, cellular, extracellular elements and environment factors play important roles in the different stages of the healing process.[10]

The most impactful external factors for wound healing are wound infection, oxygen concentration and humidity.

The environment's infection status plays a crucial role in the wound's healing process: bacterial inflammation has an inhibitory effect on wound healing due to the generation of bacterial metabolic products and the tissue responses they elicit, along with the bacteria's necrotization of the tissue.

The environment's oxygen content affects the healing process aswell. Most of the oxygen involved in the healing of wounds is derived from the local circulating blood but a portion of it comes from the environment at the wound surface: a higher environmental concentration is shown to help the healing process by providing the healing cells more oxygen. [11]

The balance of moisture is critical to wound healing. In acute wounds, a balanced moist surface facilitates the action of growth factors thus promoting cellular growth.

Excess moisture in the wound can impair the healing process and damage the surrounding skin, leading to wound maceration. Lack of moisture in the wound environment, related primarily to exposure of the wound environment to air, promotes wound desiccation and necrosis.

Other factors that influence a wound's healing status may be the pH [12] and various chemical species such as uric acid[13]in the wound's environment[14]. Any imbalance of these parameters disturbs the healing process, leading to a partial cicatrization and chronicization of the wound.

Monitoring a wound's enviroment can offer a better control of the healing process by choosing adequate therapies.

Traditionally doctors have to remove the dressing of a wound to asses its status, which may lead to infection from external influences or disturbances of the healing process. Given the dependence of healing on chemical factors the use of a non invasive electrochemical sensor that can be embedded into the dressing's surface would solve the problem of external influence, being able to monitor the wound without the removal of the gauze, leaving the healing processes undisturbed.

As the demand for wearable sensors increases, so does the need of new materials capable of being versatile, easily fabricated and electronically compatible with both biological processes and electronic interfaces.

Chapter 1

Methods and Materials

1.1 Print process

As stated before, PEDOT:PSS is an excellent material for textile bioelectronic applications due to its high conductivity, biocompatibility and flexibility. Since PEDOT:PSS commercially comes as a water-polymer solutions, a way to process it into a practical textile material is by ink printing: following the research of Xi Fan et al [15] and Dong Nyoungh Heo et al [16] we studied how to manufacture highly conductive PEDOT:PSS inks with different physical properties based on the addition of various co-solvents. The next sections will go over the different print parameters set to fabricate textile applications of PEDOT:PSS: print methods, print configurations, ink composition and substrate choices.

1.1.1 Print configurations

To study the electrical characteristics of the PEDOT ink a rectangular geometry was chosen: a 30 by 5 millimeter rectangle is printed onto a substrate and steel wire is sewn into the extremities to create a reliable connection to electronic instruments, later the sewn wire is covered in argent paste and silicon paste to ensure conductivity and insulation to liquid electrolytes.

Throughout this thesis this print configuration will be referred to as CONF1. A diagram is shown in Fig[1.1]. On top of studying the ink's characteristics this thesis aims to investigate its use as electrodes for a textile wetness sensor.

For that purpose a different print configuration is used: two 15 by 5 millimeters ink rectangles separated by a 2 millimeter gap, each threaded by steel wire as the previous configuration. When a conductive liquid is poured onto the sensor, the gap allows the liquid to seep into the substrate that is between the two PEDOT electrodes, creating a bridge between the two PEDOT strips that allows the transport of charge.

Since the substrate by itself has an high impedance, when a liquid is dropped between the

electrodes the impedance of the sensor will decrease, relying information on the wetness of the substrate. Throughout this thesis this print configuration will be referred to as CONF2. A diagram is shown in Fig[1.2].

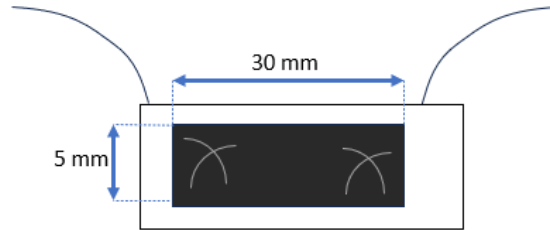


Figure 1.1: Configuration for the study of the electrical properties of the PEDOT ink, referred to as CONF1. The substrate is represented in white, the ink in black and the steel wire in grey.

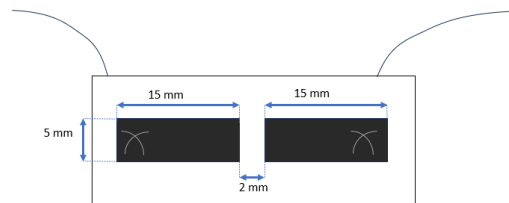


Figure 1.2: Configuration for the PEDOT wetness sensor, referred to as CONF2. The substrate is represented in white, the ink in black and the steel wire in grey.

1.1.2 Printing method choice

To print the aforementioned configurations of the PEDOT ink two methods have been used: serigraphy and 3d printing.

Serigraphic printing consists of forcing an ink, by pressing with a squeegee, through the mesh of a netting screen stretched on a frame onto the object to be printed. The non-printing areas of the screen are protected by a cutout stencil or by blocking up the mesh. In this case the mesh is made out of stainless steel but traditionally it can be made

of nylon or tergal. Serigraphy is widely used in the textile industry to print different materials onto textile fabric such as for the production of patterned t-shirts. The frame used to press the PEDOT ink onto the substrates can be seen in Figure[1.3]. Due to the frames available mesh only the CONF2 could be printed with serigraphy. The electrical properties of the serigraphy printed configurations have not been investigated as their use has already been documented [19], while their morphological properties have been studied for qualitative comparisons.

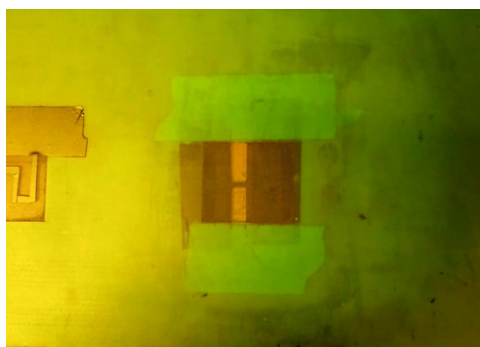


Figure 1.3: serigraphy mesh used to print the CONF2

The other method used to print the two PEDOT:PSS configurations is 3D printing. 3D printing consists of a process called additive manufacturing: the chosen object is printed by a machine that deposits material onto a surface through a needle, printing layer on top of layer to achieve a 3D product. 3D printing has been used in the industry since the 1980s but only for production of prototypes due to the cost of the required machinery that stopped it from becoming accessible to other fields. Only in the last decade it has become more affordable, portable and easy to use, introducing this technique to laboratories and even personal use.

The 3D printer used to print the two configurations onto the substrate is the Cellink Bio X 3D printer.

Most 3D printers use plastic filaments as the printing material, which is then melted as it comes out of the nozzle and is deposited following the object's geometry, solidifying due to heat transfer. Instead of filaments, the Bio X 3D printer can be loaded with syringes containing a wide range of liquid solutions, from cell cultures or pharmacological compound to organic inks, ready to be printed onto petri dish or any textile material. The temperature-controlled printhead ensures control over the print process, allowing real time viscosity changes, while an array of UV light allow for photocrosslinking, solidifying a properly prepared ink through exposure to ultraviolet light.

The Dual high-powered fans that channel air through a HEPA H14 filter and UV-C germicidal lights ensure that no external body may get in contact with the print subject. Compared to standard 3D printer the BIO X offers unparalleled flexibility in organic

tissues printing, some notable examples facilitating the fabrication of complex metabolic tissue models or the fabrication of living tissue models featuring hepatocytes and stellate cells, alongside supporting structures—such as arterial and venous structures. Fig[1.4] displays the Bio X 3D printer.

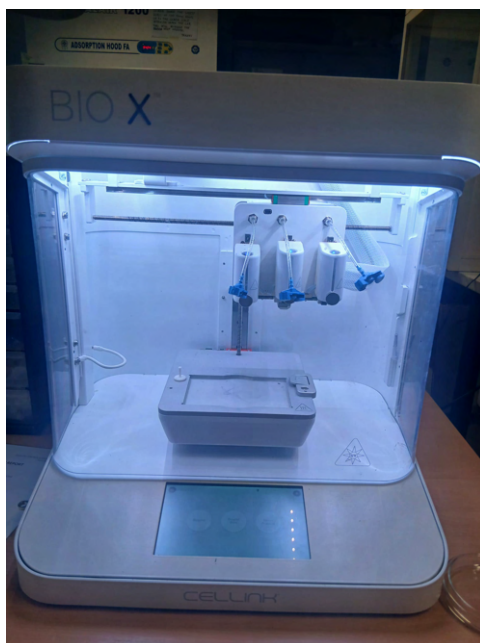


Figure 1.4: The BIO X 3D printer

1.1.3 Ink choice and preparation

Another parameter that heavily impacts the PEDOT:PSS's properties is the ink's composition.

In this thesis two inks with different compositions have been studied to determine the best PEDOT:PSS ink for a textile application.

Commercially a PEDOT:PSS complex is prepared by oxidative polymerization of ethylenedioxythiophene in aqueous dispersion using sodium peroxodisulfate as the oxidant, meaning that most available PEDOT:PSS sources are aqueous solution with a fixed percentage of the polymer: for this study the product used was the Clevious PH1000, a water solution with 1.0 – 1.3 wt.% content of PEDOT:PSS.

The first ink is a mixture of PEDOT:PSS in aqueous solution and Ethylene glycol in the ratio 95.2%:4.4% wt.

Ethylene glycol (CH_2OH)₂ is an organic molecule heavily used in the manufacture of polyester fibers and for antifreeze formulations. In a PEDOT:PSS solution the EG

(short for ethylene glycol) is shown to greatly increase conductivity: Ouyang et al.[17] observed a significant enhancement in film conductivity through immersing PEDOT:PSS films into EG baths. The film conductivity was enhanced from 0.4 to 200 S cm⁻¹.



(a) Hot plate used to stir and heat the various inks (b) syringe used to load the ink into the BIO X printer

Figure 1.5: Items used during the ink preparation

To prepare the first ink, referred to as INK1, 15 grams of PH1000 are heated in a hot plate at 130° while being stirred at 300 rpm to evaporate the water within the solution and obtain a solution with a 4% wt. PEDOT:PSS concentration, up from 1,3 % wt. of PH1000. In Fig[1.5a] the hot plate used is shown. Once enough water has evaporated EG is added to the solution, 5% wt. grams of the solution. The ink is then placed in designated syringes to be used with the BIO X PRINTER, shown in Fig[1.5b]. Once the print process is done, INK1 has to be dried in a oven at 70° for 30 minutes to evaporate the remaining water and dry the ink.

The second ink, referred to as INK2, is a mixture of PEDOT:PSS in aqueous solution, ethylene glycol (EG), poly(ethylene glycol) diacrylate (PEGDA) and a photoinitiator, lithium phenyl-2,4,6-trimethyl-benzoylphosphinate (LAP) in the ratio 64.4% : 3.22% : 32.2% : 0.1% wt.

PEGDA is a synthetic polymer that is used for a variety of drug delivery and tissue engineering based applications. Beside being non-toxic and hydrophilic, its distinctive feature is the ability of UV light crosslinking: in the presence of the LAP photoinitiator and UV light the PEGDA polymer crosslinks, connecting different polymer chains through double-bonds. The crosslinking process turns the PEGDA from a low viscosity liquid to a solid structure referred to as an hydrogel.

Hydrogels are substances composed of a three-dimensional crosslinked network of molecules,

which are capable of absorbing large amounts of water; they are extensively used as drug delivery systems, wound dressings, biosensors or contact lenses.

The PEGDA-LAP combination is extensively used in different studies and 3D printing processes, which employ photopolymerization for precise manufacturing of three-dimensional structures[18].

INK2 therefore gains a 3D structure once crosslinked, while showing conductivity due to the PEDOT:PSS molecules within it.

To prepare INK2 15 grams of PH1000 are heated in a hot plate at 130° while being stirred at 300 rpm to evaporate the water within the solution and obtain a solution with a 4% wt. PEDOT:PSS concentration. Once enough water has evaporated EG is added to the solution, 5% wt, exactly as INK1. After this the PEGDA is added: initially a 1:1 evaporated PH1000 : PEGDA weight ratio was chosen although it revealed to be too viscous for the 3D printer to print, so a 2:1 weight ratio was chosen.

Once the PEGDA is added to the solution, 0.2 % wt. grams of LAP is added to the solution. Once INK2 has been deposited onto the desired surface it has to be crosslinked: the Bio X 3D printer has a 453 nm λ UV light that is used to crosslink hydrogels. INK2 has to be exposed to UV light for 120 seconds at a 3 cm height to be crosslinked.

1.1.4 Substrate

Two different substrates have been chosen to be the base fabric of the PEDOT application in this thesis. The first, called “ROYAL” gauze, is made of 70% rayon, 30% polyethylene terephthalate and a thin anti-adherent film of polyethylene. The second gauze, called “AKENA” gauze, is composed by 100polyethylene terephthalate.

These two fabrics show different liquid absorption properties, as reported in the ”Wireless Textile Moisture Sensor for Wound Care” paper [19]. In Tab1.1 these properties are shown. In Fig[1.6] the substrates are shown.

Substrate	Absorption(g/g)	Absorption(l/m^2)
AKENA	8.0 ± 0.37	0.03 ± 1.3
ROYAL	11.0 ± 0.5	1.38 ± 0.07

Table 1.1: Absorption properties of the substrates investigated. The absorption is reported both in g/g and in l/m^2 to indicate the amount of volume absorbable by the textile material compared to its initial weight or to its planar dimensions, respectively. From the data the lower absorption capabilities of the AKENA substrate can be seen.

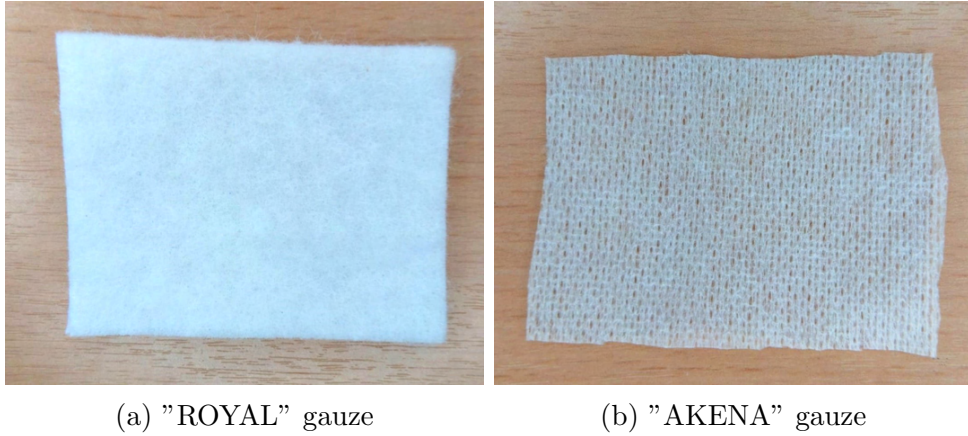


Figure 1.6: Substrate options

1.1.5 Print procedure

To print first a CAD file is needed: the file contains printing instruction and the structure of the print's object. To generate the templates for the two different configurations Freecad 1.1 was used.

Once the CAD files are loaded into the BIO X printer, an ink syringe must be inserted into one of three apposite slots. The syringe is then connected to an air pump which pushes the ink out during the print.

The printer has a touch screen which allows the user to adjust various print parameters. The print parameters for INK2 are as as follows

- Pump: pneumatic 3ml
- Nozzle: 33 gauge.
- Pressure: 70-80 kpa
- No Photocrosslink
- Nozzle Speed: 20 mm/s
- Exagonal grid
- 85 % fill density

The print parameters for INK2 are as as follows

- Pump: pneumatic 3ml
- Nozzle: 33 gauge.

