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Master of Science

Low cost stretchable thin film electroluminescent devices for display applications

Dissertation submitted in partial fulfillment
of the requirements for the degree of

Master of Science in
Micro and Nanotechnologies Engineering

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FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

September, 2018

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ACKNOWLEDGEMENTS

This thesis would not be possible without a very large group of people that helped me not specifically during this project but also throw my academic and personal life.

Firstly, I would like to thank my coordinator Dr. Kaspar Jansen, for receiving me at IDE TU Delft. But more importantly I want to thank all the guidance, support, time and patience dedicated, they made a big difference on the outcome of the project and during this phase. A special thanks to Masha and Martin, that guided through all my small tasks during the day. I learned a lot with both of you, this project would not have the same outcome without you. Thank you to all the staff in the laboratory, that helped during all these months.

Gostava de agradecer o meu orientador na FCT, o professor Dr. Pedro Barquinha, pela orientação em momentos difíceis que iluminaram o caminho e me ajudaram a completar este projeto. Obrigado pela disponibilidade e tempo dedicado à minha tese.

Aos meus pais, não vejo por onde começar. Obrigado por me terem proporcionado a aventura destes 5 anos. Obrigado por me terem carregado a bagagem com todo o tipo de instrumentos para que a sobrevivesse e nela prosperasse. Obrigado por serem o exemplo, por me terem apoiado, educado e por terem estado sempre lá em todos os momentos. Obrigado por todos o sacrifícios que fizeram e continuam a fazer, para que hoje possa escrever estas palavras. Obrigado por serem quem são que fazem de mim quem sou, pois vejo-vos todos os dias em mim, e anseio que se vejam a prosperar. Obrigado por tudo.

Aos meus avós, um especial obrigado, por serem os alicerces de uma família que me orgulho onde as qualidades são inumeráveis e que a saudade aperta em todos os momentos. Espero que um dia se orgulhem de mim o quanto eu me orgulho de vós, e que esta tese seja o inicio de tal caminho. Obrigado por estarem sempre lá, por serem um exemplo em todos os aspetos por fazerem de mim quem sou hoje e quem serei daqui para a frente.

Um obrigado a ti Pedro, pois sei que pode até ser surpresa, mas em ti vejo e aprendo, cresço e maturo. Espero que cresças, aprendas e alcances o sucesso pessoal e profissional. Espero que no futuro podamos partilhar todas essas historias e rir vendo o tempo passar.

Obrigado Adriana por fazeres parte da minha vida. Por me teres ajudado a ultrapassar difíceis momentos durante esta vida académica. Mas mais importante por seres parte integral dos melhores momentos. Obrigado por trazeres cor a esta tela de carvão, e por graças a ti crescer, maturar e aumentar o paradigma que é a vida. Obrigado por estares

ao meu lado e por continuares a estar nestas novas etapas que se avizinham.

Um especial obrigado a ti Leisico, por me teres agarrado e mostrado como sobreviver. Obrigado pela tua amizade e pelo exemplo que proporcionas. Mas mais importante obrigado por seres o amigo que és, obrigado pelos ensinamentos, palavras e conselhos. Pelas ideias partilhadas, pelos debates meticulosos, pelas gargalhadas e pela vida. Obrigado por teres sido parte importante desta vida, e por me teres recebido sendo o mentor que foste.

Agora para ti Sofia, obrigado por teres feito parte em todas as etapas desta vida académica. Obrigado pela tua amizade, pela orientação e pelos conselhos. Sem ti não seria o que sou hoje, e não tinha concluído esta epata desta forma. Obrigado por teres sido a mentora que precisei, preciso e continuarei a precisar. A tua amizade, as risadas, sermões e toda a boémia, são as memorias que levarei destes tempos. Espero que o meu trabalho te tenha deixado orgulhosa.

Aos meus afilhados, Alexandre, Barbara e Neto. Obrigado por todos os momentos, pela boémia e por me terem aberto os olhos quando necessário e com isso me feito crescer. Obrigado por fazerem parte das amizades que levarei para a vida. Espero que alcancem todo o sucesso que anseiam e mais aquele que nem sequer estarão a pensar. Estou certo que darão ótimos engenheiros e melhores pessoas. Orgulhem-se das pessoas que são, dos valores que têm e contem comigo para tudo o que necessitarem.

Um obrigado ao Miguel, por teres sido professor em milhares de situações de aperto e dislexia mental. Contigo aprendi mais do que possas imaginar. A tua ajuda foi vital no meu intelecto enquanto homem das ciências. Sem ela hoje a compreensão de muitos dos conceitos com os quais hoje estou familiarizado, seria infinitamente mais complicada. Admiro o teu conhecimento, e vejo-te como mentor de conhecimento cientifico. Mais que a mim desejo que tu alcances o sucesso académico, pois sei que o mereces a todos os níveis. Se um dia te tornares professor, estou certo que farás um trabalho incrível. A forma como encaras o conhecimento e a paciência que tens fazem de ti o melhor perfil para professor.

Aos meus amigos que não foram mencionados nestes parágrafos. Muitos de vocês mereciam estar nestas paginas, e conseguia escrever livros com memorias que guardo. Mais livros ainda com as nossas discussões. Neste 5 anos, cresci com todos vós e todos vós são parte crucial desta jornada. Obrigado pelas vossas amizades e por me terem aturado estes anos. Levo memorias que jamais esquecerei e momentos que não trocaria por nada. Na nossa vida pacata da FCT foram anos de tormentas alegrias. Sem vocês não estaria onde estou e não seria quem sou. Espero que todos vós alcancem a realização pessoal, a todos vós um muito obrigado.

"I have not failed. I’ve just found 10,000 ways that won’t work"

Thomas A. Edisson

ABSTRACT

Recent advances in materials science research have enabled the production of highly stretchable devices like sensors and displays. This new field of stretchable electronics stem from strain engineering and nanocomposite approaches, which require expensive production methods and result in fragile devices.

The emerging materials group at TU Delft Industrial Design Engineering Department large interest on expandable and stretchable light emitting devices culminated on this work where it was found a method to obtain stretchable electroluminescent devices for application on simple electroluminescent passive matrix displays. The devices were produced with all solution-based methods and non-expensive techniques as screen printing. The devices were obtained with by a sandwich structure of an emissive layer in between two electrodes. It was used as substrate a commercially available silicone rubber material called Ecoflex 00-30. The same silicone rubber material with ZnS:Cu phosphorescent powders embed were used as emissive layer. PEDOT:PSS enhanced with Bis(trifluoromethane)sulfonimide lithium salt was used as electrodes, samples with 10% enhancer show 800 Ω at 0% strain and 2 kΩ at 50% strain. Electroluminescent devices showed a transmittance of 30% limited by the fabrication technique and a satisfactory brightness in daylight. The entire structure has less than 250 µm of thickness, encapsulated and with a substrate of 100 µm. Relative luminance characterizations showed good luminance behaviour upon strain.

Keywords: PEDOT:PSS, Electroluminescence, Electroluminescent devices, Passive Matrix, Screen printing, Stretchable, Transparent

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RESUMO

O crescimento de áreas como a eletrónica transparente e/ou eletrónica extensível aumentam o número de aplicações como sensores, circuitos extensíveis, têxteis inteligentes, embalagens inteligentes, etc. Avanços nesta área provêm maioritariamente de strain engineering ou do desenvolvimento de nanocompósitos, que involvem processos complexos de custos elevados para a produção de dispositivos de baixa eficiência. Estas características aumentam as dificuldades de implementação destes processos para produção em massa a nível industrial.

O trabalho realizado no departamento de Industrial Design enginering da Tecnical University of Delft culminou no fabrico de uma matriz eletroluminescente extensível. Dispositivos são fabricados por screen printing e outros métodos de baixo custo. Como substrato é utelizado Ecoflex 00-30 um material à base silicone disponível comercialmente. Este material juntamente com pós fosfrescentes de ZnS:Cu é utilizado na camada emissora do dispositivo com estrutura sandwich utilizada para obtenção de eletroluminescência. Como elétrodos é utilizado PEDOT:PSS com propriedades melhoradas dada a adição de um sal de lítio, estes eletrodos atingem resistências de 800 Ω a 0% de extensão e 2 kΩ a 50% de extensão. Dispositvos finais possuem uma transmitância de 30% limitada pelas técnicas de fabrico e um brilho intenso mesmo na presença de luz. O dispositivo final possui uma espessura inferior a 250 µm mesmo quando encapsulados e com o substrato de 100 µm.

Palavras-chave: PEDOT:PSS, Electroluminêscencia, Dispositivos electroluminescentes, Matriz passiva, Screen printing, Extenssível, Transparente

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Symbols

ε_0	Vacuum permittivity .
A	Electrode area .
E	Electric Field .
Q	Electrodes Electric Charge .
V	Voltage .
d	dielectric width .

Acronymns

AC	Alternating Current.
AgNWs	Silver Nanowires.
CAGR	Compound Annual Growth Rate.
CB	Conduction Band.
CNTs	Carbon Nanotubes.
EL	Eletroluminescence or Eletroluminescent.
LED	Light Emitting Diodes.
OLED	Organic Light Emitting Device.
PDMS	Polydimethylsiloxane.
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate).
phosphor	Phosphorescent.
SEBS	Styrene Ethylene Butylene Styrenes.
STEC	Stretchability and Electrical Conductivity.
TFEL	Thin Film Eletroluminescent.
UV	Ultra Violet.
VB	Valence Band.

OBJECTIVE

Electroluminescence is largely used on display applications. Organic Light Emitting Device (OLED) technology offer applications as curved displays or even flexible displays. However, when looking for properties like stretchability, a new strategy is needed to achieve devices like foldable or stretchable displays. The work done with the emerging materials team at TU Delft Industrial Design Engineering Department aims to find an approach to simple stretchable electroluminescent displays using high field electroluminescence. The main objective of this thesis is to develop a stretchable and transparent electroluminescent passive matrix prototype with enough brightness to be used on daily applications as: signs with updatable information; smart labels or even for fashion applications in clothing and architecture. To develop such prototype a typical sandwich structure is used, where as emissive layer is used phosphrescent ZnS:Cu powders embed on silicon rubber and or electrodes enhanced PEDOT:PSS electrodes. It is also the objective of the present thesis to develop such technology using simple all solution-based methods that are inexpensive and applicable to mass production. This thesis work aims to:

- Produce non expensive transparent stretchable electrodes;
- Produce devices bright enough to be used with ambiance light using ZnS:Cu phosphorescent powders;
- Produce simple stretchable devices that require the lowest use of power possible;
- Produce a working eletroluminescent passive matrix;

MOTIVATION

Technologies like a curved TV or a curved smartphone display are now a reality on our daily life and flexible devices are our expectations for the coming years. OLEDs offer new approaches to flexible displays, permitting intense lighting on flexible substrates. However, OLEDs are a very sensitive technology, making it difficult to use on collapsible and stretchable devices. It is one thing to achieve flexibility and another to achieve stretchability. Stretchability is a desired property for the next step in electronics, offering countless advantages for large area applications like advertisement screens or wearable computers. Such characteristic when applied to electronics opens possible applications on the most varied areas from textile to automobile industry.

Stretchable electronics is not just an ambition, is a growing tendency, products like sensitive e-skin or stretchable solar cells, are fast arriving to our reality. On a study made by IDTechEx the stretchable electronics market is estimated to be worth 800 million dollars by 2028. [1] On another study provided by RESEARCH AND MARKETS, the global stretchable electronics market is forecast to grow at a staggering Compound Annual Growth Rate (CAGR) of over 80% by 2023. [2]

With such a growing importance there is a big effort in the scientific community to study stretchable electronics. At the current day the research on stretchable electroluminescent devices, focus on the combination of rigid elements like Light Emitting Diodes (LED) or OLEDs with soft rubbery polymers. Both referred approaches show lots of difficulties since the combination of rigid elements (LEDs) result in connectivity difficulties and increased contact resistances, compromising the devices functionality.