- Pressure: 90-100 kpa
- Photocrosslink: left module(452 nm) for 120 s at 3 cm height
- Nozzle Speed: 20 mm/s
- Exagonal grid
- 85 % fill density

The substrate is placed under the nozzle in a petri dish and adequately stretched to ensure a smooth print.

After the ink syringe, substrate and printer are set the last step is calibration: the printer's axis are calibrated manually to ensure that the nozzle is neither too close or too far from the substrate's surface. Once the calibration is done the chosen print configuration can be printed.

The samples fabricated with INK1 are dried in a oven for 30 minutes at 120° while the samples fabricated with INK2 are crosslinked with UV light in the printer following the aforementioned "Photocrosslink" parameter.

When either inks are dried steel wire is sown into the sample to provide a way to connect the samples to the instrumentation using crocodile clips. Since the sewing process can break the dried ink, silver paste and silicon paste are placed on top of the exposed steel wires.

1.1.6 Notable print precautions

Here notables issues with the fabrication process are reported and possible solutions to them:

- Electrical contacts: since sewing steel wire can break the PEDOT:PSS disposition and reduce conductivity, silver paste was used. More advanced solution may be magnetic contacts to avoid tampering with the ink or layering the substrate with carbon tape before printing the PEDOT:INK to achieve full conductivity even in the case of the ink's rupture.
- Viscosity: with a PEDOT:PSS concentration of 4% and addition of PEGDA the ink becomes quite viscous, making it impossible to print with smaller, higher precision nozzles. Either choose higher diameter nozzles or reduce the PEDOT or PEGDA concentration.
- Calibration: print calibration is different for the two substrates: the AKENA substrate is plain and fiberless, allowing the nozzle to hover at a distance of 0,4-0,5 mm from the surface while retaining high print definition. The ROYAL substrate

has many fibers near the surface that can get tangled in the nozzle and ruin the print. To evade this when printing the nozzle is hovering at a distance of 1,4 - 1,6 mm from the surface: because of this the nozzle doesn't get tangled but a higher pressure is require, usually 10-15 kpa more than what used for the AKENA substrate.

1.2 Morphological characterization

This section depicts the techniques utilized to characterize the morphological properties of the substrates and inks: optically analyzing the surface of the material can lead to useful insights about the print process and material properties.

While using any apparatus for optical imaging, light diffraction heavily restricts the scale to which a single instrument is reliable. As an electromagnetic wave moves through space, every point of the wavefront is a source of new spherical waves which interact constructively and destructively between themselves: this phenomenon is known as the Huygens–Fresnel principle. This creates a diffraction pattern that appears as an aberration on the resulting image, shown as the object having a blurry edge. A diagram is shown in Fig[1.7]. When two or more close-by objects are to be observed, aberration can make the objects impossible to distinguish. The limit to which we can distinguish two different items is given by the resolving power or resolution.

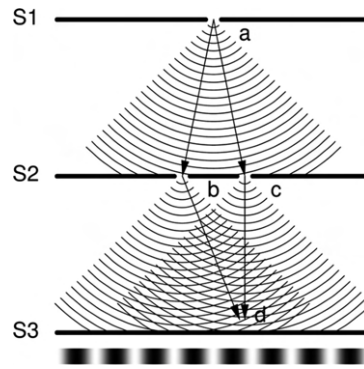


Figure 1.7: The Huygens-Fresnel principle

For a circular aperture of diameter D , the first minimum in the diffraction pattern occurs at $\theta = 1,22 \frac{\lambda}{D}$. The criterion for determining the diffraction limit to resolution based on this angle was developed by Lord Rayleigh in the 19th century. The Rayleigh criterion for the diffraction limit to resolution states that *two images are just resolvable when the center of the diffraction pattern of one is directly over the first minimum of the diffraction pattern of the other*. Given a lens or an assembly of lenses such as microscope,

the resolving power or resolution σ of the instrument is dependant on the quality of the lenses and by the wavelenght of the medium used for observation following the Rayleigh Criterion:

$$\sigma = \frac{0,61\lambda}{\mu \cdot \sin(\beta)} \quad (1.1)$$

where μ is the refractive index of viewing medium and β is the semi-angle of the microscope's aperture. Eq[1.2] shows that, given the best possible quality of an optical apparatus, the only way to have a lower resolving power is by decreasing the wavelenght of the light used.

1.2.1 Optical microscope

Optical microscopes use visible light and sets of lens to magnify the superficial characteristics of a given object. Since the wavelength of visible light ranges from 380 to 750 nanometers, an optical microscope can distinguish objects down to 100-200 nanometers. A sample is usually mounted on a motorized stage and illuminated by a diffuse source of light. The image of the sample is projected via a condenser lens system onto an imaging system, such as the eye, a film, or a charge-coupled device. The microscope used to optically analyse the material's surfaces is the Optika B-380. This microscope could accurately distinguish the sample's fiber with a resolution of 100-200 nanometers. The microscope and its working principle are illustrated in Fig[1.8].

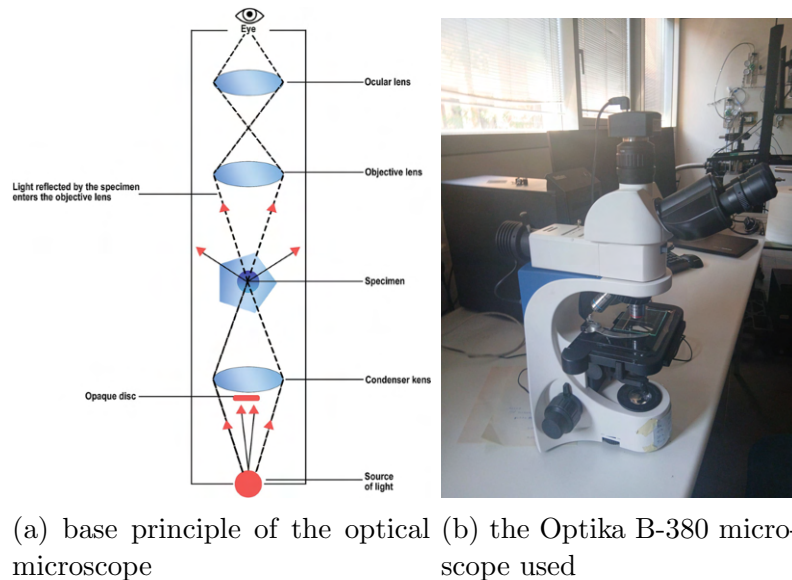


Figure 1.8: Substrate options

1.2.2 Scanning Electron Microscope

An optical microscope fails to clearly observe items on the scale of nanometers and smaller, as its resolution is tied to the wavelength of visible light, which gives a maximum resolution of a 100-200 nanometers.

Where optical microscopes use visible light in a classical wave assumption, quantum mechanics, in particular the wave-duality hypothesis, show that any particle can be considered as a wave.

The De-Broglie's wavelength is the analogous of classical light wavelength for massive particle, which shows that any particle can be described as a wave, and as such is subjected to the phenomenons of diffraction and refraction. This means that massive particles, such as electrons, can be used for optical measures aswell, given the right instruments.

Due to the particle-wave duality of quantum mechanics, for a particle with momentum p can be defined the correspondant De-Broglie wavelenght, through the relation:

$$\lambda = \frac{2\pi\hbar}{p} \quad (1.2)$$

if we consider an electron beam that is accellerated by a voltage V , using the energy-momentum relation $E = \frac{p^2}{2m_e}$ and energy of the accelerated electron $E = eV$, the relation becomes:

$$\lambda = \frac{2\pi\hbar}{\sqrt{2m_e eV}} \quad (1.3)$$

which shows that by increasing the voltage the particle's De-Broglie wavelength decreases, and following Eq[1.2] so does the resoluteive power of the beam.

Electron microscopes use a focused beam of electron to analyse the surface of samples at resolutions far smaller than that of an optical microscope, with a resolution ranging from nanometers to the atomic level. Two main types of electron microscopes are used: SEMs and TEMs.

Scanning Electron Microscopes (SEM) accellerate electrons using an accellerating voltage between 5-20 KV, which results in a resolution that goes from millimeters to nanometers; most importantly the electrons in a SEM are mostly reflected by the target's surface, providing surface topographic information, which makes the images intuitive and easy to understand.

Transmission Electron Microscopes on the other hand accellerate electrons with voltages reaching up to 300 KV, resulting in a resoluteive power from nanometers to atomic scales; the electrons accellerated in TEMs are energetic enough to penetrate the sample, providing additional information of the internal structure of a given material.

A SEM produces an electron beam by heating a tungsten filament leading to thermionic emission and subsequently accellerate and focuses the electrons through a series of magnetic lenses; once the beam has been condensed a series of magnetic coils project the

beam over the sample, scanning the desired surface.

Once the electron beam interacts with the sample multiple interactions take place between electrons and the surface's atoms :

- Primary electrons (PE): primary electrons continue to travel into the sample and spread to generate a teardrop-shaped volume from which backscattered electrons are generated.
- Secondary electrons (SE): when an electron scatters inelastically with an atom of the sample a secondary electron is created. SEs are usually loosely bound outer shell electrons from atoms close to the sample surface, making this a surface topography sensitive technique. Due to their low energy, SEs are detected through a Everhart-Thornley detector, which is essentially a Faraday cage that has a positive potential which can collect the negatively charged inelastically scattered electrons.
- Backscattered electrons (BSE): When an electron elastically scatters with an atom of the sample a backscattered electron is created. These electrons have higher energy compared to SEs and originate from below the surface, in the teardrop-shaped volume underneath the surface. BSEs are usually scattered near the opposite direction of the beam and their energy varies with the atomic number Z , making this a composition sensitive technique, able qualitatively to distinguish different materials of the sample. The approach to detect BSEs involves a neutrally charged solid- state detector placed right above the sample but below the objective lens.
- Auger electrons: Auger electrons are created when a beam electron knocks out an electron of the inner shells of a light ($Z < 12$) atom: an atom from an outer shell falls in it's place, releasing energy that is transferred to an outer electron, which is subsequently ejected from the atom. Auger electrons have very specific energies, which make them easily detectable.
- X rays: Similarly to Auger electrons, when an electron of an inner shell of a heavier element is knocked out by a beam electron another electron takes it place; in the transition the difference energy of the shells is released as form of an X ray, which is then detected through apposite detectors. This, coupled with Augur electron detection, gives great information on the atomic composition of the sample[20] [21].

Diagrams of the various electron interactions are shown in Fig[1.9] and Fig[1.10]

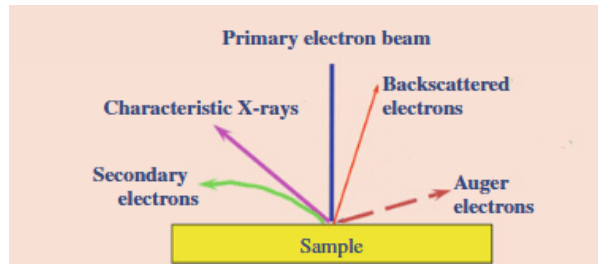


Figure 1.9: Diagram of electron beam - sample interaction

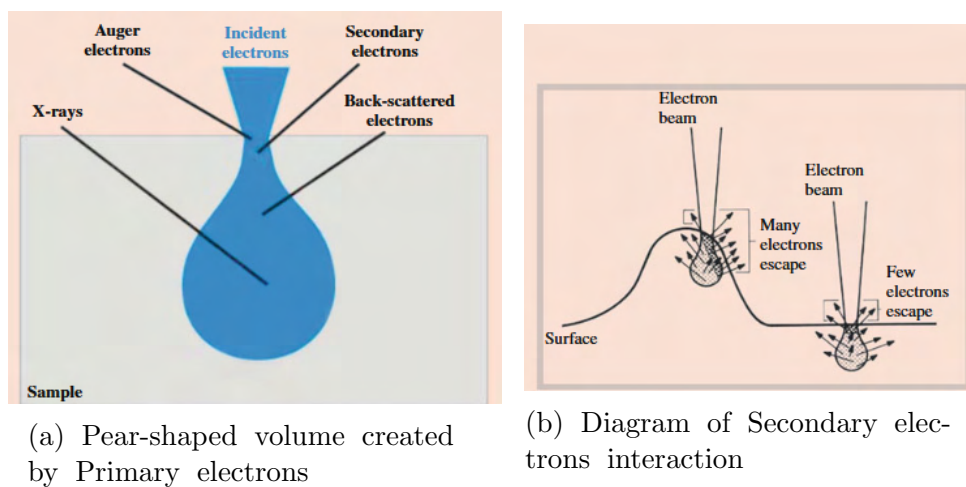


Figure 1.10: SEM diagrams

The SEM utilized to scan the sample's surface is the Cambridge Instruments Stereoscan 360 SEM Microscope System. This SEM also has an x-ray detection chamber, able to instantaneously analyze a material's composition. To acquire clear images the samples are coated in a Chromium-Gold layer, which increases the sample's conductivity; if a material has poor conductivity the beam electrons that interact with the sample's surface may accumulate on it, creating a negative charge that deflects incoming electrons, ruining the images. in Fig[1.11] the microscope is shown.



Figure 1.11: Photo of the Cambridge Instruments Stereoscan 360 SEM Microscope System

1.3 PEDOT Ink characterization

To characterize the different PEDOT:PSS inks both impedance and resistance of the ink were measured in different conditions, namely the properties in standard atmospheric condition and in a wet, ion-rich environment. To simulate the second condition a PBS (Phosphate Buffer Saline) solution was used, made by dissolving one tablet of PBS in 1 liter of water, obtaining a solution rich in ions with a pH of 7.2 - 7.4.

1.3.1 I-V characteristic

The I-V characteristic of the different ink and substrate combinations were observed by applying a voltage at the ends of the steel wires of the CONF1 (Fig[1.1]) and measuring the resulting current.

For each sample a voltage sweep was applied, ranging from -0.6 V to 0.7 V with a 0.05 V step. Once the voltage had reached 0.7 V another sweep would start, opposite to the first, bringing the voltage back down to -0.6 V and then another -0.6 V to 0.7 V sweep was applied, totaling three sweeps for each sample.

The instrument used to measure the I-V characteristic is the Keithley 2120B System

SourceMeter, shown in 1.12, along with the program supplied by the DIFA of Bologna. The I-V characteristic has been observed at the "dry" state, meaning normal atmospheric conditions.

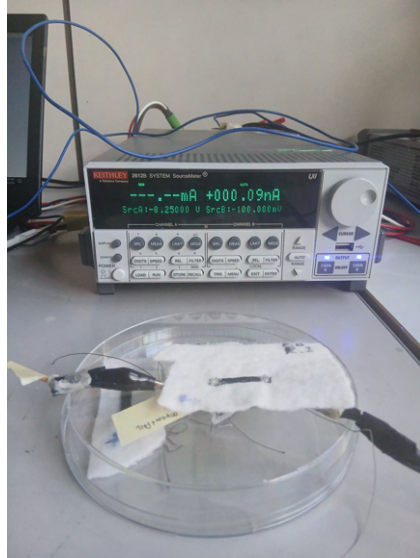
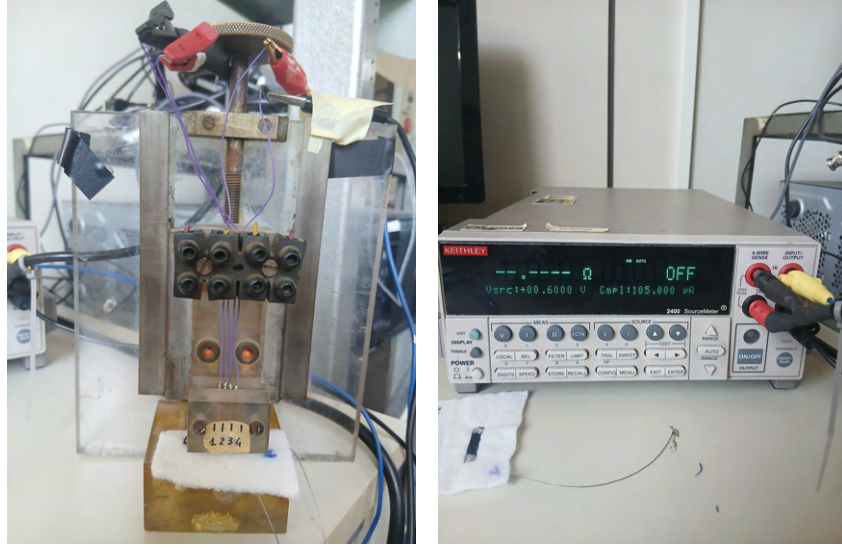


Figure 1.12: Photo of the experimental setup for the I-V characteristic

1.3.2 Sheet resistance

Whilst the I-V characteristic measures the current considering the whole CONF1 PEDOT strip, it does not provide information on the ink's own resistivity: due to the considerable volume of the INK2 current dissipates through the PEDOT:PSS ink, increasing the overall resistivity. Moreover, the resistance of the steel wire and the contacts is unknown, leading to a considerable error when estimating the ink's resistivity. To evade these problems, a 4 way probe has been used, shown in Fig[1.13], alongside a Keithley 2400 Sourcemeter. The measure was conducted in the "dry" state.



(a) 4 way probe

(b) Keithley 2400 Sourcemeter

Figure 1.13: Experimental setup for the 4 way probe

The 4 way probe is commonly used to measure the resistance of thin sheets of material, a property used to characterize thin films of conducting and semiconducting materials. A four-point probe consists of four equally spaced electrical probes, as shown in Fig[1.14].

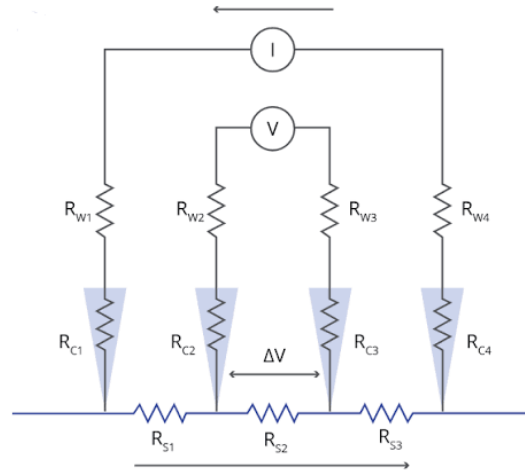


Figure 1.14: 4way probe diagram. The four probes have equal spacing (s) and are shown in contact with a surface. A current (I) is injected through probe 1 and collected through probe 4, whilst the voltage is measured between probes 2 and 3.

When a sharp probe injects current through an applied voltage into a sheet of conductive

material of height t , the current travels outwards from the point of contact through concentric cylindrical shells of equipotential, each of which have current density (J) of:

$$J = \frac{I}{2\pi r t} \quad (1.4)$$

Where r is the radial distance from the probe. By applying Ohm's Law ($E = \rho J$) with the electric field across each shell equal to the voltage drop over the shell thickness, or $-\Delta V / \Delta r$ (this term is negative as voltage decreases with r), and with the thickness of the shell tending towards zero, the following equation is obtained:

$$\frac{dV}{dr} = -\rho \frac{I}{2\pi r t} \quad (1.5)$$

where $\frac{\rho}{t} = R$ is the resistance of the sheet material. When integrated between r and an arbitrary radius r' the equation becomes

$$V - V' = \frac{IR}{2\pi} (\ln(r) - \ln(r')) \quad (1.6)$$

considering just two probes, probe 4 that injects current and probe one that collects it, the voltage in any point of the surface is:

$$V - V' = \frac{IR}{2\pi} (\ln(r_4) - \ln(r_1)) \quad (1.7)$$

where r_4 and r_1 are the radial distances from probe 4 and 1 respectively.

Consider 4 probes in contact with the conducting material, which are in a line with equal spacing (s). They are set up so that current is injected through probe 1 and collected by probe 4. The voltage at any point is equal to the sum of the voltage due to each probe separately as for Eq[1.7]. This means that probe 2 and probe 3 will measure a voltage of:

$$V_2 - V' = \frac{IR}{2\pi} (\ln(2s) - \ln(s)) \quad (1.8)$$

$$V_3 - V' = \frac{IR}{2\pi} (\ln(s) - \ln(2s)) \quad (1.9)$$

so that the difference $\Delta V = V_2 - V_3$ is:

$$\Delta V = \frac{IR}{\pi} \ln(2) \quad (1.10)$$

which gives us the sheet resistance:

$$R = \frac{\pi}{\ln(2)} \frac{\Delta V}{I} \quad (1.11)$$

Therefore, by measuring the change in voltage between the inner probes and the applied current between the outer probes, we can measure the sheet resistance of a sample [22]. This equation is only valid if the material being tested is no thicker than 40% of the spacing between the probes, requiring otherwise a correction factor. Most importantly, using the 4 way eliminates contact and wire resistances from the measurement. Consider the measure of resistance of a Device Under Test (DUT) through the use of an Ohmmeter: the ohmmeter measures all resistances in the circuit loop, including the wires' and contacts'.

To evade this problem an ammeter and voltmeter are used in tandem: due to Ohm's law measuring the current passing through a resistance and the voltage across it immediately gives the resistance of the sample. At a first glance this may sound a convolution, since both the ammeter and voltmeter require wires and contacts to properly measure a sample's characteristic, resulting in the same problem as before. Consider a measure apparatus as shown in Fig[1.15].

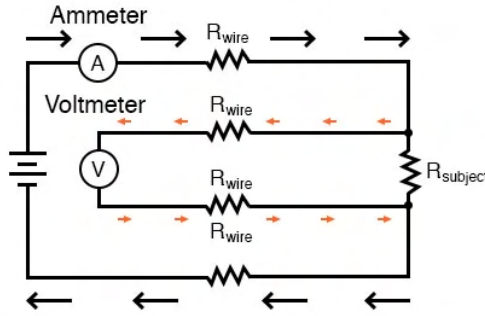


Figure 1.15: Circuit diagram of a 4 way probe

By choosing a voltmeter with an high resistance the current passing through the voltmeter is minimal, and so is the voltage drop caused by the stray resistances of the wires and contacts, resulting in a voltmeter indication that is very nearly the same as if it were connected directly across the subject resistance. Any voltage dropped across the main current-carrying wires will not be measured by the voltmeter, and so do not factor into the resistance calculation at all.

The aforementioned considerations on the 4 probe sheet measures have been obtained considering a sample with infinite area and thickness that is 40 % or less compared to the distance between the probes. When considering a rectangle with finite area, such as the one of CONF1(Fig[1.1]), a correction factor must be applied. Moreover for samples such as the ones printed with the INK2 a correction factor must be applied due to the increased thickness of the crosslinked ink. Following F.M.smits [23] in Tab[1.2] and Tab[1.3] tables of these correction factors are reported. The unit of measure for sheet resistance is $\Omega/\square$, where $\square$ is the numbers of squares of the measured sheet. This means

that for a 3 mm by 0,5 mm sheet the number of squares is 6, so the total sheet resistivity is the sheet resistivity times six.

W/S	F(W/s)
0.4	0.9995
0.5	0.9974
0.6250	0.9898
0.7143	0.9798
0.8333	0.9600
1.0	0.9214
1.25	0.8490
1.4286	0.7938
1.6666	0.7225

Table 1.2: Correction factor F for a sheet of conductive material with notable thickness. W is the thickness of the material and S the spacing between the probes

D/S	A/D = 1	A/D = 2	A/D = 3	A/D $\geq$ 4
1.0			0.9988	0.9994
1.25			0.9973	0.9974
1.5		0.9859	0.9929	0.9929
1.75		0.9826	0.9850	0.9850
2.0		0.9726	0.9737	0.9737
2.5		0.9413	0.9416	0.9416
3.0	0.8192	0.9	0.9002	0.9002
4.0	0.7784	0.8061	0.8062	0.8062

Table 1.3: Correction factor for a finite rectangle of conductive material. D is the height of the rectangle, A the length and S the spacing between the probes

1.4 Wetness sensor characterization

This section shows the methods used to characterize the properties of the various combinations of PEDOT INK, substrate and printing technique when used as cathodes for a wetness sensor, as shown by the CONF2(1.2). To do such, the ink by itself was analyzed through a impedance spectroscopy at different wetness levels using the CONF1 to understand the ink's own impedance behavior. Once the behavior of the ink has been determined the CONF2 was analyzed, first by doing an impedance spectroscopy of one sample of every substrate and ink combination at different wetness levels, then

the remaining samples' impedance were analyzed over time, dropping increasingly higher volumes of PBS in the gap between the two electrodes.

1.4.1 Impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) offers great insights into the properties of various electrochemical systems and is widely used in corrosion studies, semiconductor science, energy conversion and storage technologies, chemical sensing and biosensing. EIS is based on the perturbation of an electrochemical system via the application of a sinusoidal signal over a wide range of frequencies and the monitoring of the sinusoidal response (current or voltage, respectively) of the system.

Considering the CONF2 as our electrochemical system, the goal of the impedance spectroscopy is to understand the behavior of this system when it is exposed to different wetness levels, meaning that both the electrodes and the whole configuration have to be studied to accurately understand the use and utility of the PEDOT:PSS ink as an electrode material.

In first approximation, following McGhee et al. [24], in a porous materials (such as the indium tin oxide used by McGhee) each dielectric particle - particle boundary in the dielectric can create an electric field having a capacitive element, with the particle itself also being resistive, therefore, the dielectric layer can be modeled as an essentially infinite amount of RC circuits, each with its imperfect capacitance. Textile polyethylene substrate similar to those reviewed in this thesis exhibit poor dielectric properties when dry [25] while showing greater conductivity: when wet a continuous permittivity increase during water absorption indicates the higher (moisture - induced) polar content in the polymer, creating dielectric particle - particle boundary in the dielectric, similarly to what McGhee et al [24] hypotized [26].

It is not out of reach to consider then the substrate in the CONF2 between the two PEDOT ink cathodes as an infinite amount of RC circuits, each with its imperfect capacitance. To accurately model the behavior of impedance generated by electrochemical processes the Walberg Impedance is used. Following Byoung-Yong Chang [27] an electrochemical system can be represented by using a Constant Phase Element(CPE).

The constant phase element (CPE) is a variation of a capacitor, it was invented to describe impedance observed only in electrochemical systems. The impedance of the CPE, is expressed in Eq[1.12]

$$Z_{CPE} = \frac{I}{(i\omega)^n Y_0} \quad (1.12)$$

where n and Y_0 are parameters characterizing the CPE. A CPE almost inherits properties from a capacitor, but a slight difference in phase shift and magnitude responding to AC signals distinguishes the CPE from a capacitor. The degree of the phase shift of a capacitor is $\pi/2$ while that of a CPE is $n\pi/2$, where n ranges from 0 to 1 (practically 0.8 to 1). When $n = 1$, the CPE is an ideal capacitor and the Y_0 presents its capacitance.

Otherwise, the CPE deviates from a capacitor and the Y_0 does not directly present the capacitance any longer. Having made these considerations, the CONF2 can be expressed as a combination of CPEs and resistances given by the materials, as shown in Fig[1.17]. Determining the constant n of a real CPE is a complex subject that goes beyond this thesis' goal, so all the CPEs will be considered with $n = 1$, effectively considering them ideal capacitors.

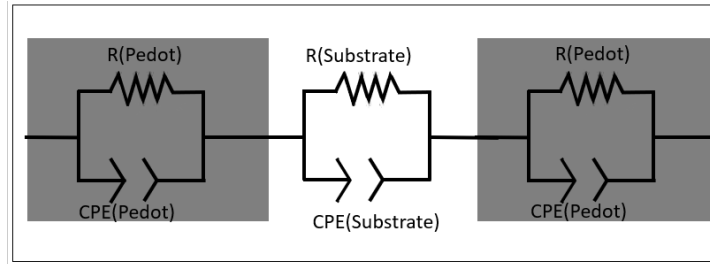


Figure 1.16: Circuit diagram of the CONF2

For the impedance spectroscopy a Zurich Lock In Amplifier has been used, alongside the necessary software for data analysis. The experimental setup for the impedance spectroscopy is shown in Fig[1.17]. The frequency sweep has been carried from 1 KHz to 1Mhz .

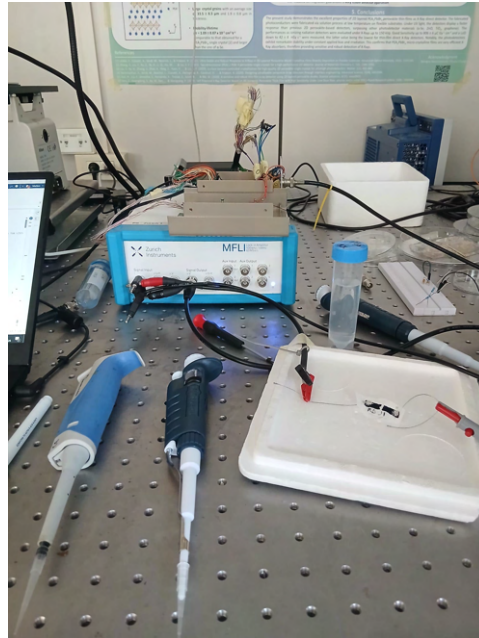


Figure 1.17: experimental setup for the impedance spectroscopy

Chapter 2

Results

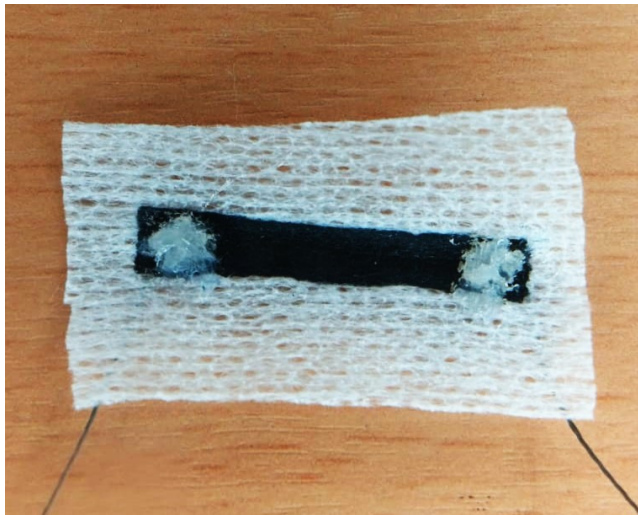
2.1 Photos

2.1.1 Print results

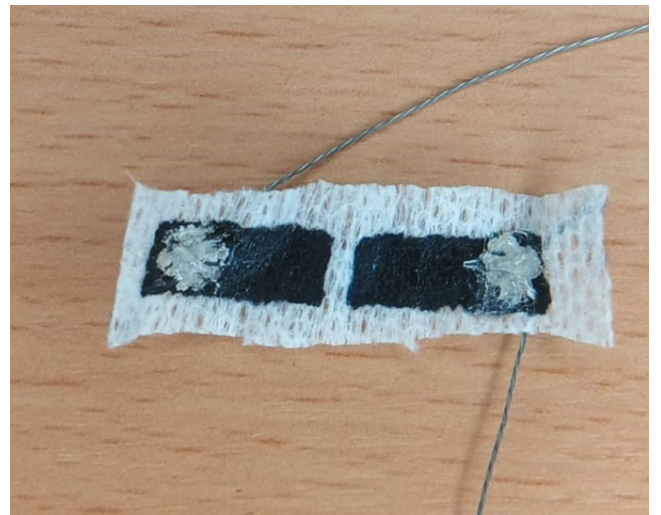
In this section the photos of the different configurations are reported. For each configuration the nomenclature is as follows:

”INK_SUBSTRATE_CONFIGURATION”

For each configuration three samples were made to confirm the configuration’s behavior.