The use of OLEDs share some of the same difficulties of using LEDs for stretchable technologies. But also a great number of other problems, like the reduced life expectation given the extremely sensitiveness to oxygen and moisture. Or the difficulties to encapsulate devices which cause an aggravation on the degradation, making the devices very sensitive and not efficient for stretchable applications. More importantly, this sensitiveness demands highly controlled production environment, which requires complex methods of fabrication and an increased production cost. Given all these problems and more, other alternatives to achieve fully stretchable devices need to be studied. One of them is building stretchable light emitting devices using electroluminescence.

Chapter 1

Introduction

1.1 Contextualization

The massification of computers and smartphones brought a growing dependence on these devices, turning them into essential pieces not only at work but also on our daily life. With such a big role in our lives consumers demand higher quality, convenient and portable digital devices. [3, 4] So, flexible, foldable and stretchable pieces of technology are now on the imagination of costumers and engineers. Flexible and stretchable displays have attracted great attention due to many advantages such as lighter weight, less fragility, and higher portability than existing displays. These devices have potential to open up future applications on areas like expandable and foldable screens for smartphones; wearable or fashionable electronic clothing; rollable or collapsible wallpaper-like lamps; biocompatible sources for in vivo or epidermal medical devices; wearable computers; smart cards, etc, enabling more freedom for devices design. [5–7]

1.2 Electroluminescence

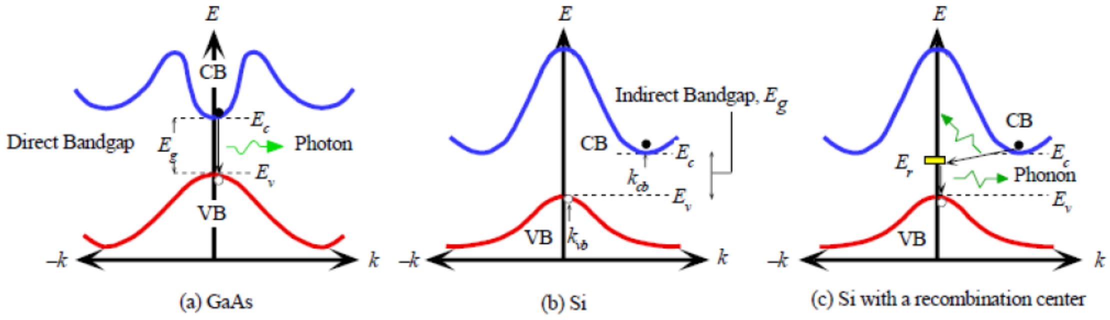
Electroluminescence is a nonthermal generation of light, resulting from the application of a electric field to a specific kind of material. [8] This effect was discovered in 1936 by the french physicist Destriau when he observed that light was emitted from a ZnS compound upon application of a large electric field. [9] There are two classes of Eletroluminescence or Eletroluminescent (EL) in inorganic materials: high-field EL and injection EL.[8]

In injection EL, light is emitted upon recombination of minority and majority carriers across the band gap of crystals, this type of electroluminescent is very common on LED devices. [8] On the other hand, high field EL is the excitation of luminescence centres (lattice defects caused by impurities that create prohibited states on the bandgap) which enables electron excitation and radiative relaxation (see figure 1.1c). [10] On this type of EL, the majority of charge carriers are accelerated by a strong electric field, usually around 1×10^6 V/cm. The high-energy electrons raise the luminescent centres to excited quantum states via impact ionization and/or impact excitation. These excited centres must eventually relax to ground state, emitting photons (process known as the radiative relaxation). [11, 12]

Semiconductor materials are categorized by direct-gap materials (all the II-VI and most III-V compounds) or indirect-gap materials (group IV semiconductors and some III-V compounds). The schematic of figure 1.1 shows the difference between these types of bandgap. As observable on figure 1.1 direct band gap materials have the minimum Conduction Band (CB) height directly above the the maximum Valence Band (VB) height.

On the contrary indirect-gap materials have the maximum VB heigh misaligned with the minumum CB which usually require emission or absorption of a phonon to complete the lowest energy transition across the energy gap.

Such conditions make band-to-band radiative transitions much more probable across a direct bandgap materials than indirect bandgap materials, since on a direct bandgap material the recombination does not require a momentum change. [13] However, it is possible to obtain high efficient emitting indirect bandgap materials recurring to impurities. With semiconductor doping, a recombination center within the band gap is created. So, the electron is firstly captured by the recombination center and the change in energy and momentum caused by the capture provokes a lattice vibration (phonon). [13] However, with the right doping the emission can be electromagnetic and in the visible range, when such happens the recombination center can be called luminescence center. The doping can also be used on direct bandgap semiconductors in order to tune a desired frequency emission, which can be a specific colour.



(a) GaAs (b) Si (c) Si with a recombination center

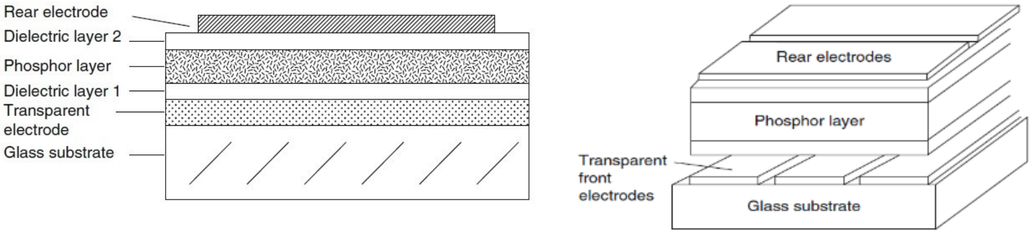
Figure 1.1: Illustrative schematic for diferent tipes of bandgap, (a) GaAs direct bandgap; (b) Si indirect bandgap; (c) Si indirect bandgap with a recombination centre.[13]

In this work it is used ZnS phosphor powder embed on an insulating material. ZnS is a II-VI semiconductor with an energy bandgap of 3.6 eV. [14] There are two structural variants, cubic phase and hexagonal phase. In either phase, each Zn^{2+} ion is coordinated by $4S^{2-}$ ions in a tetrahedral configuration condition, making ZnS a good emitter. ZnS is a relatively stable sulphide at atmospheric conditions, yet it requires moisture protection when subjected to an electric field. [14] Such is due to the field-assisted dissociation of water that form OH^{-} ions and compromise ZnS and its fucntionality as eletroluminescent material. [14]

ZnS is the most common material on research and development of eletroluminescent phosphor applications as TFEL. [8] ZnS is a luminescent material tipicallyused as X-ray source however as described before, semiconductors can be doped with impurities to form luminescent centres and enable controlled electroluminescence. On the EL phenomena the electro-optical characteristics of the EL phosphor are determined by the host (ZnS), however the wavelength of the emission (colour) is determined by the impurity added to the host. On this work it was used copper (Cu), which forms ZnS:Cu phosphor powder that emits a blue greenish colour, it is also typical to see ZnS doped with manganese (Mn) which as an orange color however the ZnS:Cu offers a more intense light for the same power. ZnS is widely used in all types of high-field EL devices, specially for (Alternating Current (AC)) powder EL devices as the one demonstrated on this work.

1.3 Electroluminescent Devices

The devices developed in this work use a insulating/phosphor/insulating layer structure first proposed by Russ and Kennedy in 1967. Such design was a major development when compared with previous developed TFEL devices. [8] This simple EL phosphor device structure is presented in figure 1.2. These devices follow four simple steps for light emission that will be described ahead. [8, 15]



(a) (b)

Figure 1.2: (a) Thin film double-insulating-layer TFEL typical device structure showing sequence of layers; (b) Typical TFEL display with rows and columns.[13]

The display structures rely on important processes that occur within the phosphor layer and at the phosphor interfaces. [15] This phosphor layer must satisfy some criteria to enable efficient light emission, it must contain impurities with localized quantum states; it must be an electrical insulator; it must exhibit an avalanche-type breakdown process once a critical electric field is reached (on the order of 1×10^8 V/m) and the electrons that generate light must be able to fall into a localized ground state to cause light emission even in the presence of a high electric field in the phosphor layer. [15]

The electric field (E) is related with the electrode distance (dielectric width (d)) and with the voltage applied (V). However the electric field is directly related with the charge in the electrodes (Q) and inversely related with the electrode area (A) and to vacuum permittivity (ε_0). The equation 1.1 translates this relationship. From this it is assumable a relationship between the electrode conductivity and the electric field.

$$E = \frac{V}{d} \iff E = \frac{\frac{Qd}{\varepsilon_0 A}}{d} \iff E = \frac{Q}{\varepsilon_0 A} \tag{1.1}$$

The light emission process starts with a voltage application across the TFEL device electrodes, causing the phosphor layer to sustain a high electric field. [8] The electric field will allow trapped electrons in the interface between phosphor and insulating layer, to tunnel into the CB of the phosphor layer. Once traveling on the CB, electrons possess kinetic energy (they become “hot”) and may impact-excite impurity centers (luminescence centers) causing their ground state electrons to become excited. When these excited electrons return to the ground state, light is emitted. [15]

Conduction band electrons may also excite other valence band electrons into the conduction band, by a avalanche process. [15] These further excited electrons may excite luminous centers, causing more light emission. Eventually electrons that are travelling from one interface layer may arrive to the opposite interface layer where they are trapped until the electric field is reversed (AC power supply) and all the process repeats it self. So, on these EL devices light emission is pulsed and an AC voltage is necessary to sustain the device operation. This voltage usually consists in a series of peak voltage pulses, with alternating polarity. [15]

1.4 Electroluminescent transparent and stretchable devices

To build stretchable EL devices a structure similar to the structures shown on section 1.3 with stretchable layers should be used. For the emission layer the phosphor powders are embedded on a silicone rubber material.

A more significant challenge is transparency, given that usually these phosphor powders are not transparent, as the case of the powder used on this work (ZnS:Cu phosphor powder) that has a white colour. Despite the difficulties for fabricating a stretchable semi-transparent emissive EL layer, a bigger difficulty is to obtain transparent and stretchable electrodes.

1.4.0.1 Stretchable and transparent electrodes

Stretchable conductors are an important component on deformable EL devices. [16] This kind of stretchable conductors have been fabricated via two main routes: strain engineering and nanocomposites. [17, 18] In the first approach, nanostretchable inorganic materials, such as metals, are patterned into wavy lines that can be extended when an underneath elastomer substrate is stretched. [17, 19] It is also common to deposit a thin layer of conducting materials such as metals, carbon nanotubes, or graphene on a pre-strained substrate, that leads to the formation of periodic buckles upon the release of strain, allowing materials to accommodate further cycles of stretching up to the initial pre-strained value. [20, 21]

The second major route toward stretchable conductors is embedding a conductive filler in a insulating elastomeric matrix to form a nanocomposite. [20, 22] For applications as a filler, one-dimentional materials such as Carbon Nanotubes (CNTs) and Silver Nanowires (AgNWs) are chosen given their high aspect ratios. [20, 22, 23] It is also common to use metal nanoparticles or flakes as a filler under specific conditions due to their ability to self-organize upon stretching. [20] Despite this big variety of materials to choose from, the percolation dependent conductivity is highly strain-sensitive and remains hurdle for device miniaturization and cycling stability. [20]

Hydrogel ionic conductors are also a popular alternative when compared to stretchable electronic conducting structures, which usually show difficulties in circumventing their low stretchability, mechanical stability and transmittance. These hydrogels are easily formed with a solid polymer host (like polyacrylamide) and yield extraordinary mechanical properties (stretchability higher than 400%) and transparency. [16, 24]

Stretchable ionic conductive electrodes are conductive enough for generating the required electric field required for a functional EL device. However, all these hydrogel electrodes require an ionic conductor, as $LiClO_4$ (like the work of Jiangxin Wang team) or LiCl (in the work of Larson et al.) which are expensive materials. [16, 25] Moreover, the high toxicity of these materials require large laboratory safety measurements, making mass production more expensive. Hydrogels produced by all solution-based methods are difficult to pattern which hinder the work to obtain complex designs, as passive or active matrixes. Also, these patterning difficulties will cause complications for miniaturisation or mass production.