(a) INK1_AKENA_CONF1

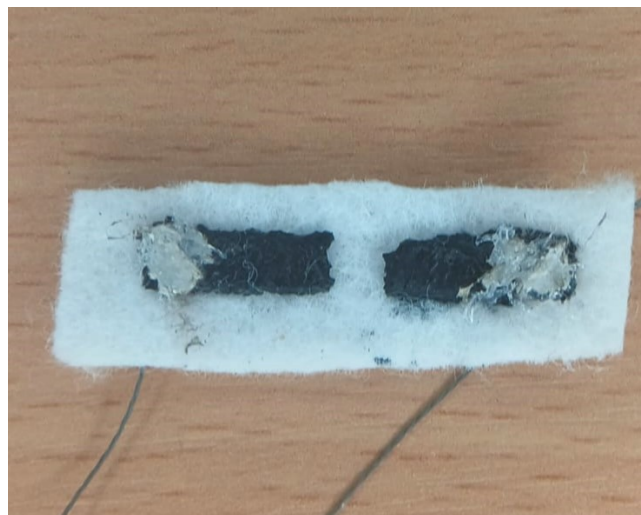


(b) INK1_AKENA_CONF2

Figure 2.1: Photos of CONF1 and CONF2 printed on the AKENA substrate with INK1

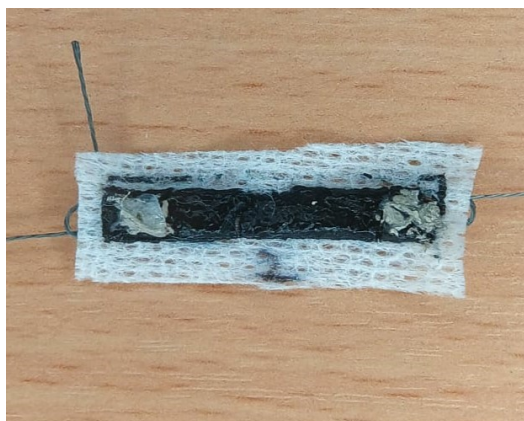


(a) INK1.ROYAL.CONF1



(b) INK1.ROYAL.CONF2

Figure 2.2: Photos of CONF1 and CONF2 printed on the ROYAL substrate with INK1

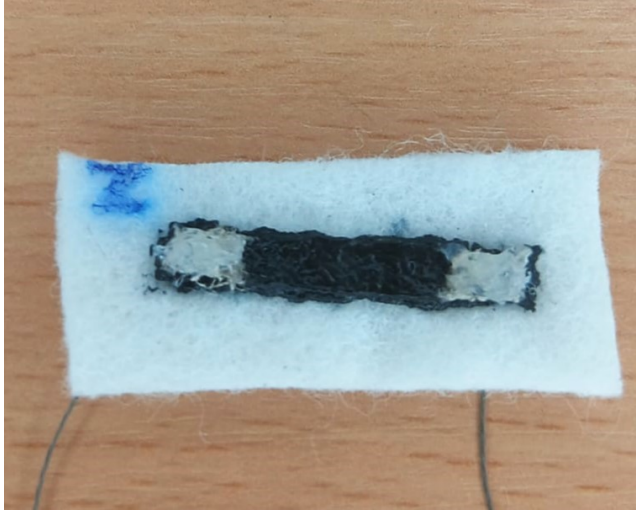


(a) INK2.AKENA.CONF1



(b) INK2.AKENA.CONF2

Figure 2.3: Photos of CONF1 and CONF2 printed on the AKENA substrate with INK2



(a) INK2.ROYAL.CONF1



(b) INK2.ROYAL.CONF2

Figure 2.4: Photos of CONF1 and CONF2 printed on the ROYAL substrate with INK2

Observing the PEDOT strips even without any instrument can give insight to each configuration's practical capabilities.

INK1, being completely absorbed by the substrate's fibers, presents a sturdy 2 dimensional structure but it has slight hydrophobic properties while INK2 has a notable thickness, appearing as a 3 dimensional strip and capable of absorbing the PBS solution, at the cost of being prone to cracking.

During the production of the samples many samples of the CONF1 printed with INK2 on the AKENA substrate would form cracks when slightly deformed.

On top of that the AKENA substrate presents slight hydrophobic capabilities, as shown in Fig[2.5]: when testing the CONF2 response to additions of PBS inbetween it's electrodes the samples fabricated with the AKENA substrate and INK1 would not absorb the PBS, creating drops on the substrate's surface, impacting the wetness sensor capabilities. Configurations fabricated using the ROYAL substrate showed greater resistance to textile deformation and immediate PBS absorption, although the substrate presents many superficial fiber as can be seen in Fig[2.4a] and Fig[2.4b], making the print process harder.

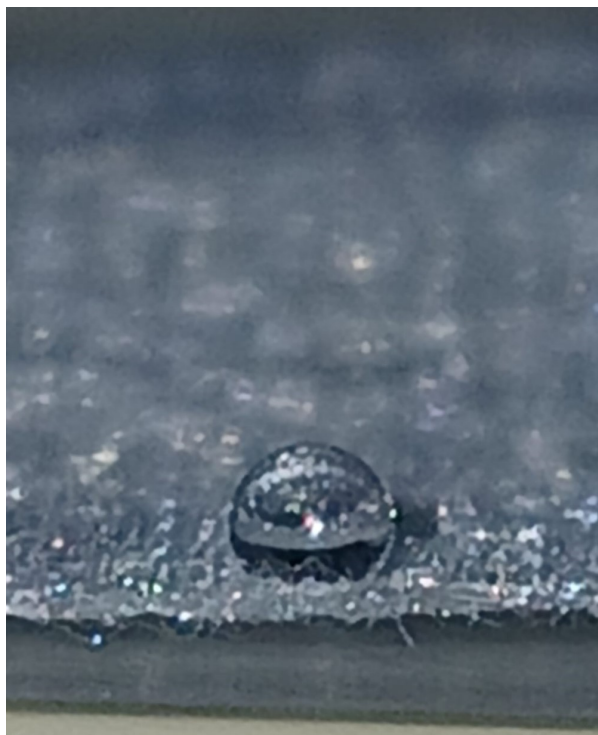
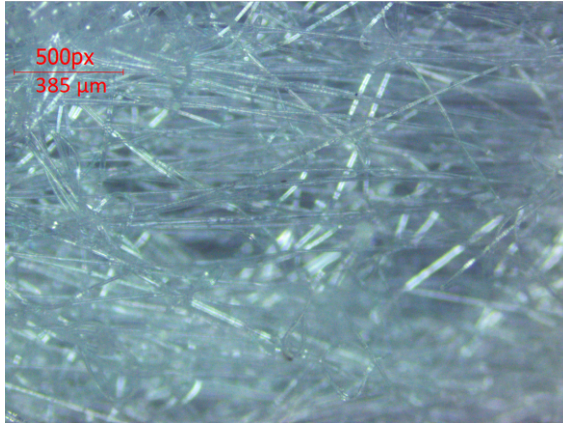


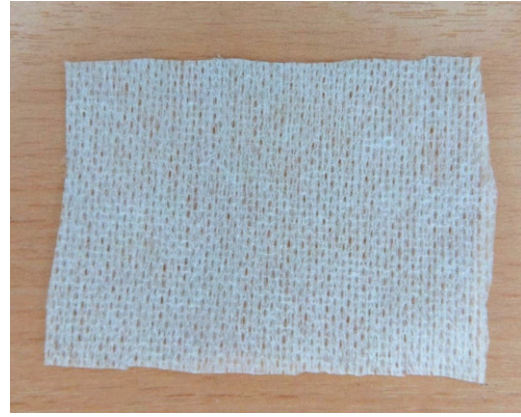
Figure 2.5: PBS drop formed onto the AKENA substrate.

2.1.2 Optical microscope images

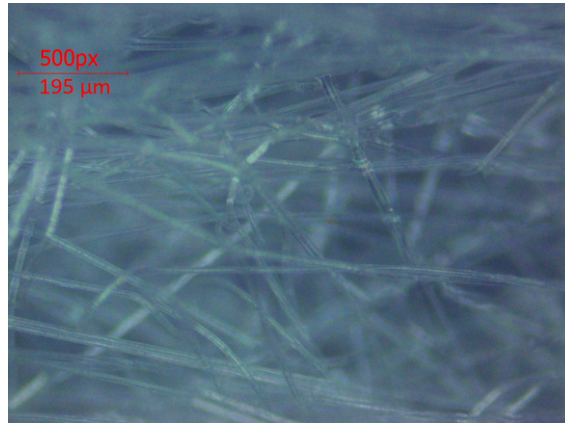
In this section the optical microscope photos of the different substrates and inks are reported. Each combination of ink and substrate was photographed at 5X, 10X and 20X but the photos reported are only the most significant.



(a) 5X magnification: 500 px = 385 μm

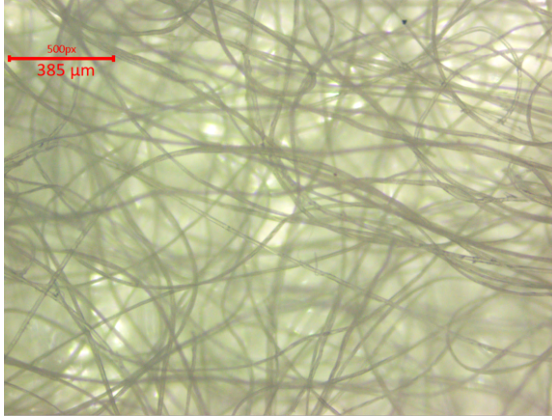


(b) Akena substrate

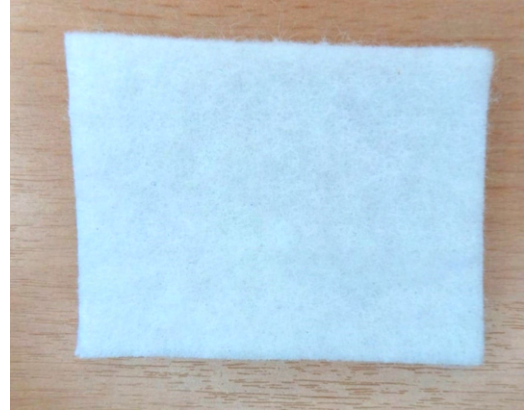


(c) 10X magnification: 500 px = 195 μm

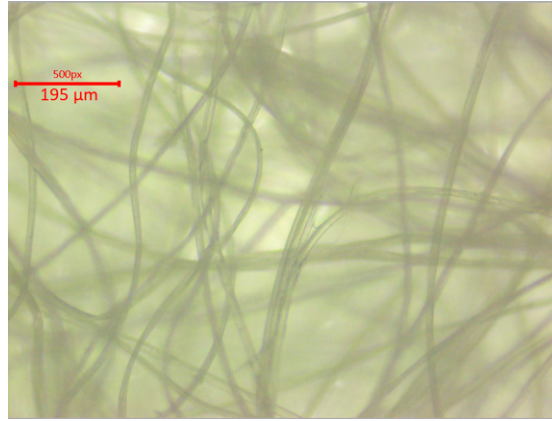
Figure 2.6: Microscope images of the AKENA substrate at different magnifications



(a) 5X magnification: 500 px = 385 μm



(b) Royal substrate

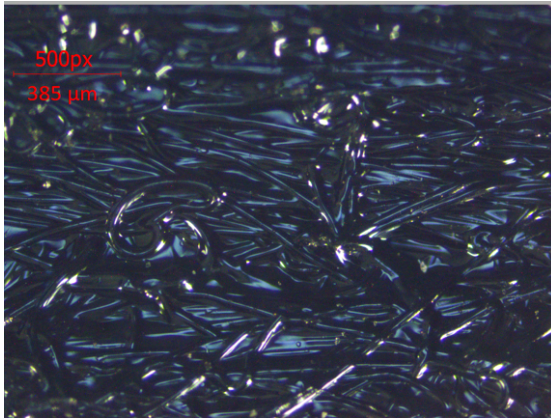


(c) 10X magnification: 500 px = 195 μm

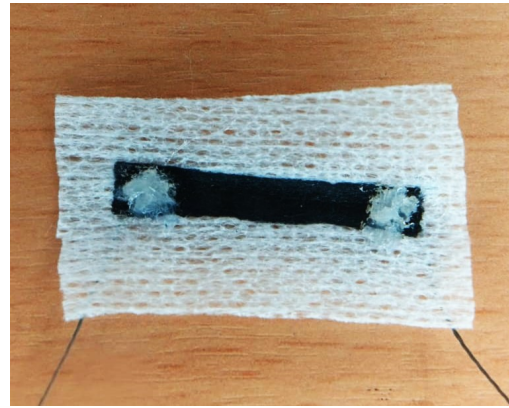
Figure 2.7: Microscope images of the ROYAL substrate at different magnifications.

Comparing the microscope images of the AKENA substrate [2.6] with the microscope images of the ROYAL substrate[2.7], we can see that the AKENA substrate fibers appear translucent, probably due to the 100% polyethylene terephthalate composition compared to the 70% composition of the ROYAL fibers. This difference in composition may be one of the factors leading to AKENA's hydrophobicity, shown in Fig[2.5].

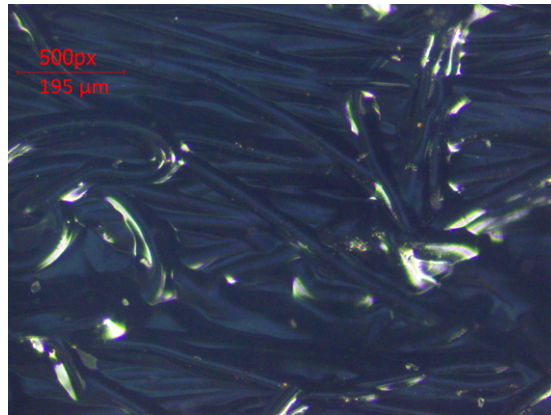
On top of the different optical properties, the AKENA substrate appear to have holes in it's surface, as seen in 2.6a, although they seem to be an intentional part of the fabrication process.



(a) 5X magnification: 500 px = 385 μm

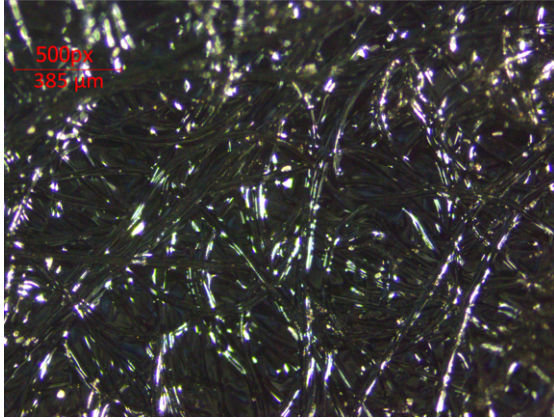


(b) Akena substrate INK1

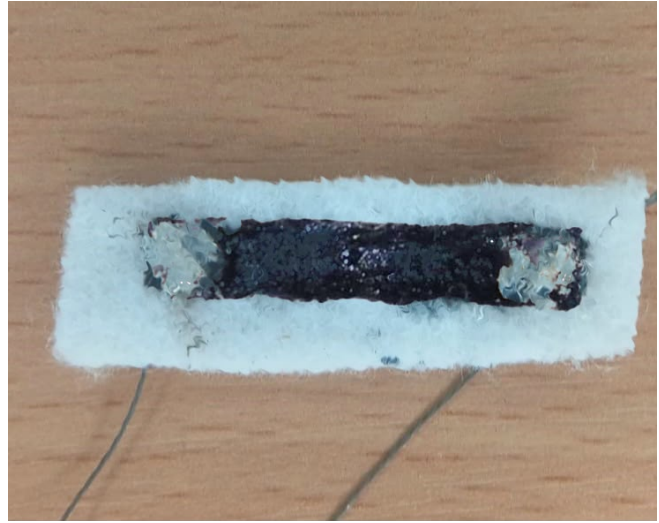


(c) 10X magnification: 500 px = 195 μm

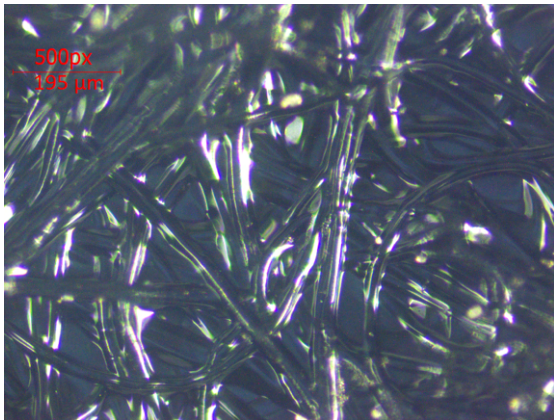
Figure 2.8: Microscope images of the INK1 on the AKENA substrate at different magnifications



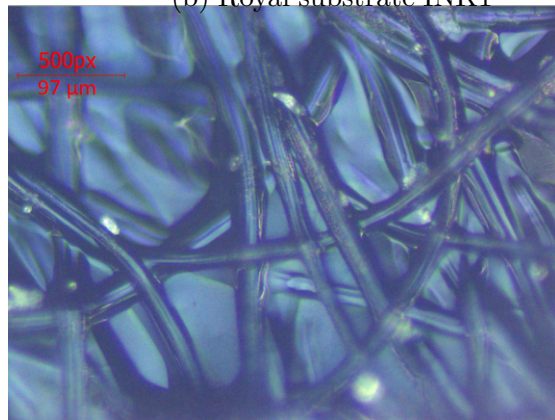
(a) 5X magnification: 500 px = 385 μm



(b) Royal substrate INK1



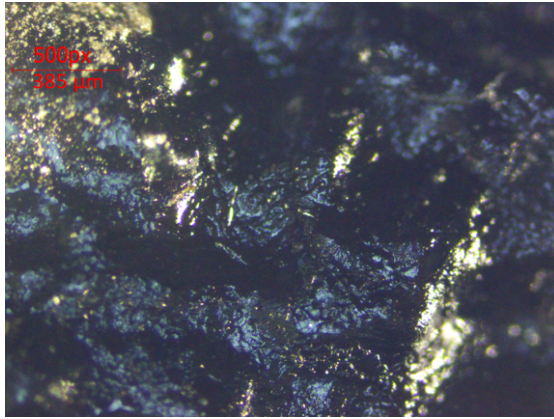
(c) 10X magnification: 500 px = 195 μm



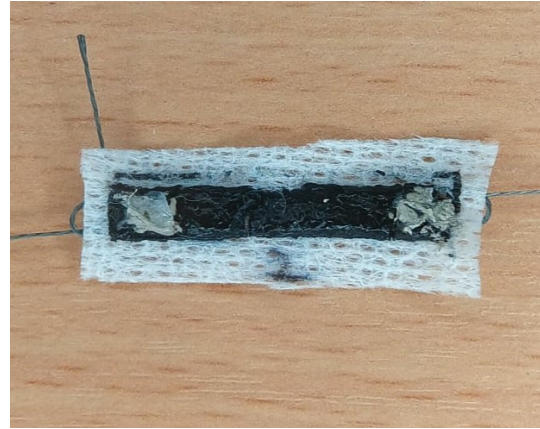
(d) 20X magnification: 500 px = 97 μm

Figure 2.9: Microscope images of the INK1 on the ROYAL substrate at different magnifications

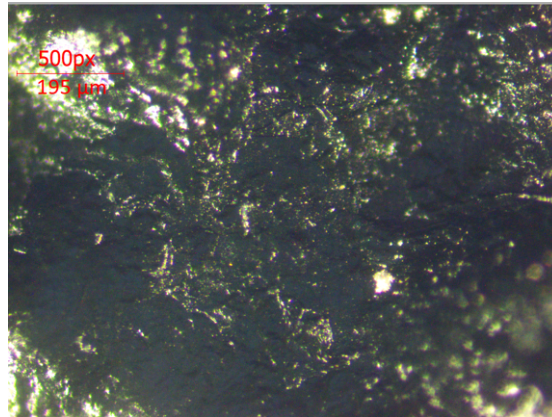
Reviewing Fig[2.8a] and Fig[2.9a], the INK1 completely permeates into the substrate, evenly coating the fibers and filling any gap inbetween them, even in the case of the AKENA substrate, which as already stated contains macroscopic gaps in the fabric's surface.



(a) 5X magnification: 500 px = 385 μm

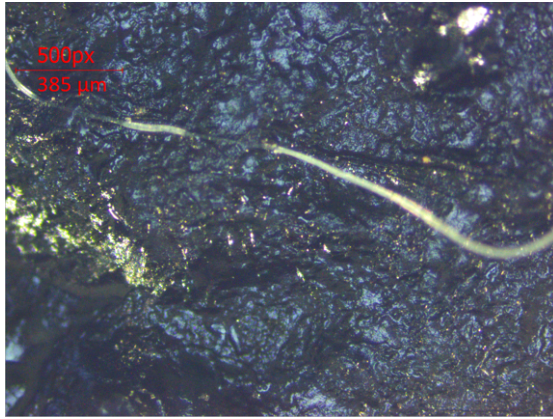


(b) Akena substrate INK2

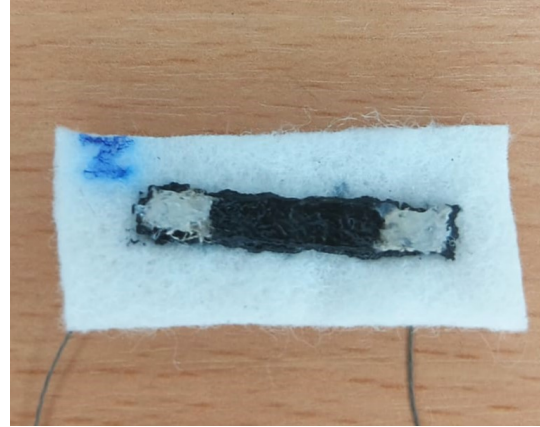


(c) 10X magnification: 500 px = 195 μm

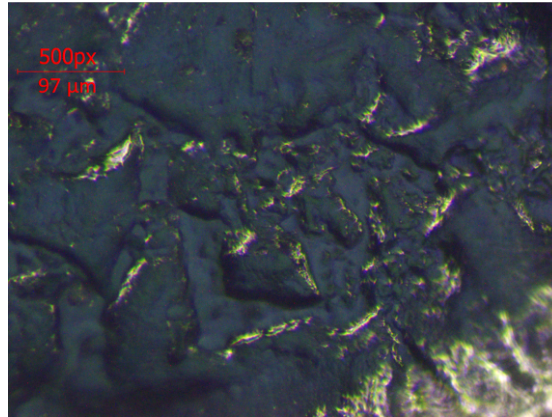
Figure 2.10: Microscope images of the INK2 on the AKENA substrate at different magnifications



(a) 5X magnification: 500 px = 385 μm



(b) Royal substrate INK2



(c) 20X magnification: 500 px = 97 μm

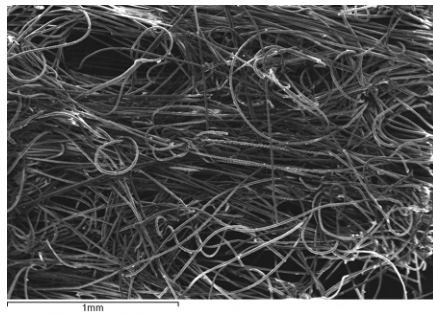
Figure 2.11: Microscope images of the INK2 on the Royal substrate at different magnifications

As can be seen in Fig[2.10] and Fig[2.11] INK2 completely covers the substrate, creating a thick homogeneous layer of hydrogel despite the different fabric. Due to the ROYAL substrate's high superficial concentration some strands may be able to surface even after being coated with INK2, as shown in Fig[2.11a].

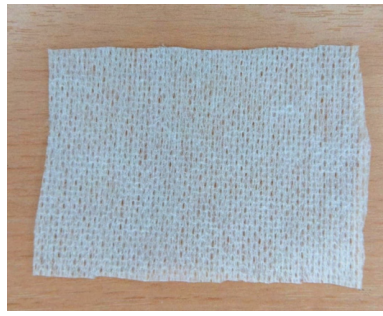
2.2 Morphological characterization

In this section the SEM photos of the different substrates and inks are reported. Each combination of ink and substrate was photographed at 50X, 100X and 300X but the photos reported are only the most significant. For the INK2 the photos shown also depict

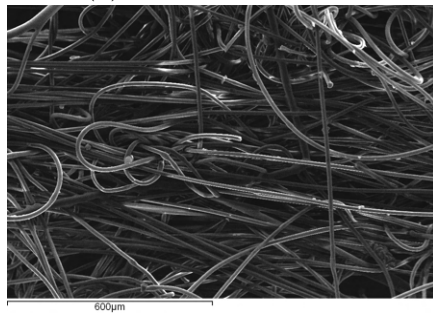
the border between the substrate and ink to show the height of the crosslinked PEDOT PEGDA ink. Serigraphic printing is shown aswell to compare its performance with 3D printing



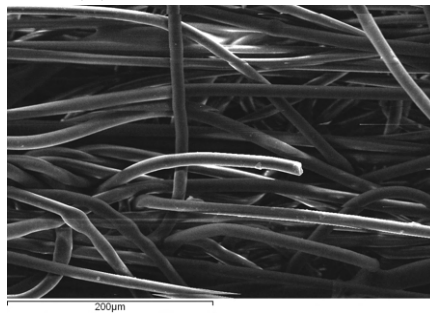
(a) 50X magnification



(b) Akena substrate



(c) 100X magnification



(d) 300X magnification

Figure 2.12: Scanning Electron Microscope images of the Akena substrate

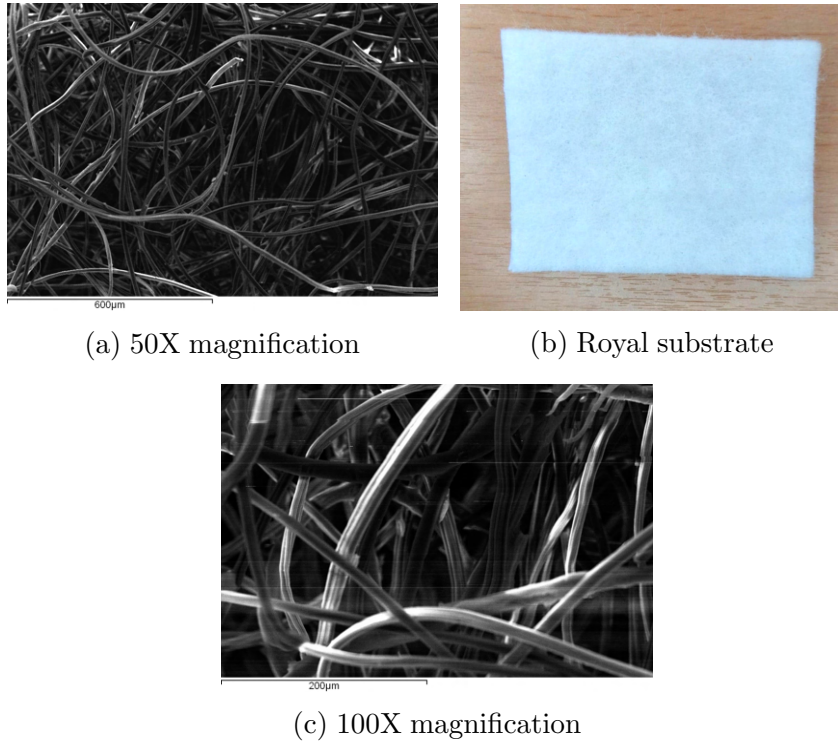


Figure 2.13: Scanning Electron Microscope images of the Royal substrate

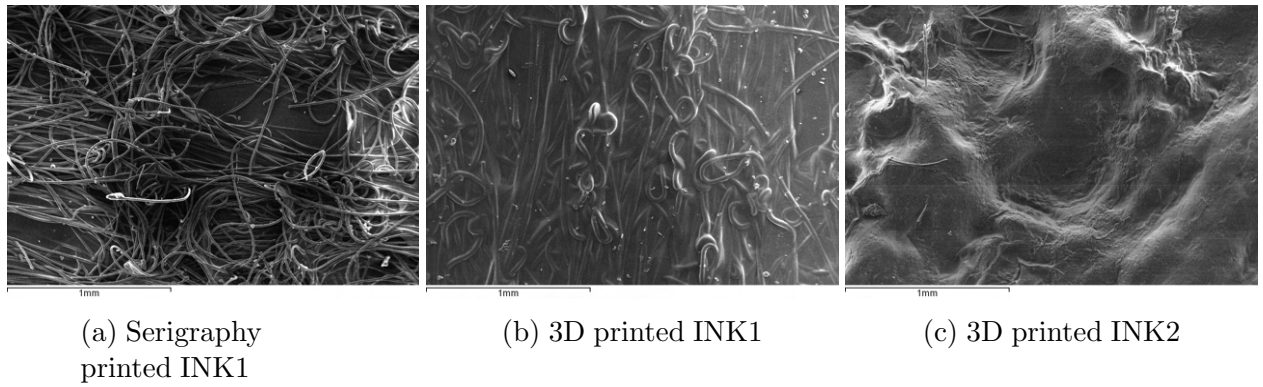


Figure 2.14: Scanning Electron Microscope images of the PEDOT:PSS inks printed on the AKENA substrate at 50X magnification

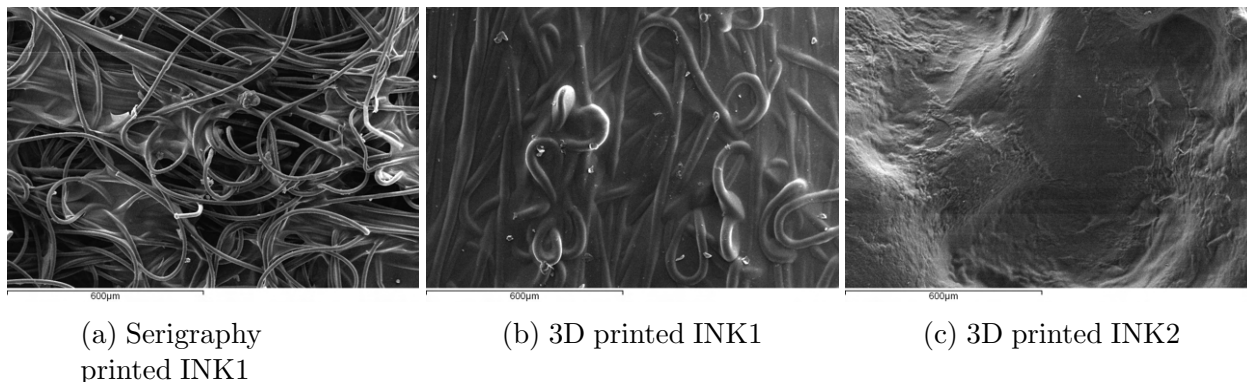


Figure 2.15: Scanning Electron Microscope images of the PEDOT:PSS inks printed on the AKENA substrate at 100X magnification