To achieve a highly stretchable conductive material that is readily solution-processable and patternable, an intrinsically stretchable conductor is desirable. [17] With this in mind, conductive polymers become good candidates given the combination of good intrisically electrical and mechanical properties that can only be achieved by this kind of polymers. Also, its solution processability brings advantages for mass production and patterning. However, the drawback of these materials are the difficulties to achieve high conductivity and stretchability at the same time. [17, 26, 27]

(Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)) has the highest reported conductivity among solution processed polymers, but it has a fracture strain as low as 5%. [17, 26] PEDOT:PSS conductivities can vary on the form and concentratons the material, on this work PEDOT:PSS 1.3wt% water dispertion was used which show a conductivity of 1 S/cm and also a PEDOT:PSS sceenprintable ink wic show a conductivity of $50\,\Omega/\square$ to $150\,\Omega/\square$. Efforts have been made to enhance the stretchability of PEDOT:PSS by incorporating plasticizers such as Zonyl or Triton. [17, 26, 27] However, an enhanced stretchability often results in lower conductivities, which usually decreases with strain. [20] Yue Wang et al. reported in 2017 at Science Advances Journal a method for obtaining highly stretchable and conductive PEDOT:PSS films with high cycling stability. This was achieved by simply incorporating ionic additives that assisted stretchability and electrical conductivity, to which they called Stretchability and Electrical Conductivity (STEC) enhancers. On the work of Yue Wang and his team results showed conductivities higher than 4100 S/cm under 100% strain. [17]

High stretchability requires polymer films with both hard and soft domains, typically seen with hydrogenated Styrene Ethylene Butylene Styrenes (SEBS) block copolymers, or polyurethane elastomers.[17, 28] In the case of PEDOT:PSS both PEDOT and PSS are semi crystalline polymers, with observable glass transition temperatures. [17, 29] To achieve a good conductivity between PEDOT-rich domains it is required a weakened electrostatic interaction between PEDOT and PSS. Which allows PEDOT to partially aggregate and form a “hard” conductive network inside the soft PSS matrix. As the figure 1.3 illustrates this can be done by the STEC enhancers. [17]

STEC enhancers are ionic compounds and ionic liquids that have sulfonate or sulfonimide anions, which are effective dopants for conducting polymers such as PEDOT:PSS. [17, 30] STEC enhancers soften the PSS domains promoting better connectivity and higher crystallinity in PEDOT regions while further enhancing electrical conductivity through hoping. These compounds are commercially available and effectively reduce the PEDOT:PSS Young's moduli by 50 times preserving and/or increasing conductivity. [17] Both characteristics are achieved when the STEC fills two specific characteristics: (i) good solubility in water and in the PEDOT:PSS matrix (ii) highly acidic anions that can act as effective dopants for PEDOT. [17]

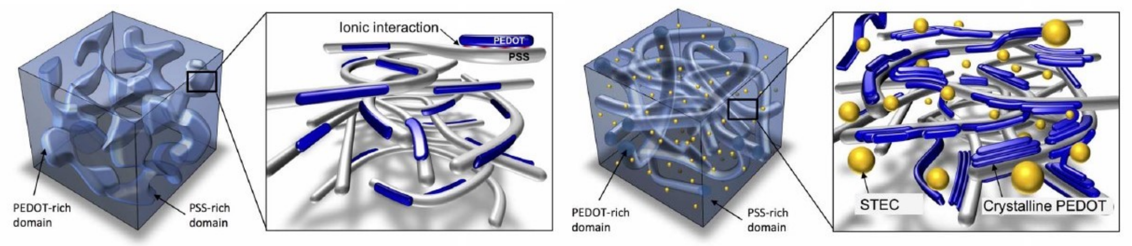


Figure 1.3: Illustrative schematic for the STEC ionic interaction with PEDOT and PSS chains.[17].

In the reported paper of Yue Wang et al. a solution with PEDOT:PSS 1.3 wt% in water and STEC enhancer is deposited via spin coating and/or Ink jet printing on a stretchable substrate of Polydimethylsiloxane (PDMS). This substrate is previous treated via UV/O_3 treatment or O_2 plasma etching. For some of these treatments like O_2 plasma treatment, the effects are temporary which make the electrode easily pealed off after periods like 20 days. [31, 32] Even for less specialized and less expensive treatments like the corona treatment (high frequency discharge that increases the adhesion of a plastic surface) the same temporary effect is visible. [33] More than that, these methods are expensive and not available to nonprofessional users. [32] Being the aim of this work to develop a low cost easy reproducible by non experts method for producing stretchable EL devices, alternatives were explored.

The work of Michael Wessely and his team at the Université Paris-Saclay suggests the deposition of a binder layer between the PEDOT:PSS thin film and the hydrophobic surface. The suggested material is *AQUAPLAST-DIY* a inexpensive, transparent ink commercially available and commonly used for fabric printing. [32] Since *AQUAPLAST-DIY* transparent binder contains a lower percentage of water than the PEDOT:PSS ink, the use of it as intermediate layer permits the adhesion of the PEDOT:PSS to the substrate. Also given the its high viscosity it hinders the formation of drops commonly caused by the hydrophobic PDMS, facilitating the deposition of uniform thin films.

On this work it will be produced a stretchable EL device using silicon rubber materials, studies will be conduct to find the best production method that fulfil the objectives. Both Hydrogels and PEDOT:PSS enhanced electrodes will be tested in order to find the best approach to build an EL stretchable passive matrix.

Chapter 2

Methodology

This chapter will be divided in three main parts. First it will be described the methods used to obtain the Hydrogel and PEDOT:PSS enhanced electrodes. After it will be presented how final EL devices were built and for last it will the characterizations carried on electrodes and devices.

2.1 Electrode Production

2.1.1 Hydrogels ionic conductors

To obtain the hydrogel it was reproduced the method achieved by Larson et al. [25] This procedure is presented on section I.1 of annex I. Various attempts to obtain desired characteristics were tried, the amount of LiCl was varied between 8M to 2M and it was also tried the use commercially available sodium chloride (NaCl). Given the lack of desired properties by following the procedure reported, the reaction time was varied to obtain satisfying results, and also to study the influence of its variation on the cured electrode mechanical behaviour.

2.1.2 Conductive polymer electrodes

To produce these electrodes it was bought PEDOT:PSS 1.3 wt% dispersed in water (483095; Sigma Aldrich) and PEDOT:PSS ink 5 wt% (768650; Sigma Aldrich). The STEC enhancer Bis(trifluoromethane)sulfonimide lithium salt was aquired from Sigma Aldrich (544094) and for the substrate it was bought Ecoflex 00-30 from Smooth-On Inc. For last it was obtained a commercially available binder AQUAPLAST-DIY for promoting adhesion to the substrate.

To obtain the stretchable substrate, a glass is pre-cleaned with acetone and sprayed with a mold releasing spray (Ease Release from Smooth-On). Next the Ecoflex is prepared by mixing the two available parts of the material (part A and B) in 1:1 ratio. The final solution is taken to low vacuum (800 bar) for 1 minute and then casted using a manual thin film applicator. The thin films must have around 100 to 150 µm in order to achieve the searched mechanical properties. Substrates were then cured in an oven at 100 °C for 10 minutes.

Different approaches to PEDOT:PSS electrodes were tried by mixing PEDOT:PSS 1.3 wt% in water or PEDOT:PSS 5 wt% ink with AQUAPLAST-DIY and STEC on different ratios. The solutions were mixed for 10 minutes and casted with different thicknesses, which varied between 3 to 8 µm using the film applicator. The thin films were cured in oven at 100°C for 10 minutes. The use of AQUAPLAS-DIY as intermediate layer as it is shown on the schematic of figure I.1 at annex I was tested first by casting and later by screen printing (always using a 120T mesh).

The final method achieved for the electrode production was the following. A solution of PEDOT:PSS 5 wt% screen printable ink and STEC enhancer was mixed for 15 minutes. In order to find the best ratio, various samples were prepared and characterised culminating on a solution with 10% to 15% STEC and 90% PEDOT:PSS. This enhanced PEDOT:PSS ink was screen printed on a ECOFLEX 00-30 substrate with a intermediate layer of AQUAPLAST-DIY, also screen printed to ensure good adheasion of the PEDOT:PSS to the substrate. All layers were cured before a new layer was screen printed. Curing was done a blow dryer at a hand distance from the sample, until the layer appeared dried. To produce an electrode at least 3 layers must be screen printed, cured and given the time to cool down between depositions.

2.2 Devices and passive matrix production

The device structure is shown on figure I.2 at section I.3 of annex I. To build this device, different layers were screen printed with a 120T mesh and dried with a blow drier, as described on section 2.1.2 for the electrode production. The emissive layer is then screen printed directly on top of the cured electrode.

For the emissive layer, phosphor powders of ZnS:Cu (EL phosphor D512B from KPT Shanghai Dongzhou Industrial CO.,LTD.) were embed on different weight ratios of 10 to 70 % on Ecoflex 00-30 (taking in consideration the Ecoflex 00-30 method of preparation). The phosphor powders were mixed first with part B and only then the part A was added. The solution is taken to low vacuum (30 seconds) to reduce the trapped air bubbles. After removed from vacuum the solution must be rapidly screen printed on top of the electrode, otherwise it gets too viscous to screen print using a high resolution mesh. After the deposition, the thin films must be dried by the blow drier and given the time for cool down. At least two layers must be screen printed to obtain uniform light emission from the EL device. On top of the emissive layer, a layer of Ecoflex 00-30 was screen printed with a larger area than the top electrode to avoid short circuits. Before the deposition of the top electrode, a AQUAPLAST-DIY layer must be screen printed to guarantee the electrode adhesion. The enhanced PEDOT:PSS ink is then screen printed on top the AQUAPLAST-DIY. A detailed procedure to obtain these devices is shown on section I.2 of annex I.The matrix was produced using the same method, however the design used on the mesh were different.

The designs for the matrix are shown on figure I.4a at section I.1 of annex I, while the designs for the EL devices are shown on figure I.4b. The patterns were drawn using Adobe Illustrator and then cut on vinyl using a vinyl cutter (USCutter). The vinyl cut patterns were stuck to the mesh as suggested by figure I.3a and I.3b at section I.1 of annex I. The material was deposited on top of the cut pattern and it was followed a common screen-printed technique. It is advised the use of an already patterned mesh to reduce the production time, improve alignment and permit less damaged samples.

2.3 Electrodes and devices characterization

Electrodes were characterized for thickness, transmittance and resistance behaviour upon strain. While devices, were characterized for transmittance and relative luminance with and without strain as illustrated on schematic of figure I.7 in annex I.

To study different characteristics, various samples were produced. Electrodes with different number of layers were produced having two, three and five screen printed layers. For each thickness three different PEDOT:PSS enhanced electrode samples were produced, with STEC enhancer ratios of 0, 10, 15 and 20%. The majority of the samples with 20% of STEC enhancer showed poor mechanical properties so they were disregarded.