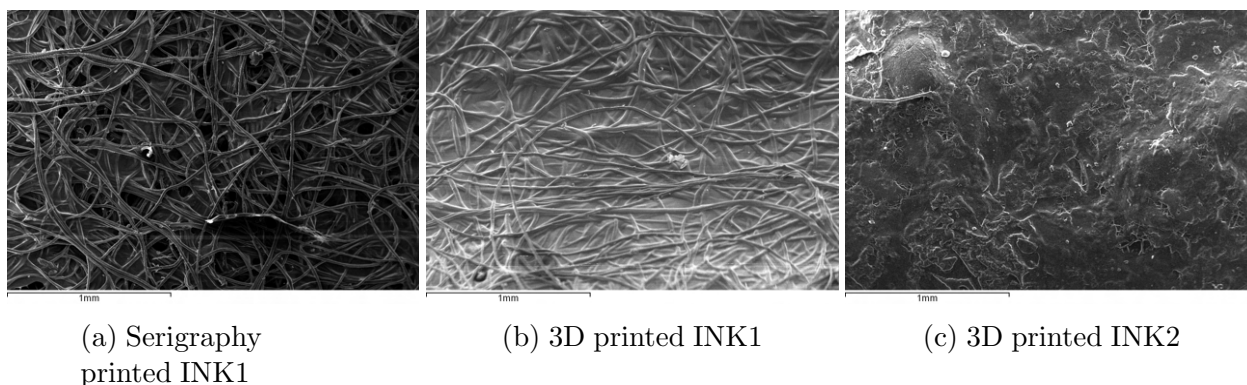


Figure 2.16: Scanning Electron Microscope images of the PEDOT:PSS inks printed on the ROYAL substrate at 50X magnification

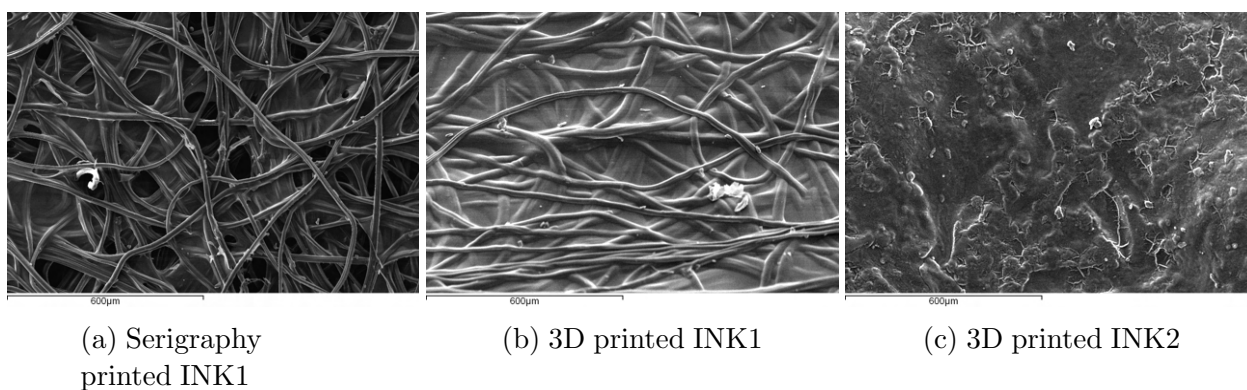


Figure 2.17: Scanning Electron Microscope images of the PEDOT:PSS inks printed on the ROYAL substrate at 100X magnification

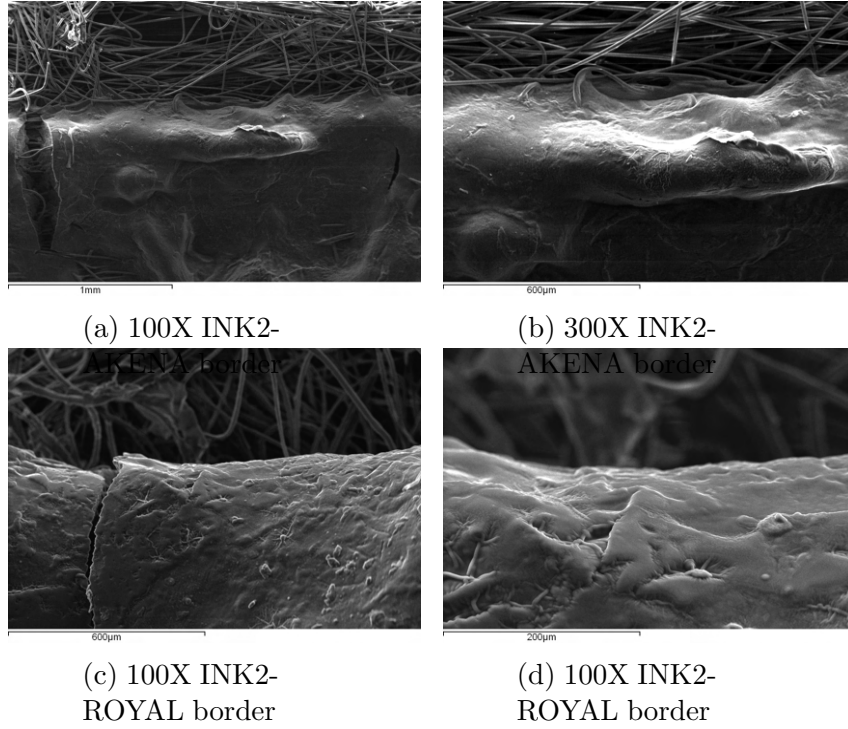


Figure 2.18: Scanning Electron Microscope images of the INK2-substrate borders

SEM images provide many additional information on both the substrate and the ink's properties. Notably the difference between serigraphy printing and 3D printing can be seen for the AKENA substrate in Fig[2.14a] and Fig[2.14b] and for the ROYAL substrate in in Fig[2.16a] and Fig[2.16b]: serigraphic printing of INK1 is inconsistent in filling gaps in the substrate, which may impact the material's properties such as resistivity, durability and reproducibility, while 3D printing of INK1 is able to evenly coat all of the substrate.

In Fig[2.18a] and Fig[2.18c] cracks in the photocrosslinked INK2 are visible. Comparing these images with those of INK1 it can be seen how INK1 lacks cracks and other imperfections, which strengthens the hypothesis of it having the higher mechanical resistance out of the two inks, as seen during the print process.

Finally if we compare the images of the AKENA substrate [2.12a] and ROYAL substrate[2.13a] at 50X it can be seen how the AKENA fibers are much more dense than ROYAL's, possibly leading to the aforementioned slight hydrophobicity, due to tighter gaps between the fiber for a liquid to flow into.

2.3 Electrical characterization

2.3.1 I-V Graphs

In this section the I-V curves of the different CONF1 substrate-ink combinations are reported, obtained as described in the Methods section. Three samples for each configuration were analyzed. In the case where all three samples' I-V curves overlap to the point of being indistinguishable the mean and standard deviation of the three sets of point is shown. For each sample three sweeps from -0.7 V to 0.6 V have been applied, resulting in three points for each value of tension, the mean of which has been used for the final result.

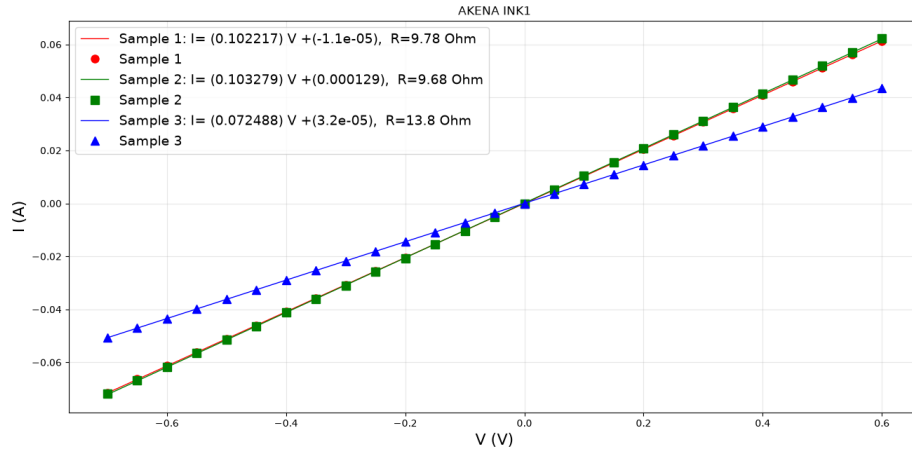


Figure 2.19: IV curves of the three AKENA INK1 samples.

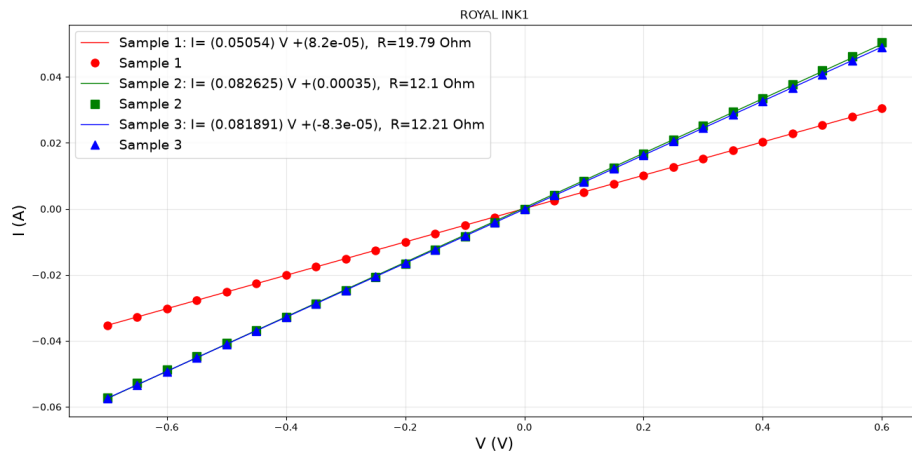


Figure 2.20: IV curves of the three ROYAL INK1 samples.

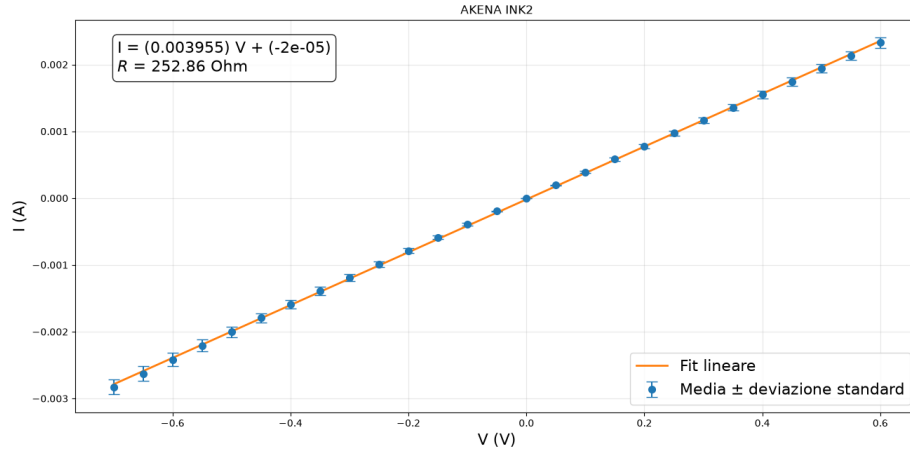


Figure 2.21: IV curves of the AKENA INK2 configuration. Due to the sample's similarity, the current values of the three samples were averaged, showing mean and standard deviation

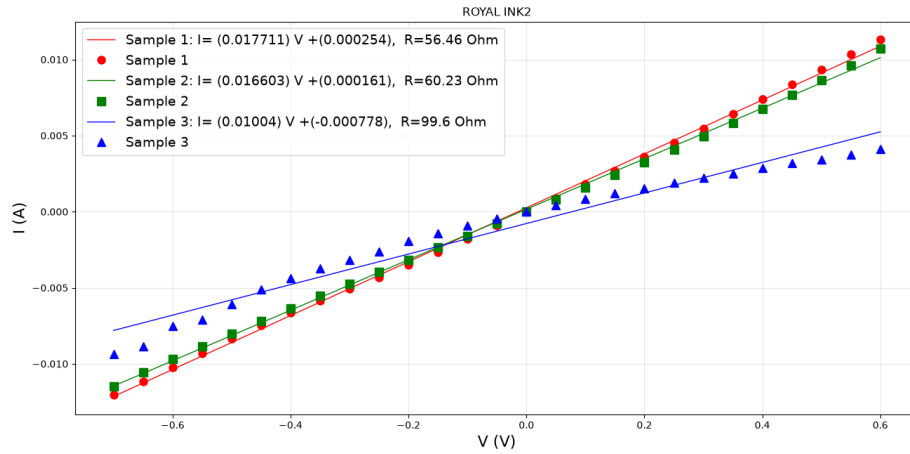


Figure 2.22: IV curves of the three ROYAL INK2 samples.

As shown in the graphs all the samples of a certain configuration share similar resistance. The resistances for each substrate-ink combinations are reported in Tab[2.1]. The presence of outliers between samples is a result of the print process: despite the fabrication steps being the same for every samples, the 3D printing process is not always perfect and along with the wire's resistance and the substrate's complexity leads to variations in the resistances values, as can be seen most notably for the ROYAL INK2 samples [2.21].

Substrate	Ink	CONF1 Resistance (I-V)(Ω)
AKENA	INK1	10.78 $\pm$ 0.51
ROYAL	INK1	13.94 $\pm$ 0.01
AKENA	INK2	252.86 $\pm$ 0.73
ROYAL	INK2	67.47 $\pm$ 0.55

Table 2.1: Resistance values of all substrate-ink combination. The data shown is a mean of the resistances of all three samples

Comparing the AKENA INK1 and INK2 configuration with their correspondent ROYAL configuration it is reasonable to assume that the INK2 has an higher overall resistance, the main reason for this may reside in the 3 dimensionality of the INK2 configurations: throughout these the current may disperse in the volume of the INK2, increasing the overall resistivity, while in the case of INK1 the current may be bound to a more confined path, due to the ink being essentially two dimensional.

On the other hand comparing the configurations with same ink shows that when considering INK1 the ROYAL INK1 configuration appears to be the most resistive compared to the AKENA INK1 configuration: this may be caused by the presence of the surface fibers of the ROYAL substrate along with it's thickness.

When comparing the INK2 the situation is reversed: the AKENA INK2 configuration appears to be the most resistive: this may be a result of the INK2 fragility when printed on AKENA, as reported in the "Print results" section.

2.3.2 4 Way sheet resistance

The 4 way probe sheet resistance measures are reported in Tab[2.2] while in Tab[2.3] the thickness of the substrates and INK2 are shown.

The measures are a mean of three samples for each sample of a given combination of ink and substrate.

The resistances at each point of the sampling interval have been shown intentionally to highlight a property of INK2: when the polarization of the applied voltage changes a rapid increase in resistivity can be observed, most notably for the INK2 AKENA samples.

This may suggest the presence of an hysteresis cycle for the INK2. In Fig[2.23] the I-V graph of an AKENA INK2 sample is shown where each different dataset corresponds to a different subsequent sweep: for each subsequent sweep the slope of the I-V changes showing a change in resistance, which may again hint at the presence of an hysteresis cycle.

Comparing the sheet resistances before the voltage polarity change we can see that the PEGDA ink is on average less resistive than it's counterpart for each substrate: as already stated the PEGDA INK is 3 dimensional, which may lead to the surface ink to

be completely free of resistive substrate fibers. This behavior is lost once the polarity of the voltage is changed.