For the EL devices characterization, samples with the same area but with different electrodes were characterized in transmittance and luminance with and without strain. The electrodes of these EL devices all had three screen printed layers but different STEC enhancer ratios (0, 10 and 15% of STEC). The emissive layers had different number overlapped layers and different phosphor powder concentrations .

2.3.1 Electrical characterization

The resistance behaviour upon strain was observed using two separated pieces of equipment, one for measuring resistance and another to stretch the sample, as suggested by the figure I.6 at section I.3 of annex I. The stretching equipment by ZWICK/Roell was attached to the sample by compressing the clamps to it. To avoid cutting the sample and bad resistance readings, the clamps were protected with isolation tape. The sample size (3 cm) was input on the equipment software in order to calculate the strain applied. The attached cables to the electrode on figure I.6, were connected to a copper tape which was attached to the electrode in order to avoid piercing the sample and to promote a better contact. A Squirrel data logger (Grant 2020 Series) to measure the resistance upon strain. Samples were stretched to a maximum of 80% strain, however when achieved the data logger measurement capacity of 300 kΩ the tests were stopped.

2.3.2 Transmittance and thickness characterization

To observe transmittance a spectrometer Lambda 950 from Perkin Elmer was used. The measurements were taken in the visible range from 300 nm to 800 nm. The same technique was used to observe transmittance of EL devices. The electrodes thickness was measured using a profilometer XP-200 by AMBIOS Technology.

2.3.3 Luminance characterization

For the luminance measurements it was used a luminance meter LS-100 from MINOLTA in a dark room. The samples were placed perpendicularly to the equipment as figure I.8a at section I.3 of annex I suggests and powered by a EL inverter with two homemade connectors made of clothespins as it can be seen on figure I.8b. For the luminance characterization upon strain it was used a stretching equipment made in the laboratory, given the need of a darker room to conduct the tests. The strain was always applied at a constant velocity by manual moving a joystick, the strain calculations were previously calculated. The set-up is shown on figure I.8c.

CHAPTER 3

RESULTS AND DISCUSSIONS

In this third chapter all experimental results will be presented, the chapter will be divided in five distinct parts. First it will be discussed the results obtained with hydrogels and the reasons for looking to different alternatives. On the second part it will be presented the results of different attempts to obtain a low cost method to produce stretchable and transparent EL devices with PEDOT:PSS enhanced electrodes. For the third part it will be observed and discussed the characterizations carried on the enhanced electrodes. On the fourth part of this chapter it will be presented the EL devices properties such as transmittance and luminance with and without strain. For last it will be presented the passive matrix display produced using the methods studied.

3.1 Ionic Hydrogels

Polyacrylamide hydrogels containing ion salts are popular to use as stretchable and transparent electrodes. However they easily dry out loosing their desired mechanical properties. [34, 35] One of the ways to achieve desired mechanical properties of high stretchability is to use highly hydratable salts to retain water in the polyacrylamide matrix avoiding the loss of water and maintaining the mechanical properties. [34, 36] The method presented on section 2.1.1 was demonstrated by Larson et al. and used to obtain these hydrogels. [25] The results obtained by Larson's team show EL devices with extraordinary mechanical properties as stretchability up to >480% strain, for luminescences of 43.2 mlm/W. These devices were operated at 700 Hz under an electric field of 25 kV/cm, using a voltage source of 2.5 kV.

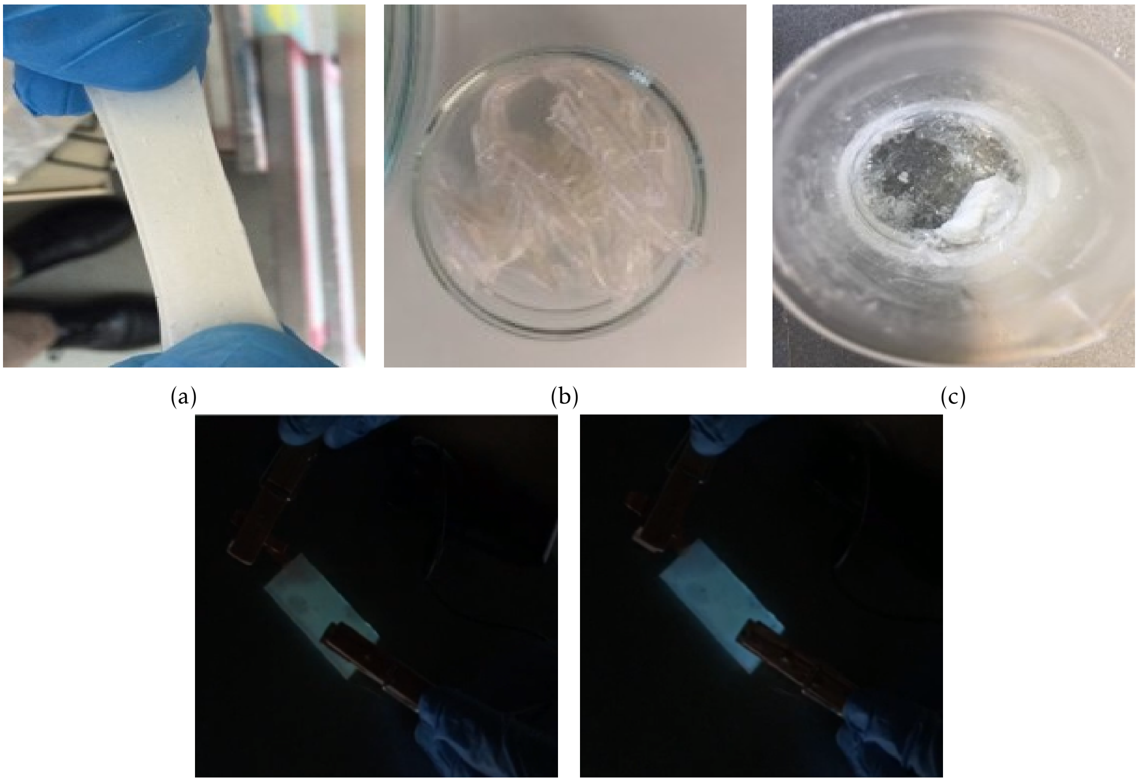
Attempts to obtain the same results failed. The inability to have the solution at a stable temperature of 60 °C, given the lack of a proper hot plate may have caused the reaction of copolymerization to be altered which provoqued the drying out off the gel sooner than expected. It is thought that the tempeature variations caused by the method used to stabilize the temperature was enough to variate the PAM matrix polymerization time, since the reaction is senstive to temperature variations. [37] It is also thought that the quantity of the hydrogel solution produced (10 to 20 ml), affects the required time for polymerization at given temperatures. Such is thought since the quantity of LiCl and acrylamide in these solutions significantly affect the amount of water in the gel, which may cause deviations of the ideal temperature for the polymerization and more importantly deviations of the reaction time. Various tests with shorter reaction times and different LiCl salt concentrations were tried, however these attempts failed to fulfil the objectives and when these were achieved could not be reproduced.

On the few times that was possible to produce a viable solution, the uncured gel was casted and cured via UV. The cured samples looked humid, sticky, fragile and they did not properly adhere to ecoflex 00-30. The best samples looked like figure 3.1a. To avoid these properties, longer periods of curing were tried however samples curled up as figures 3.1b show. The samples produced with longer curing times were less sticky but extremely fragile, breaking when pulling from the glass substrate where they were casted. When casted on top o ecoflex 00-30 the adhesion was still poor which may be due to the lack of surface treatment and/or due to the curling. The curling may have happened not just due to the curing time, but also to the film thickness (20 to 150 µm) which was significantly thinner than the reported samples (1 mm). This is thought since some of the samples curled up even with only 5 more seconds than the original curing time, and also because the most thin samples curled on the curing time. However, the objective of the thesis was to obtain devices thinner than 1 mm, so a manual thin film applicator was preferable than 1 mm dispersion mold used on the work by Larson et al. This decision could be a contributor factor for the poor properties obtained.

Samples that were not compromised were used to build simple devices as it can be seen on figure 3.1a. These were extremely fragile and broke under little strain. Moreover, the adhesion of the cured hydrogel to the Ecoflex 00-30 phosphor layer (emissive layer) was poor, compromising the device cohesion mainly when flexed or stretched. It was also tried using another salt to verify the influence on the hydrogel properties. It was used NaCl to meet the objective of producing low cost devices. The solution crystallized with less than half of the reaction time, the result can be seen on figure 3.1c.

Despite all the mechanical properties issues the electrodes were conductive even for lower concentration of LiCl, demonstrating conductivity even with 2M of LiCl. However, it must be taken in consideration that the LiCL functionality is not just to enable conductivity but also to retain water on the PAM matrix permitting higher stretchability. Meaning that a lower concentration of LiCl compromises mechanical properties and also the electrodes lifetime. [36] With the conductive electrodes an EL device was build as it can be seen with no light emission on figure 3.1d and emitting light on figure 3.1e. The light is not intense, and the device broke after the stretch seen on figure 3.1a.

Lithium Chloride is extremely expensive, concentrations of 8M for 10 ml takes 3.39 g of LiCl which makes the final EL device extremely expensive. Being one of the objectives producing a low-cost method to obtain stretchable and transparent EL devices, using LiCl as ionic conductor is not the best option. Moreover, LiCl is also toxic when in contact with skin, which is a problem since the project aims for biocompatibility. Using encapsulation to have biocompatibility was thought, however for this hydrogel it was difficult since the results showed a lack of adhesion to the Ecoflex 00-30, making it difficult to encapsulate the devices. The high toxicity of the materials require the use of safety equipment which turns the process more difficult and costlier.



(a) (b) (c)

(d) (e)

Figure 3.1: (a) Stretchable device built with Acrylamide electrodes; (b) Curly hydrogel electrodes; (c) Solidified hydrogel, using NaCl as conducting ionic salt; (d) EL device with hydrogel electrodes, not emitting; (e) EL device with hydrogel electrodes, emitting.

High viscosity and toxicity of the uncured gel makes it very difficult to pattern, which makes the hydrogel a not suitable approach to produce applications on displays. Also the high viscosity of the solution limits the method for future applications that require miniaturization. The lack of a simple method for the electrode production adds difficulty to adapt to roll to roll methods typical from industry production. So, taken all these considerations and the poor results achieved with the given conditions, the method was abandoned and another one was carried.

3.2 PEDOT:PSS enhanced electrodes

To obtain enhanced PEDOT:PSS electrodes as described by Wang et al. at first it was added Bis(trifluoromethane)sulfonimide lithium salt to a solution of PEDOT:PSS 1.3% in water. [17] Various concentrations of the STEC enhancer were experimented, however at the beginning it was used 40% since this was the minimum reported value to obtain significant results. [17] The lack of spin coater and the objective of using simple production methods made thin film manual casting the preferable alternative method to produce uniform thin films.