	-0.7 V	-0.375 V	-0.05 V	0.275 V	0.6 V	Mean $\pm$ std variation
INK1 AKENA	3.36	3.42	3.43	3.76	3.78	$(3.5 \pm 0.2) \Omega/\square$
INK1 ROYAL	4.25	4.26	4.29	4.20	4.17	$(4.2 \pm 0.2) \Omega/\square$
INK2 AKENA	3.49	3.41	3.41	6.17	6.14	$(4.4 \pm 1.5) \Omega/\square$
INK2 ROYAL	4.54	4.54	4.62	5.03	5.07	$(3.43 \pm 0.2) \Omega/\square$

Table 2.2: Sheet resistance measures of all INK substrate combinations. All the measures are in $\Omega/\square$. The mean and standard variation have been corrected using the geometric factors found in Tab[1.3]. The resistances have been measured at equal intervals from -0.7 V to 0.6 V for consistency with the I-V measures of the same samples.

Material	thickness(mm)
AKENA	0.22 ± 0.01
ROYAL	0.85 ± 0.01
INK2 AKENA	0.70 ± 0.24
INK2 ROYAL	1.61 ± 0.23

Table 2.3: Thickness of the substrates and mean of three samples of crosslinked INK2. For the substrates the error used is the sensitivity of the caliber used while for the INK2 the standard deviation was used.

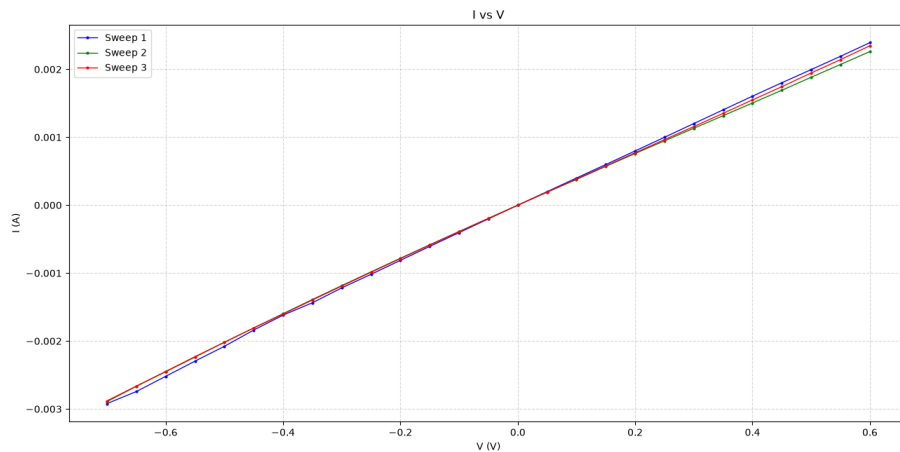


Figure 2.23: IV curves of an INK2 AKENA sample. The three lines represent each a subsequent sweep. The change in the slope of the curves is visible, showing a change of resistance through subsequent sweeps

2.3.3 Impedance spectroscopy measures

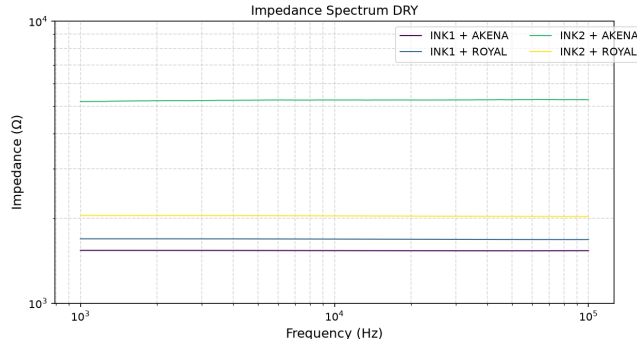
Impedance spectroscopy measures of the different substrate ink combinations of CONF1 are shown in Fig[2.25], conducted at different volumes of PBS present on the surface of the PEDOT ink .

INK1 is shown to have constant impedance throughout all PBS levels, which may indicate that it does not interact electrochemically with the ions within the solution: this behavior is coherent with the ink's hydrophobicity, as the liquid cannot enter between the substrate's fibers.

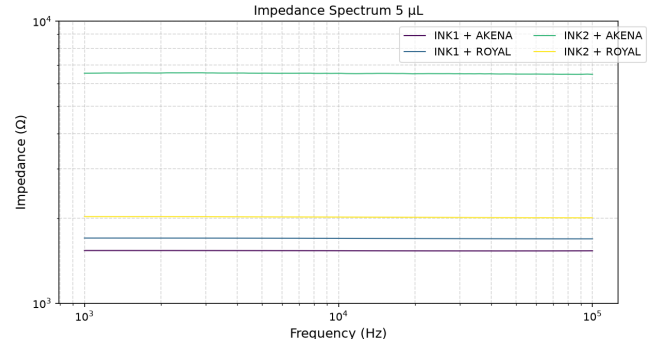
INK2 acts differently for each substrate. The INK2 AKENA samples show increasing impedance as the volume of PBS increases, a behavior that is alone throughout all samples and it may be caused by defects in the printing process. The INK2 ROYAL combination shows a decreasing impedance throughout increasing PBS volume levels: this hydrogel is hydrophilic, being able to absorb the PBS solution that interacts with it. This absorption of the PBS may be what leads to a lower impedance.

The behavior of all the different combinations' impedance remains constant at different frequencies, which suggests that the single strip of PEDOT ink can be modeled as a resistance instead of more complex element containing a CPE as initially hypothesized in Fig[1.16].

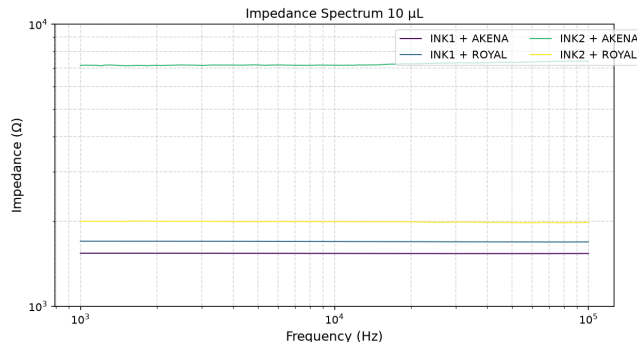
Following the behavior observed in the I-V curves the INK2 shows higher impedance compared to INK1, whilst the substrate choice affects the impedance based on which ink is printed. The impedance values of the CONF1 for different substrate-ink combinations are shown in Tab[2.4]



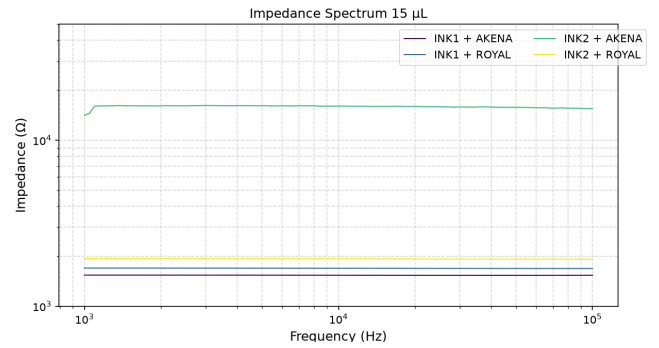
(a) Dry(no PBS volume) spectroscopy



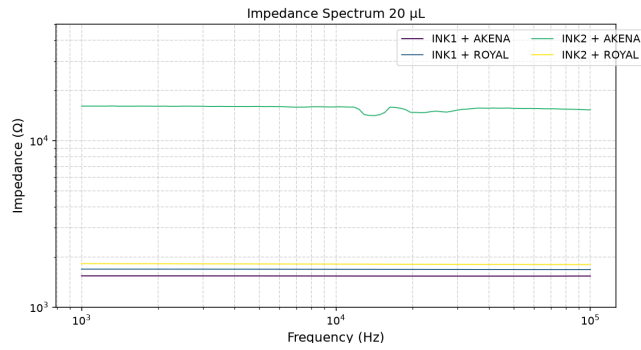
(b) 5 μ L PBS spectroscopy



(c) 10 μ L PBS spectroscopy



(d) 15 μ L PBS spectroscopy



(e) 20 μ L PBS spectroscopy

Figure 2.24: Impedance spectroscopy of the CONF1 of the four ink-substrate combinations.

	DRY	5 μL	10 μL	15 μL	20 μL
INK1 AKENA	1536.0 ± 1.3	1534.3 ± 1.8	1538.6 ± 1.8	1535.9 ± 1.9	1536.7 ± 1.8
INK1 ROYAL	1687.7 ± 3.7	1697.9 ± 3.9	1696.1 ± 3.9	1692.8 ± 3.9	1686.2 ± 3.8
INK2 AKENA	5258.5 ± 22.2	6537.2 ± 23.5	7158.7 ± 84.8	16061.4 ± 294.5	15935.6 ± 490.5
INK2 ROYAL	2039.9 ± 5.8	2020.4 ± 6.8	1995.4 ± 7.5	1932.1 ± 6.6	1812.3 ± 7.2

Table 2.4: Impedance of all INK-substrate combinations at different wetness levels measured at 10 Khz. All the measures are in Ω .

Fig[2.25] through Fig[2.28] show the impedance spectroscopies of the CONF2 for each one of the 4 ink-substrate combinations at different volumes of PBS absorbed in the exposed substrate inbetween the cathodes.

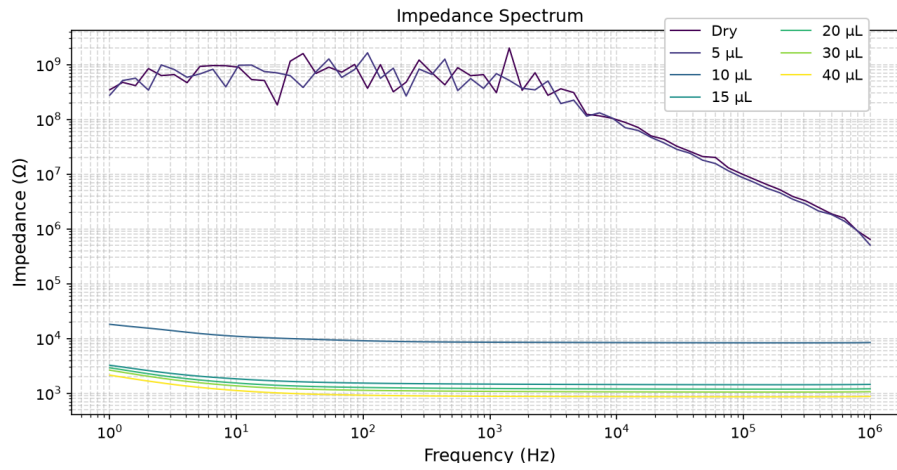


Figure 2.25: Impedance spectroscopy of the INK1 AKENA CONF2 at different PBS levels.

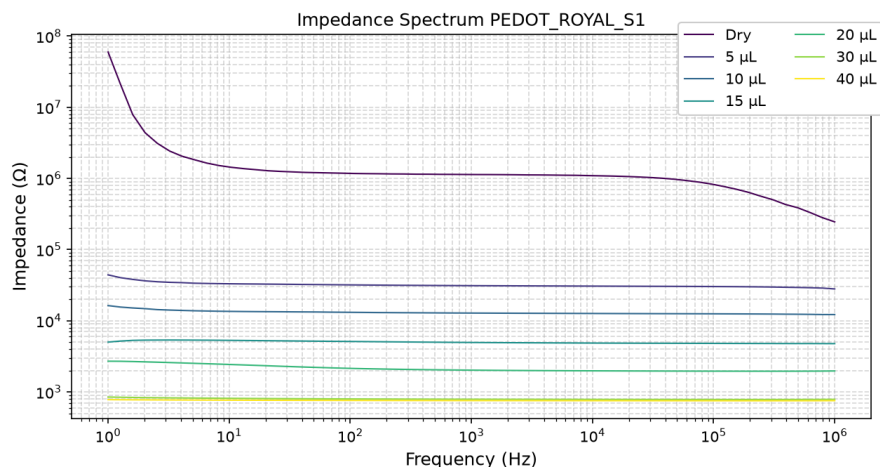


Figure 2.26: Impedance spectroscopy of the INK1 ROYAL CONF2 at different PBS levels.

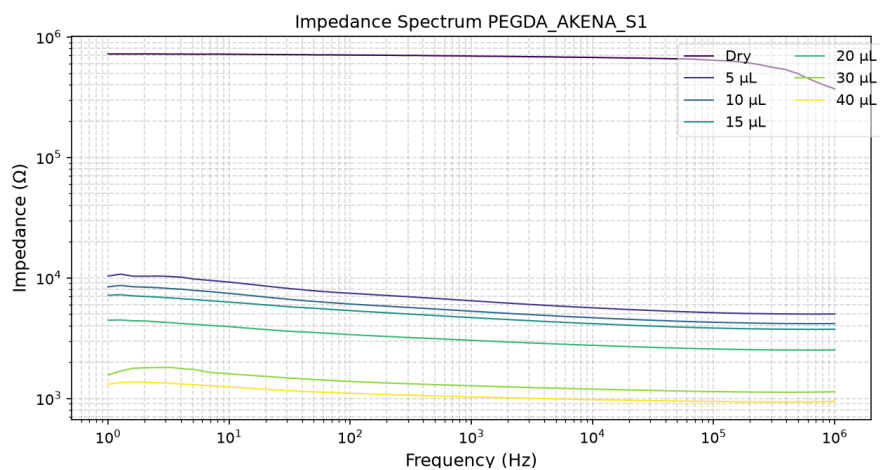


Figure 2.27: Impedance spectroscopy of the INK2 AKENA CONF2 at different PBS levels.

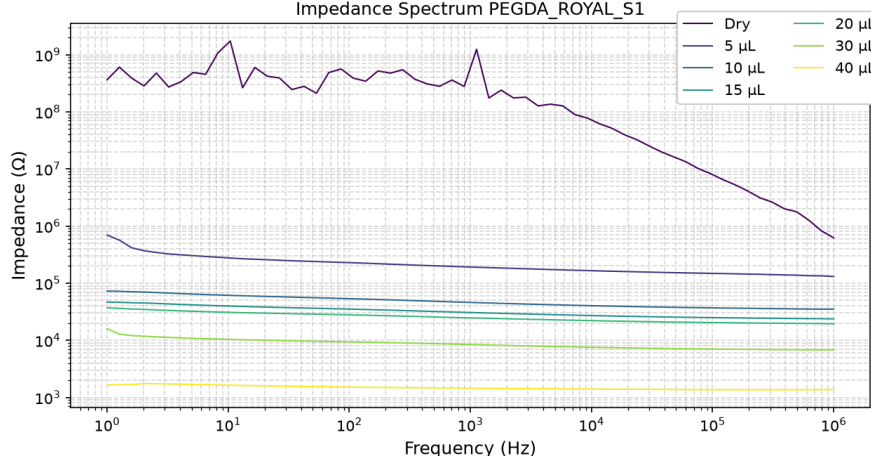


Figure 2.28: Impedance spectroscopy of the INK2 ROYAL CONF2 at different PBS levels.

Comparing Fig[2.25] through Fig[2.28] giveS many insight on the influence of each ink-substrate combination on the wetness sensing capabilities of the CONF2.

Observing Fig[2.26] and Fig[2.27] we can see how the INK2 AKENA and INK1 ROYAL configurations present a stable impedance profile, compared to the other two configurations. At high frequencies all of the combinations standardize their behavior, assuming an impedance of $10^6 \Omega$: if we consider the possible circuit scheme of the CONF2(Fig[1.16]) and the impedance of an ideal capacitor, we consider the CPE as such, $\frac{1}{i\omega C}$, we can see that at high frequencies the impedance of the CONF2 is given by the resistances of the cathodes and the resistance of the PBS imbued substrate. This behavior is repeated in all of the spectroscopies.

Once 10 μL PBS have been added inbetween the electrodes (Fig[2.27]) all combinations start conducting due to the PBS soaking the substrate.

As the volume of PBS inbetween the electrodes increase beyond 10 μL we can see different behavior between the combinations:

- INK1 AKENA: once 10 μL of PBS have been deposited between the electrodes the impedance value remains similar throughout all subsequent wetness levels, staying in the range of 1-3 $\text{K}\Omega$: as stated before both INK1 and the AKENA substrate are slightly hydrophobic, which results in creation of PBS drops on top of the substrate (Fig[2.5]). As a consequence, once the PBS drop became large enough to cover the 2mm gap between the electrodes the current most likely would pass through the PBS, ignoring the substrate. Any subsequent addition of PBS then would not influence the impedance since a passage between the two electrodes would have been already created. This combination may be unfit for sensing wetness change: when observing the impedance of the configuration if the impedance is too similar between wetness levels a wrong estimation of the wetness may occur.

- INK1 ROYAL: the impedance drops throughout additions of 5 μL PBS, staying in the range of 10^3 - $10^5 \Omega$: we can estimate that for every 5 μL of PBS the impedance drops by around $0.5 \text{ K}\Omega$, significant and constant enough to be easily detected.
- INK2 AKENA: the impedance drops slightly throughout additions of 5 μL PBS, staying in the range of 10^3 - $10^4 \Omega$. Compared to the INK1 AKENA case, the impedance values appear to be more spaced out throughout the additions of 5 μL , making this configuration useful for wetness sensing.
- INK2 ROYAL: the impedance drops throughout additions of 5 μL PBS, staying in the range of 10^3 - $10^6 \Omega$. For every 5 μL of PBS the impedance drops are significant and constant enough to be easily detected. This combinations presents the highest overall impedance throughout all PBS levels and all frequencies, most likely due to the combination of INK2's and ROYAL's combined increased resistivity.

Fig[2.29] through Fig[2.32] show the impedance-time response to additions of PBS in-between the electrodes of CONF2. This helps visualize the effect of the additions of PBS on each CONF2 combination. The red arrows indicate an addition of 5 μL of PBS while the green one indicate an addition of 10. The generated AC signal used for the impedance-response had a frequency of 1 Khz.

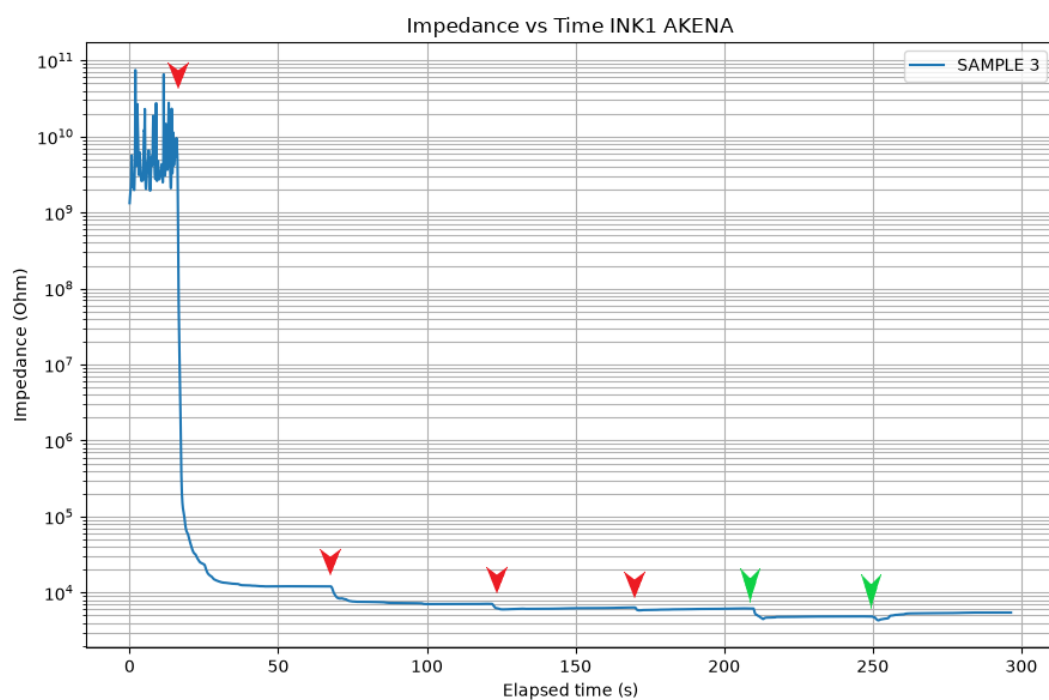


Figure 2.29: Impedance vs time response of the INK1 AKENA configuration after subsequent additions of PBS. The red and green arrows indicate respectively an addition of 5 μ L and 10 μ L of PBS solution.

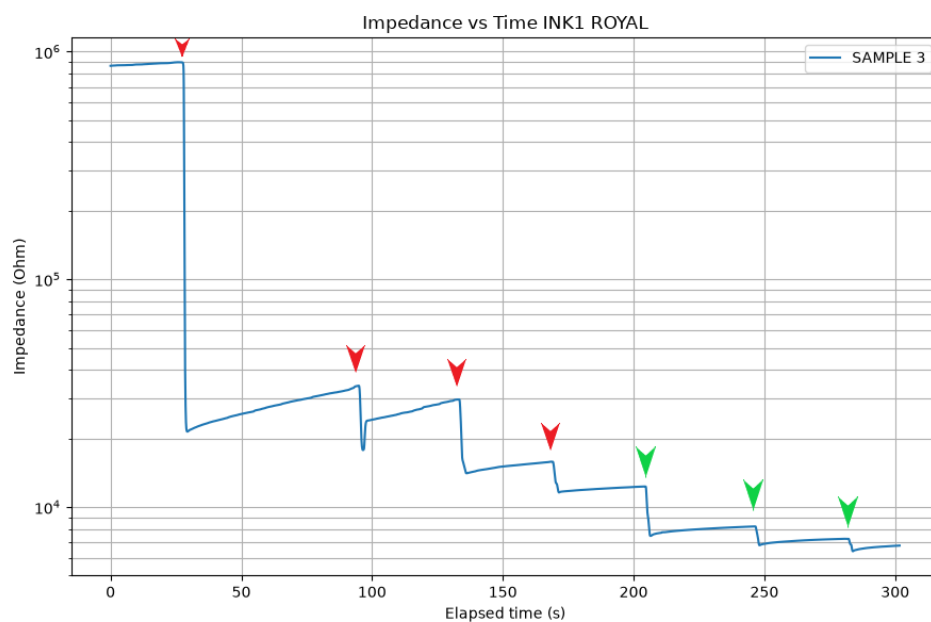


Figure 2.30: Impedance vs time response of the INK1 ROYAL configuration after subsequent additions of PBS. The red and green arrows indicate respectively an addition of 5 μL and 10 μL of PBS solution.

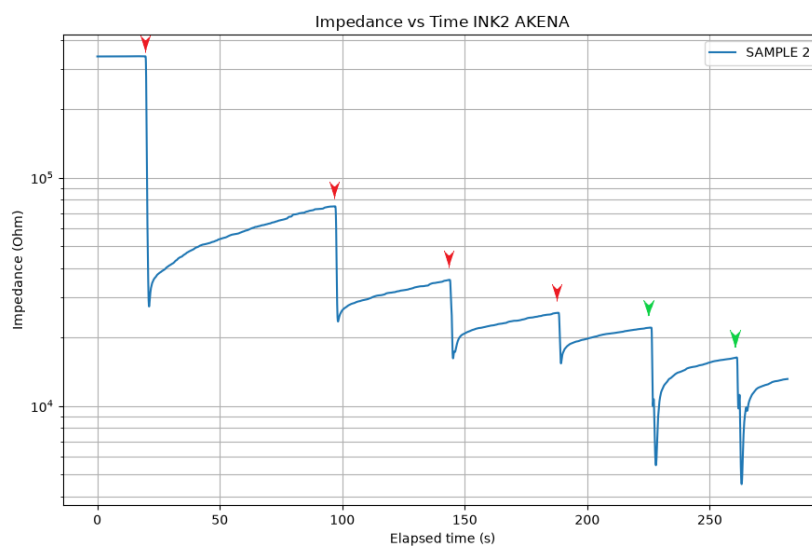


Figure 2.31: Impedance vs time response of the INK2 AKENA configuration after subsequent additions of PBS. The red and green arrows indicate respectively an addition of 5 μL and 10 μL of PBS solution.

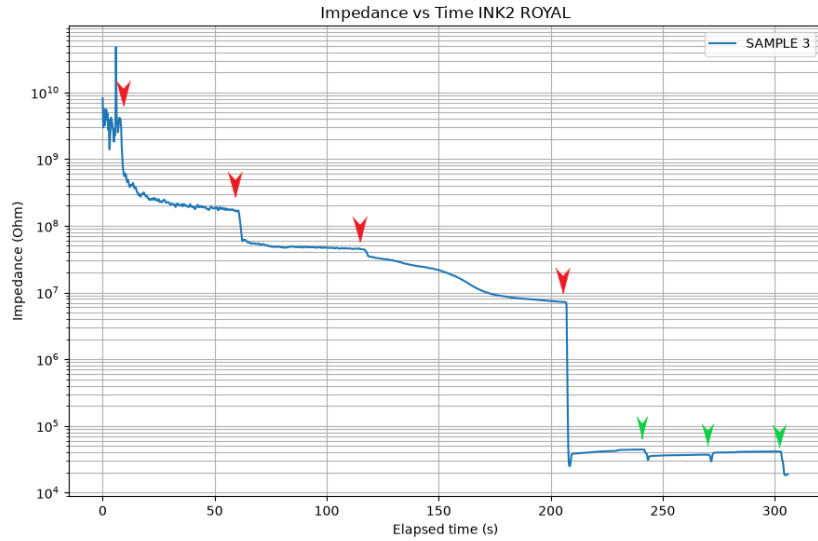


Figure 2.32: Impedance vs time response of the INK2 ROYAL configuration after subsequent additions of PBS. The red and green arrows indicate respectively an addition of 5 μL and 10 μL of PBS solution.

Fig[2.29] shows the INK1 AKENA samples when subjected to additions of PBS. We see a rapid decrease in impedance at 5 μL of PBS, followed by a stabilization of the impedance, which makes the INK1 AKENA unfit for wetness sensing: if multiple PBS level show very similar impedance level it becomes hard to precisely assess the wetness level of the configuration.

Fig[2.30] shows the INK1 ROYAL samples when subjected to additions of PBS. Each wetness level has a distinct impedance value making this combination good for wetness sensing. Particularly it can be seen that after each addition of PBS the impedance suddenly decreases, slowly increasing right after until reaching a more stable value: as the PBS drop is absorbed by the substrate it soaks the area between the electrodes, uniforming the impedance across the electrodes. As the substrate becomes saturated with PBS this effect is no longer present, as can be seen in the latter PBS additions.

Fig[2.31] shows the INK2 AKENA configuration when subjected to additions of PBS. Its behavior closely follows that of INK1 ROYAL, albeit with some differences due to the different materials used: the initial dry impedance is lower, as the AKENA substrate is less resistive than ROYAL, while when saturated (second green arrow) the impedance is higher. When saturated it is reasonable to assume that both substrates have similar electrical properties, so what changes the impedance of the CONF2 is the ink's choice, resulting in a higher impedance for INK2 AKENA compared to INK1 ROYAL.

Fig[2.32] shows the INK2 ROYAL configuration when subjected to additions of PBS. Its behavior follows that of INK2 AKENA. Due to ROYAL's higher resistivity when dry

it has higher impedance than it's AKENA INK2 counterpart, with similar impedance when fully saturated.

In Tab[2.5] the electrical properties of all substrate-ink combinations are summarized.

Substrate	Ink	CONF1 Resistance (I-V) (Ω)	CONF1 Sheet resistance ($\Omega/\square$)	CONF2 Impedance dry (Ω) (1 kHz)	CONF2 Impedance 5 μL (Ω) (1 kHz)
AKENA	INK1	$10.78 \pm 0.51 \Omega$	$3.5 \pm 0.2 \Omega/\square$	$7.13 \times 10^8 \pm 6.57 \times 10^8 \Omega$	$4.62 \times 10^8 \pm 1.30 \times 10^8 \Omega$
ROYAL	INK1	$13.94 \pm 0.01 \Omega$	$4.2 \pm 0.2 \Omega/\square$	$1.13 \times 10^6 \pm 5.55 \times 10^3 \Omega$	$3.10 \times 10^4 \pm 9.16 \times 10^1 \Omega$
AKENA	INK2	$252.86 \pm 0.73 \Omega$	$4.4 \pm 1.5 \Omega/\square$	$6.90 \times 10^5 \pm 3.27 \times 10^3 \Omega$	$6.26 \times 10^3 \pm 1.74 \times 10^2 \Omega$
ROYAL	INK2	$67.47 \pm 0.55 \Omega$	$3.43 \pm 0.2 \Omega/\square$	$3.82 \times 10^8 \pm 4.24 \times 10^8 \Omega$	$1.86 \times 10^5 \pm 5.44 \times 10^3 \Omega$

Table 2.5: Electrical properties of all substrate-ink combinations for both CONF1 and CONF2.

Chapter 3

Conclusions

The use of an organic 3D printer inks has shown to be a reliable and efficient technique for printing the PEDOT:PSS electrodes, assuring reproducibility and precision. The versatility of 3D printing allows for virtually the fabrication of any geometry that is required, along with being compatible with most ink compositions. The photocrosslinking features of the BIOX printer allows for the use of hydrogels, opening many fabrication possibilities.

When compared to 3D printing, serigraphic printing showed less consistency and versatility, being heavily restricted by the available mesh.

The AKENA substrate has shown the best conductivity and while easier to print on, has been shown to compromise the structural stability of the PEDOT:PSS electrodes; the ROYAL substrate instead appears to give the PEDOT:PSS electrodes good flexibility and resistance to deformation, albeit having lower conductivity and being more challenging to print on.

The liquid INK1 has shown good conductivity in DC and low impedance when used in AC, whilst showing slight hydrophobic capabilities and a higher susceptibility to the substrate used, possibly due to its property of fully seeping and covering the substrate's fibers.

The hydrogel INK2 has shown lower conductivity than INK1, possibly due to current dissipation in its 3 dimensional structure, but its ability of being crosslinkable through UV light makes the fabrication process more reliable. Its complex structure allows it to be less dependent of the substrate choice and a possible framework for more advanced uses.

The single electrode behavior, simulated by the CONF1, is consistent for each ink-substrate combination. The electrode is describable by a resistance since its behavior remains similar at any frequency and wetness level.

The AKENA INK1 and ROYAL INK1 configuration show similar behaviors but the hydrophobicity of the INK1 can cause issues when used in more complex application.

The AKENA INK2 combination shows the highest resistivity, sheet resistivity and impedance,

possibly due to the mechanical instability of the INK2 when printed on the AKENA substrate. On the other hand the INK2 ROYAL combination has shown good resistance, good sheet resistance and impedance, making it the prime candidate for textile use.

As for the behavior when used in a wetness sensor configuration, the four ink-substrate combinations have shown similar properties. All combination, except INK1 AKENA, show notable impedance change at 1 KHz when exposed to additions of PBS. Particularly the INK2 ROYAL configuration shows great promise for the wetness sensor electrodes: the impedance drops up to 20 μ L of PBS are notable enough to safely estimate the wetness level, the substrate absorbs the PBS with no issue and the ink-substrate combination is the most resistant to deformations and textile stress.

In conclusion, the PEDOT:PSS based inks have proven to possess useful electric properties, good flexibility, ease of fabrication and along with the ease of use and reliability of 3D printing they show promising capabilities for use in textile applications, especially in electrochemical sensors destined for medical use.

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