The use of an enhanced PEDOT:PSS watery solution makes it difficult to cast thin films in non-treated silicon rubber substrates such as Ecoflex 00-30 given the hidrophoicity characteristic from the materials. The absence of surface treatment equipment as

UV/O_3 or O_2 plasma, to reduce the hydrophobicity of the surface made it impossible to obtain consistent and uniform films that adhere to the ecoflex substrates. This condition compromised the PEDOT:PSS enhanced thin film formation (see figure 3.2). The thin films were let to dry and then cured at 130°C as suggested, however their final form always resemble the films shown on figure 3.2. Since the substrate was not treated for better wettability there is no adhesion to the surface and when compared to the method reported by Wang et al., this difference will hinder the polymer curing upon heat exposition, mainly because these thin films had microns of thickness instead of nanometres as some of reported films. [17]

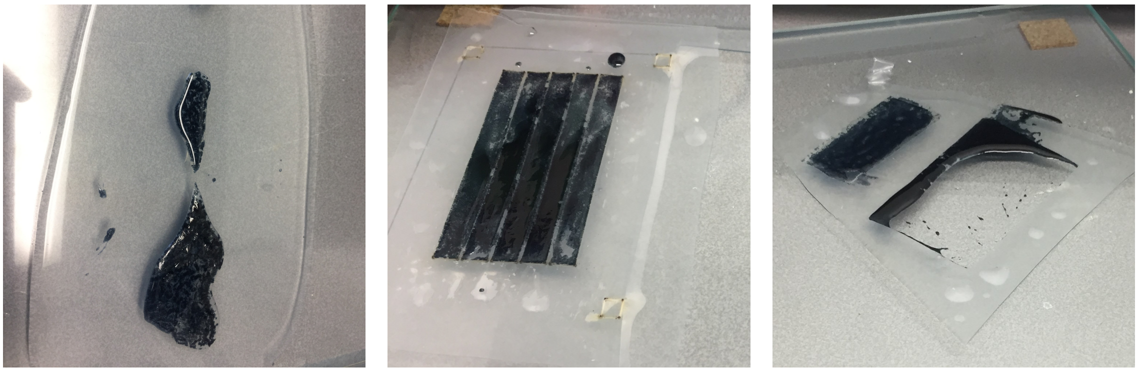
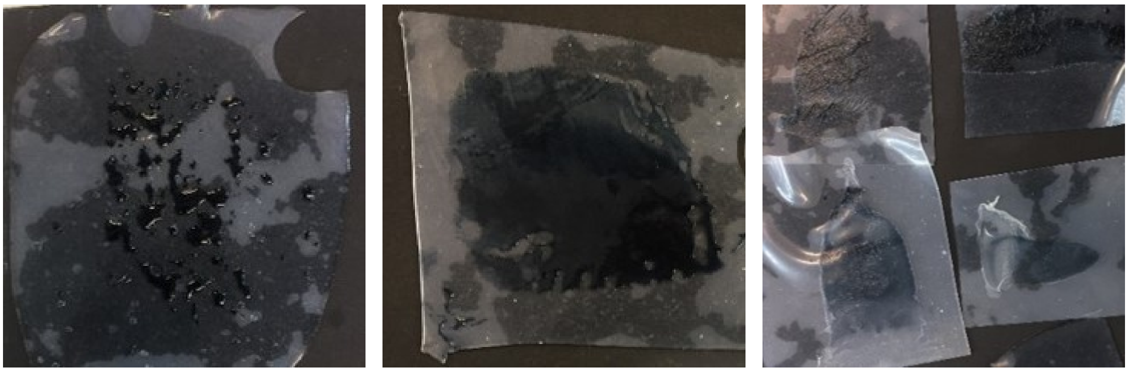

(a) (b) (c)

Figure 3.2: (a) Enhanced PEDOT:PSS 1.3% in water solution dropcasted on top of Ecoflex 00-30; (b) Electrode pattern laser cut on Ecoflex 00-30 as mold for electrode production on top of Ecoflex 00-30 substrate; (c) Simpler ecoflex 00-30 laser cut molds for bulkier electrodes production.

3.2.1 Enhanced PEDOT:PSS and AQUAPLAST-DIY

Solutions to enhance the film adhesion without the use of UV/O_3 or O_2 plasma treatment were needed. The reported use of AQUAPLAST-DIY as a binder to obtain better adhesion to silicon ruber substrates as ecoflex 00-30, had satisfactory results for this kind of applications. [32] The water presence in the AQUAPLAST makes it soluble on the PEDOT:PSS solution. So, it was thought that the binder could add viscosity and promote adhesion to the substrate, permitting more consistent uniform thin films after curing. Different solutions of enhanced PEDOT:PSS and AQUAPLAST were casted and the results were observed. These results are shown on table II.1 of annex II.

The attempts carried shown that adhesion is only significantly improved if PEDOT:PSS is deposited on top of an intermediate layer of AQUAPLAST-DIY. This better adhesion achieved with the aquaplast intermediate layer as shown on improved mechanical properties such as stretchability. As it can be seen on figure 3.3a the casting of the PEDOT:PSS 1.3 wt% enhanced solution with a percentage of AQUAPLAST directly on silicone, revealed to not be enough to improove adheasion to the susbtrate, however the samples produced with an aquapalst intermediate layer proved to adhere to the substrate building electrodes with better properties.



(a) (b) (c)

Figure 3.3: PEDOT:PSS 1.3 wt% in water enhanced solution (PEDOT:PSS:STEC:AQUAPLAST) casted with different conditions.(a) 40/40/20% casted on ecoflex; (b) 35/45/20% casted on ecoflex; (c) 35/45/20 casted on AQUAPLAST.

The difference in between figure 3.3b and 3.3c as well as other results on table II.1 of annex II, show clear evidence that a binder intermediate layer results in better mechanical properties of the electrodes. On the other hand, by observing figure 3.3b, 3.3c and figure III.1b from annex III, it is perceptible how the films appear humid despite already being cured and dried for a couple of days. A closer look on table II.1 show that the humidity is present even on films casted with the AQUAPLAST intermediate layer and it will continue to be observable but not so significantly on other approaches later discussed on section 3.2.2. Humidity presence on the thin films is relevant because it will made it difficult to other top layers to adhere, causing difficulties on the device production.

When the thin films leave the oven, they appear cured. However, with exposure to atmosphere they tend to get wet, accumulating small water droplets on the surface. This condition changes the adhesion of upper layers and makes the electrodes easily peeled off upon slight contact. It is thought that the water presence is due to the STEC enhancer since it is a lithium chloride sulphide and it absorbs water. The layer thickness of some microns has enough salt to attract water and trap it on its surface. This water adsorption makes the surface of the films humid and in some cases after prolonged exposure to the atmosphere it is even possible to see the water droplets on top of the film by naked eye.

Electrodes on figure 3.3c show a lack of uniformity on the deposition, which happened given the amount of PEDOT:PSS not being enough for the extension of the film causing the fade up to appear. The same phenomena is visible on the devices of figure 3.4, but in this case an excess colloidal particles is accumulated on the end. This problem is also responsible for the last visible line at the end top part of some electrodes like sample 5 and 9 from table II.1 of annex II.

The lack of uniformity visible on the electrodes of figure 3.4 (casted with ±4 µm) is due to the holes caused by either small defects on surface, or accumulated material on the film applicator. As mentioned before, due to casting the excess stay in the end. This characteristic is more accentuated for watery films like the ones casted with PEDOT:PSS 1.3% in water, which is the case of devices on figure 3.4.

The working device on figure 3.4 shows only emission on the corner. It is thought that this is due to the larger electrode thickness on that corner, since thicker films have lower resistance. So, it is plausible to assume that only on that corner the electrodes were conductive enough to generate the strong electrical field required for the electroluminescence phenomenon.

In an attempt to solve the humidity problem, the electrodes were cooled under low vacuum and rapidly isolated with a top layer (usually the emissive layer). This could minimize the time exposed to the atmosphere and therefore the thin film humidity adsorption. The problem with such a rudimentary solution is that on a top layer deposition that took more time , the deposited layer would easily peel off given the humidity presence (figure 3.5f). This condition made it difficult to encapsulate the device and even if the device was encapsulated, the presence of a connection to hard electronics to apply power (like copper tape or copper wires), will cause the encapsulation layer and the electrode to peel off at the slightest movement. The adhesion problems seen on figure 3.5f, are a non-desirable condition when looking for properties like stretchability and/or flexibility.

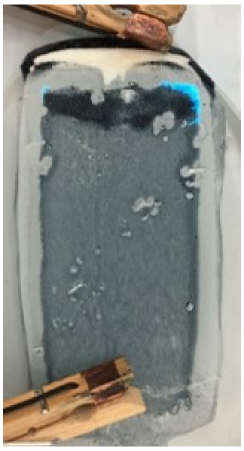
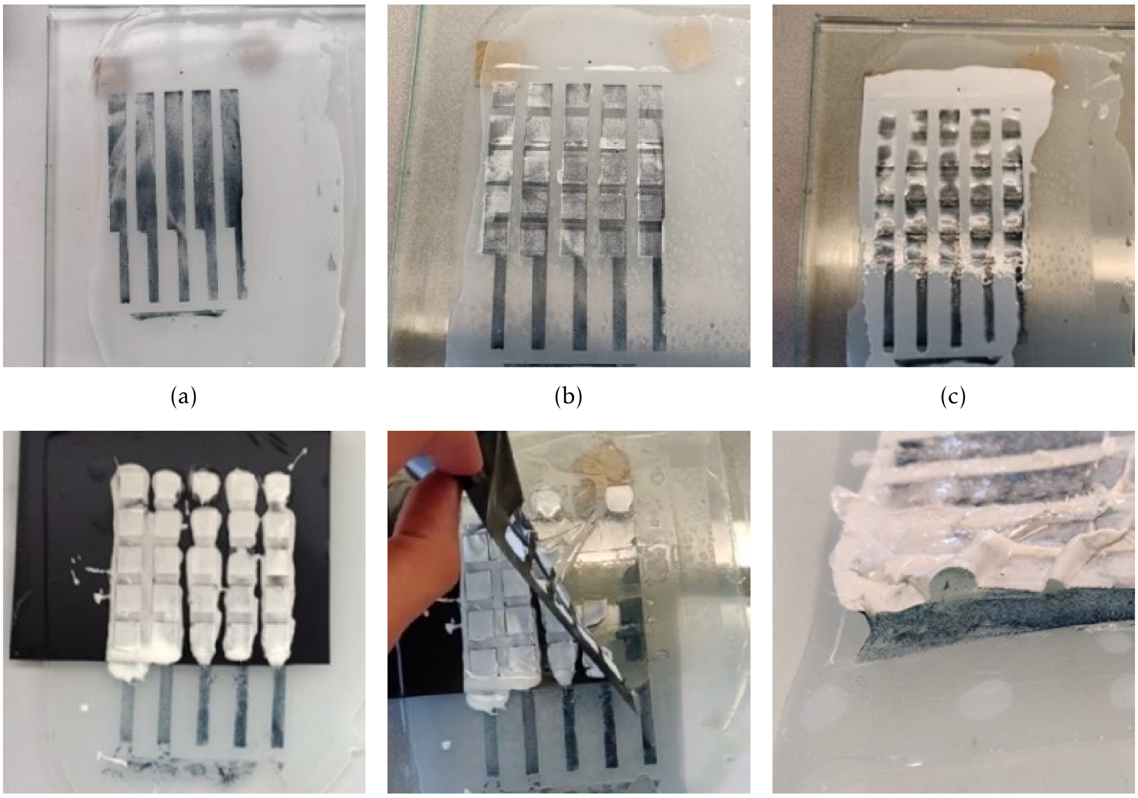


Figure 3.4: Working device (only on the corner) produced by manual casting and powered by EL inverter of 9V;

In figure 3.5a it is visible the lack of uniformity on the electrodes. Thisis due to the colloidal PEDOT:PSS 1.3 wt% watery solution not being viscous enough to form a uniform cast by the manual film applicator. Due to the solution being too much or too less for the pattern wich can cause excess solution on the end of the deposition. Or due to a phenomenon common on casting methods, where dispersed particles tend to go towards the center or to accumulate on the beginning or end of the casting given the surface tensions that agglomerate particles.

For last, the thin films low adhesion and lack of consistency compromised the matrix patternization using the manual film applicator. As it can be seen by figure 3.5d and 3.5e, during the emissive layer deposition the excess of the emissive layer solution cures on top of the mask. So, when removing the mask, the electrodes stick to the emissive layer (see figure 3.5d) and peel off. In order to avoid this problem, the emissive layer was shaped on a uniform square. However, as figure 3.5f shows the layer did not adhere to the electrodes and more importantly, on the emissive layer deposition, the lines where the electrodes were previously deposited had less thickness (see figure 3.5f) which could cause short circuiting with the top electrode.

It was tried to screen print the pixels but as it can be seen on figure 3.3b, when the aquaplast is deposited (after the screen printing of the emissive layer) the electrodes absorb part of the aquaplast water compromising the device fabrication. For solving this it was casted a ecoflex layer, however the same problem of adhesion observed in figure 3.5f happened with frequency. More importantly the presence of an intermediary ecoflex layer between the electrodes and the phosphor layer could dramatically reduce the electric field. The problems experienced with the matrix were experienced in some degree of similarity with simpler devices which made it difficult to pursue this method. Moreover, since the matrix is the ultimate objective of this thesis a better solution for device fabrication must be found.



(a) (b) (c)

(d) (e) (f)

Figure 3.5: (a) Deposited and pattern PEDOT:PSS/STEC electrodes. (b) Deposited emissive layer by screen printing. (c) Binding layer deposition to facilitate top electrode adhesion and to stabilize thickness. (d) Vinyl mask with pixels casted. (e) Mask Matrix removal, causing electrodes peeling off; (f) Low adhesion of the emissive layer to bottom electrodes and substrate.

3.2.2 PEDOT:PSS Screen printing ink electrodes

The results until this point did not fulfil the objectives. In order to get better results, it was produced PEDOT:PSS enhanced solution with different concentrations of aquaplast binder and it was also tried to use a different kind of PEDOT:PSS. It was used PEDOT:PSS 5wt% screen printing ink, which has an increased concentration of PEDOT:PSS and other components as diethylne glycol and ethanol, that permit better PEDOT:PSS solubility in the ink and also bind the overall solution, enabling better, uniform consistent films.

Similar to the process with the PEDOT:PSS 1.3 wt%, different concentrations of STEC and AQUAPLAST were tried. The results for these experiments are summed on table II.1 of annex II. The use of PEDOT:PSS ink enabled more uniform films solving the fade out problem seen before. The ink use also permitted to obtain better overall mechanical properties as stretchability (films showed less cracks after stretching) and better adhesion (given the reduced presence of moisture). Combined with better mechanical properties it was achieved a better conductivity, the thin film electrodes with these properties are shown in figure 3.6.

The electrode in figure 3.6c is not conductive since it is a mixture between a dielectric material (AQUAPLAST) and PEDOT:PSS which is a poor conductive. When compared to the films with STEC presence, it is visible a consistency difference and a more opaque dark blue tone. This shows that the STEC enhancer does not just change the electrical properties of PEDOT:PSS but also the mechanical and optical properties. [17] Despite the better electrode properties, they continued to be easily peeled off by a harder touch, making it difficult to connect with hard electronics for power supply (see figure III.3a and III.3b of annex III).

The problem with humidity in the films observed on section 3.2.1 was partially solved with the use of the PEDOT:PSS 5 wt% ink. It was still visible some humidity in the films, however this did not caused significant problems in adhesion. Moreover, the use of the PEDOT:PSS ink significantly diminished the transmittance, a commitment that was considered relevant given the improvements on the mechanical properties and conductivity of the electrodes. It was observable that the increase concentration of STEC and/or AQUAPLAST reduced the viscosity of the enhanced solution. Condition that at first was considered positive, since enabled the casting of thinner films with transmittance improvements. However, latter this would be revealed a problem.

Given the difficulties to pattern devices using casting methods and since it was been used a screen printable ink, it was tried to use screen printing as patterning method. As section 3.2.3 shows the results were promising.

(a) (b) (c)

Figure 3.6: PEDOT:PSS enhanced electrodes (a) and (b)obtained with 40% of PEDOT 5 wt%, 20% of STEC and 40% of AQUAPLAST-DIY. On figure 3.6c is shown a casted film of 50% PEDOT:PSS 5wt% and 50% of aquaplast.

3.2.3 Screen printed enhanced PEDOT:PSS electrodes

With so much problems due to the casting method and given the reported properties achieved by Wessely et al. where EL devices electrodes were fabricated by screen printing a PEDOT:PSS 5wt% ink thin film, it was thought to screen print the enhanced PEDOT:PSS:STEC:AQUAPLAST solution to obtain better conductivity, transmittance and stretchability. [32]

Rapidly it was conluded that the use of AQUAPLAST in the enhanced solution was making it too waterly for screen printing. The same was observed for high STEC concentrations (40% STEC and 60% of PEDOT:PSS 5wt%) as it had been reported by Wang et al. for electrodes of PEDOT:PSS 1.3wt% in water. [17] So, studies were carried and it was concluded that electrodes must be produced without AQUAPLAST and with a maximum 20% of STEC on a solution with 80% of PEDOT:PSS 5 wt% ink. Given this, different electrodes with 5%, 10% , 15% and 20% of STEC enhancer were produced to verify which one had the better overall properties: transmittance, stretchability and conductivity. Samples with 20% STEC were easily peeled off and too fragile, so they were disregarded.

The combination of only PEDOT:PSS 5wt% ink and STEC described on this section could certainly alter properties on devices produced by casting methods. However, screen printing offered easier ways to obtain patterns and is highly adjustable to mass production. Given these advantages, it was decided to use the enhanced PEDOT:PSS solution by screen printing rather than casting. Moreover, screen printing opens more doors for different applications and is a low-cost option applicable to mass production.

3.3 Characterization of screen printed enhanced PEDOT:PSS electrodes

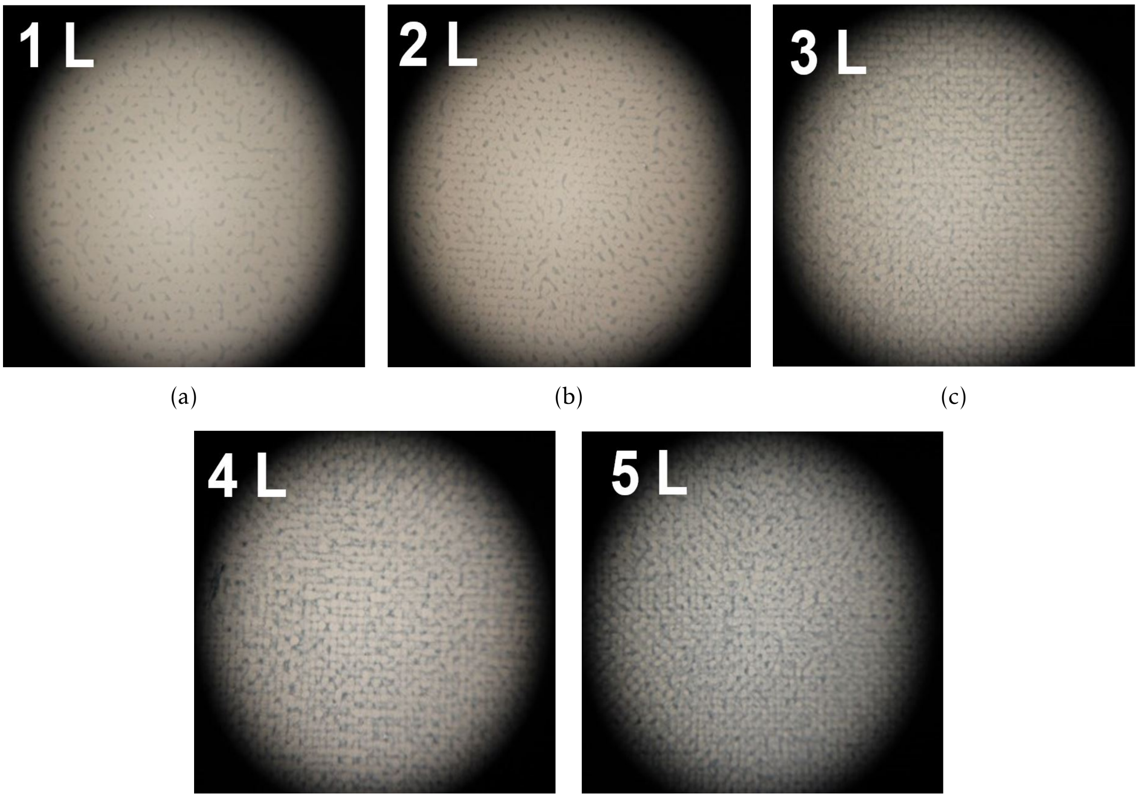
To observe the overall behaviour of the enhanced PEDOT:PSS electrodes, samples were subjected to different characterization processes explained on section 2.3. The results of these characterizations are shown on this section that will be divided in two different subsections. First it will be observed the electrodes aspect under microscope as well as their transmittance and thickness. Secondly it will be discussed the electrodes electrical behaviour under strain and how different STEC concentrations and layer number affects this behaviour.

3.3.1 Microscope observations, thickness measurements and transmittance considerations

Figure 3.7 show micrographs taken with a camera attached to a microscope with 10X amplification lens. This figures do not show scale since the equipment did not revealed it. However the intent of this pictures is just to observe the increasing amount of PEDOT:PSS on the thin film at each screen printed layer.

Figure 3.7a; 3.7b; 3.7c; 3.7d and 3.7e show samples with one, two three, four and five layers, respectively. On figure 3.7a; 3.7b it is possible to see dispersed small droplets of the deposited PEDOT:PSS. Since the conduction on polymers like PEDOT:PSS happens by electron hopping between the PEDOT and PSS chains, it is easily assumed that the electrode is not conductive given the lack of a PEDOT:PSS continue network.

On the other hand on figure 3.7c, 3.7d and 3.7e it is possible to observe a network of PEDOT:PSS caused by the screen printing mesh. If the polymer maintains a network between the two ends of the electrode there are always PEDOT:PSS chains in contact, permitting conduction by hopping on all the electrode.



(a) (b) (c)

(d) (e)

Figure 3.7: Micrographs with 10X magnification of screen printed enhanced PEDOT:PSS electrodes with different number of layers: (a) one layer; (b) two layers; (c) three layers; (d) four layers; (e) five layers.

The presence of the enhanced ink network can be better observed under a microscope. Figure 3.8a shows a sample with two layers of PEDOT:PSS enhanced ink where it is clear the presence of holes on the film caused by the 120T mesh. At the same magnification, figure 3.8d shows a five layers sample, where it is visible a uniform film caused by the overlap of various screen printed layers.

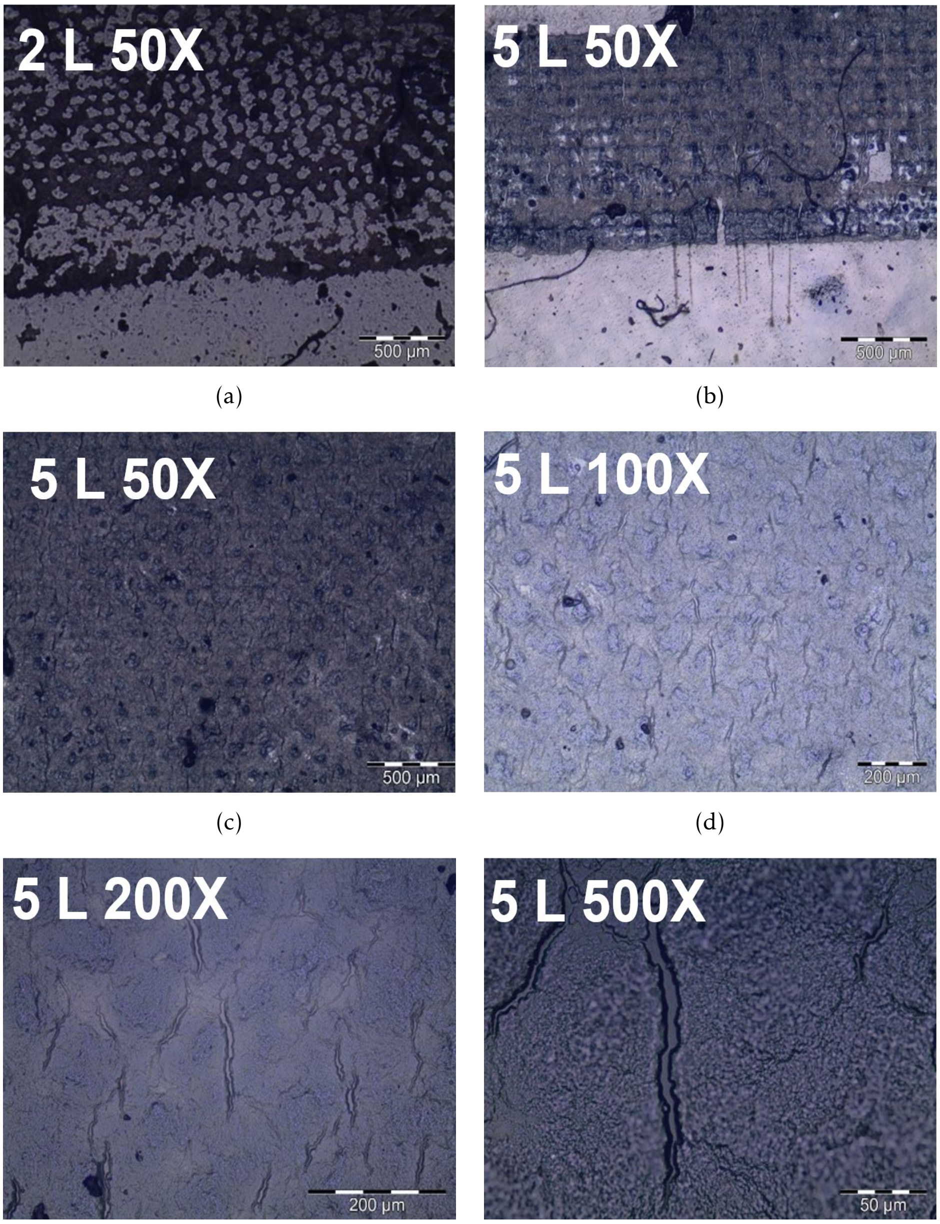
On figure 3.8d where it is showed the same sample under 100X amplification, it is observable the presence of micro cracks, caused by stretching the sample. These cracks can be better seen on figure 3.8e and 3.8f. Despite the number of cracks, electrodes are still conductive. The electrical behaviour upon strain will be discussed on section 3.3.2

The thickness measurements were done with a profilometer as mentioned before. The sample with five screen printed layers was measured but samples with two and three layers were not, since the profilometer could not make proper measurements due to the samples softness. Such could be solved by using a larger tip on the profilometer. However suc was not available and measurements taken on the five layers sample indicated an average thickness of $14 \pm 0.5 \mu m$. The thickness of the film was lower than expected, but it demosntrates the good overall electrode properties. Thicker samples could improve conductivity which is favourable for faster electrode responses when adressing pixels. However, thicker samples significantly loose transmittance, which could agravate wich is already one of the limitations of this work. The thickness is limited by the fabrication method in use, since the thin film thickness will always depend on the mesh thickness and network aperture. [38] To achieve better transmittance, methods as spin coating must be used, as reported by Wang et al. [17]

With five screen printed layers an electrode has a thickness of 13 µm. However, since it was not possible to make other measurements with different number of layers, it is not accurate to assume the thickness of one layer. From figure 3.8b it is possible to observe the lines cut by the profilometer on the interface between PEDOT:PSS film and ecoflex. Such observation indicates that despite the small thickness of the screen printed electrodes, they were harder than the ecoflex, which is an indicator of good mechanical properties and good adhesion to the substrate.

The graph of figure 3.9 shows the electrodes transmittance. The transmittance is presented in relation to the number of screen printed layers instead of thickness and the values were obtained by calculating the average transmittance from the wavelength of 300 nm to 800 nm, the error is represented on the graph. The spectrum of the samples showed a peak on the left side of the spectrum around 400 nm to 520 nm corresponding to the transmittance of the blue tone. From the graph, it is possible to study the influence of STEC concentration on the electrode transmittance. The graph indicates a transmittance decrease from 75% to 50-60% with the increasing number of PEDOT:PSS enhanced layers. This decreasing in transmittance is predictable given the expected increase in the electrode thickness caused by the increased amount of screen printing layers. Moreover, the decreasing number of holes in the thin film caused by the increase number of overlapped layers will also contribute to the reduced transmittance (as it can be verified on figure 3.8).

It is also observable from the graph of figure 3.9 that an increasing concentration of STEC enhancer increases the transmittance. However, the effect of the STEC concentration on the transmittance is much weaker than the layer number. So, given the not perfectly clear correlation, a bigger number of tests is needed to take conclusions. However, the tendency from figure 3.9 graph is that a higher STEC concentration increases transmittance.



(a) (b)

(c) (d)

(e) (f)

Figure 3.8: (a) PEDOT:PSS sample with two layers at 50X ampliation; (b)PEDOT:PSS sample with 5 screen printed layers at 50X focused on the zone where thickness measurements with profilometer were taken; (c) PEDOT:PSS sample with five screen printed layers at 50X ampliation; (d) PEDOT:PSS sample with five screen printed layer at 100X ampliation; (e) PEDOT:PSS sample with five layers at 200X ampliation; (f) PEDOT:PSS sample with five screen printed layers at 500X ampliation on a microcrack ;

Despite the non significant transmitance variations, given the graph of figure 3.9 it is still plausable to assume an increased transmittance with increased STEC concentration. This is plausable since the presence of STEC enhancer softens PEDOT:PSS chains which have an impact on viscosity, causing more dispersion when screen printing. Moreover, this statment is supported by the work of Wang et al. where a higher STEC enhancer concentration shown significant transmittance increases on PEDOT:PSS 1.3 wt% in water thin films. [17] It is thought that, this increment is caused by the presence of sulphides wich soften the PEDOT:PSS chains elongating them. This elongation creates spaces between chains which can increase the amount of light that passes through the polymer, increasing the overall transmittance. [17] This associated to the change in viscosity of the enhanced solution can justify this tendency, however in order to make more secure affirmations more tests need to be carry.

For the sample with 5 layers and 10% STEC, the transmittance is lower than for the sample with 5 layers and 0% STEC which contradicts the affirmations referred before. However, it must be considered that the difference is only 2% which is not significant. Such variation could be caused by a faulty sample or a corrupted test. A major broad of samples should be characterized in order to verify the influence of an higher enhancer concentrations in the PEDOT:PSS ink transmittance. The three layer sample with 15% STEC also deviate from the observed overall correlation, by showing a significantly higher transmittance. The reason for this deviation is not clear and a bigger number of tests must be done in order to verify this.

Transmittance is very high for low number of PEDOT:PSS layers. However as pointed on section 3.3.2 the resistance increases significantly with the decreasing number of layers. It is thought that this can be surpassed by increasing the amount of STEC in the solution, however this brings other problems like high resistance for a low strain. An alternative to increase conductivity and reduce the amount of layers is to use a mesh with a smaller aperture in order to provide a more closed network, avoiding spaces in the film which increase resistance. Moreover, it is estimated that with a smaller mesh it will not be necessary such a big number of layers to achieve proper conductivity and the transmittance will also be increased.

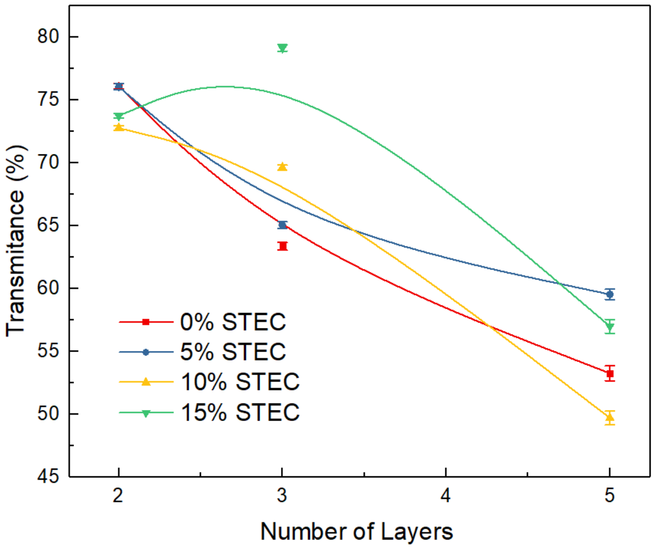


Figure 3.9: Graph to describe the influence of number of screen printed layers on transmittance for electrodes with different concentrations of STEC.

3.3.2 Electrical characterization

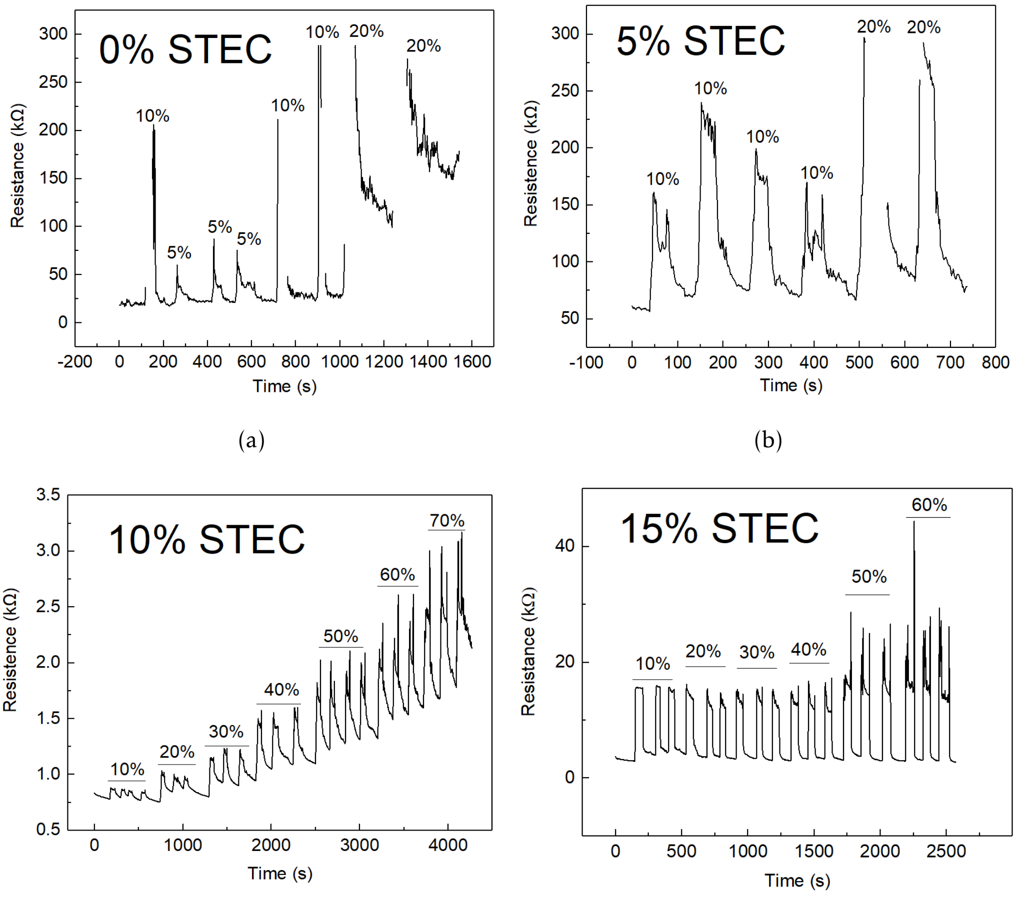
The graphs presented on figure 3.10 describe the electrode electrical behaviour upon strain of samples with 5 screen printed layers, but with different STEC enhancer concentrations. It were tested samples with 0, 5, 10 and 15% of STEC which correspond to graphs 3.10a, 3.10b, 3.10c and 3.10d, respectively. The graphs 3.10a and 3.10b show some fraction of time without measurement points, which is due to the value measured being higher than the maximum measurable by the equipment (300 kΩ).

From the graphs it is possible to verify the decrease in resistance upon the increase in STEC concentration. On the graph 3.10a where it is showed the behaviour of the PEDOT:PSS electrode with 0% STEC enhancer, at the strain of 10% the resistance is the same as the sample with 15% STEC at 70% strain (graph 3.10d). This is not just related with the increase in conductivity caused by a higher STEC enhancer concentration, but also because a higher STEC concentration improves the electrode mechanical properties which reduce the number of cracks created by the strain. With less cracks on the electrodes there is a decrease in resistance upon strain.

It also can be understood by the graphs of figure 3.10 (principally by graph 3.10c) that electrodes do not totaly recover the same resistance value from the previous stretch. This supports the relationship between the cracks caused by stretching and the resistance. When compared the graph 3.10c with the graph 3.10d this effect is attenuated, since as discussed the increase STEC concentration elongates the PEDOT:PSS chains improving the mechanical properties wich reduce the number of physical cracks upon strain, enabling the resistance restoration after strain. [17]. The graph 3.10d shows the resistance behaviour of the highest STEC concentration tested and it is visible that the values of resistance are restored even for high strains as 60%.

The sample of graph 3.10d showed an abrupt increase on resistance at 70% strain which was not completely clear the reason for such. It could be a defective test or could represent the break of the sample. For better understanding more samples should be characterized and also a more precise test like a two probe characterizations should be done. However it should be mentioned that tests done with that strain showed resistance lower than 300 kΩ.

The graphs 3.10a and 3.10b go only until 20% strain since the maximum resistance value measurable by the equipment was already been achieved for this strain while for bigger concentrations of STEC the electrode stands with a low resistance significant more high strains. Which once more shows the influence of STEC on mechanical properties which have repercussions on the electrical properties, due to the micro-cracks observed on figure 3.8f the network of PEDOT:PSS is broken causing the resistance to increase. An increased concentration of STEC softens the PEDOT:PSS chains which permit a less fragile electrode, distinguishing the number of micro-cracks impacting resistance.



(a)

(b)

(c)

(d)

Figure 3.10: Resistance behaviour upon strain with multiple cycles of stretching for different strains(a) Non-enhanced PEDOT:PSS, 0% STEC; (b) 5% STEC enhanced PEDOT:PSS electrode; (c) 10% STEC enhanced PEDOT:PSS electrode; (d) 15% STEC enhanced PEDOT:PSS electrode

The resistance measurements were taken with only 2 electrodes placed diagonaly. So, it is inaccurate to obtain extrinsic values as sheet resistance or intrinsic values like resistivity or conductivity. Given the importance of closely observing the electrodes resistance, it was summed up in table 3.1 the direct resistance values measured.

From the table 3.1 it is understood that the STEC presence on the electrodes significantly decreases resistance. When compared samples with 0% and 5% STEC enhancer it seems that the resistance values do not significantly decrease. However, a close look to the same samples at 10% strain and it is observable a significant discrepancy on resistance. On the sample of PEDOT:PSS without enhancer, at 10% strain the resistance measured surpasses the equipment limit (300 kΩ) while for the sample with 5% enhancer the resistance measured goes to a maximum of 240 kΩ (value observed from the graph of figure 3.10b). This discrepancy gets even more significant for higher STEC concentrations, which again can be attributed to the improvement of the mechanical properties from the presence of STEC enhancer.

The values of table 3.1 show that samples with STEC enhancer concentrations of 10% and 15% have a big discrepancy from the electrodes with only PEDOT:PSS ink, principally for strains above 10%. The resistance of the samples with 10% and 15% STEC enhancer show that resistance does not decrease linearly with the increase in STEC concentration, since the sample with 15% STEC enhancer show higher resistance than the electrode with 10% STEC. Such may be due to the pre-stretching (various cycles up to 80% like demonstrated on figure 3.10) done to the sample with 15% STEC before the measurements showed on table 3.1 and on figure 3.10. However, this discrepancy is not significant and the overall data supports the increase in conductivity with the presence of STEC enhancer. Moreover the behaviour does not have to be linear, a juice point for the concentration of STEC can be achieved however more samples and a bigger number of tests tests must be carried to better verify these ideas.

With the current electric measurements it is not possible to compare this work to Michael Wessely's team work since no intrinsic electrode properties or sheet resistances were possible to obtain. [32] However, taking in consideration that Michael Wessely team used PEDOT:PSS 5wt% screen printing ink to build their electrodes and the production method is almost the same, it is plausible to assume that this work should show better reistance behaviour upon strain and better mechanical properties. Although, a bigger number of tests like and a two probe characterization should be carried to better understand the electrical behaviour of the electrodes.

Table 3.1: Resistance values measured under strain and presented by electrode concentration of STEC.

	Resistance (kΩ)				
STEC (%) \ Strain (%)	0	10	20	40	60
0	24.7	206	> 300	>300	>300
5	58.8	164	>300	>300	>300
10	0.808	0.875	0.988	1.58	2.61
15	3.11	15.6	16.6	14.6	23.3

The graph of figure 3.11 illustrates better what is observable in table 3.1 where it is possible to easily verify the influence of strain in the resistance. The values used on this graph were the average of points measured for different strains and samples from the graphs of figure 3.10, the same method used for the values of table however repeated. As it also is observable on the table 3.1 the increased concentration of STEC decreases the resistance of the electrodes, principally for high strains. From the graph it is clearly visible that the best sample is the sample with 5 layers and 10% STEC given the values of resistance close to 1 kΩ. However a big number of samples must be characterized in order to better verify this conclusions.

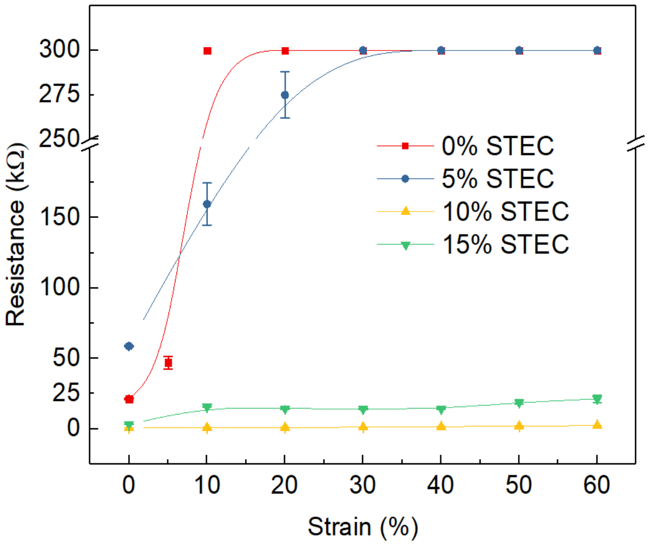


Figure 3.11: Graph to describe the influence of strain in resistance for the different samples with different concentrations of STEC.

3.4 EL devices characterization

3.4.1 Transmittance characterization

The structure used for fabricating EL devices on this work is shown on figure I.2 at section I.3 of annex I. On this figure it is visible the presence of the AQUAPLAST transparent layer as interface of phosphor/electrode and substrate/electrode, used to promote adhesion to the hydrophobic ecoflex.

The increment of a phosphor layer in between the electrodes and adding one more electrode will reduce the overall transmittance of the EL device when compared to the electrodes characterization even knowing that the AQUAPALT-DIY layer will not significantly affect the transmittance given its high transparency. However, in order to verify the influence of the phosphor layer on the overall device transmittance, studies were carried. The phosphor powder concentration is important since a high concentration of it increases the luminance of the device, since an increase number of phosphor particles will cause more EL phenomenon. The devices characterized had enhanced electrodes with 10% STEC and 5 screen printed layers and can be seen on figure 3.12a,3.12b and 3.12c.

A phosphor layer composed of 30% phosphor and 70% ecoflex 00-30 is shown on figure 3.12a, while figures 3.12b and 3.12c show phosphor layers with 50 and 70% phosphor, respectively. The transmittance values measured for those samples are presented on table 3.2 and were obtained by the average of the transmittance values measured to wavelengths from 300 nm to 800 nm. Contrary on what expected and as the data of table 3.2 reinforces, there is no significant variation in transmittance between the different concentrations of phosphor powder. It is even possible to verify by table 3.2 that samples with an emissive layer of 70% phosphor powder show more transmittance than samples with 30% phosphor powder. Although, these transmittance variations are very small (maximum discrepancy of 4%) so they should not be taken in consideration, more samples need to be characterized in order to take better conclusions.

It is understood that for lower thickness the phosphor powder concentration of the emissive layer do not play a significant role on the overall device transmittance. Which may be related to the similar thickness of the devices emissive layer. It is thought that only two layers by screen printing will not cause a big increase in thickness given the layers overlapping.

Devices show an overall transmittance of 30% making them far from transparent. Devices must be produced with 70% of phosphor powder given the lack of influence in transmittance by the phosphor concentration of the emissive layer but the significant increase in brightness caused by an increased concentration of the phosphor powder as studied in section 3.4.2. Higher percentages than 70% make the solution of phosphor:ecoflex too viscous for screen printing principally if used high resolution meshes.

(a) (b) (c)

Figure 3.12: (a) El device with 2 screen printed layers of 30, 50 and 70% phosphor powder concentration in ecoflex as screen printed emissive layer

Table 3.2: Transmittance data of EL devices samples with different concentration of phosphor powder and different number of phosphor layers.

Phosphor quantity (%)	Transmittance (%)	
	nº of layers	
	1	2
30	36 ± 0.7	30 ± 0.7
50	26 ± 0.6	28 ± 0.6
70	30 ± 0.5	26 ± 0.5

3.4.2 Luminance characterization

3.4.2.1 Luminance characterization without strain

Luminance characterization is one of the most important characterizations for EL devices, since it is the ultimate functionality of this kind of devices. This luminance characterization was carried with stretching and without stretching. Although various samples were characterized without strain, only the sample with the strongest luminance was characterized upon strain.

The characterization method is described on section 3.4.2 and the results are summarized on the graph of figure 3.13 on this section, where it is shown how the electrode STEC enhancer concentration influences the devices luminance. It is important to take in consideration that all the results presented on this section are shown in relative luminance and were taken on samples with 2 layers.

Absolute values will not be discussed since all the luminance measurements were done with an inadequate set-up for the luminance meter in use, the angle of measurement was not taken in consideration. However, all the measurements were taken under the same conditions which validates the use of relative luminance, being it enough to explore the relationships that make the objective of this chapter.

Figure 3.13 shows that a higher STEC concentration increases the device brightness. As referred on section 1.2, electroluminescence is provoked by the collision of electrons with luminescence centers causing their excitation followed by de-excitation and emission of light. A higher STEC concentration increases conductivity which enables the electrode to have a higher current density which means an increased charge on the electrodes. As equation 1.1 on section 1.3 shows, an increased charge in the electrode increases the electric field which stimulates the impact excitation phenomena as well as the avalanche phenomena resulting in a luminance increase. This is the reason why an increased current on the electrodes can cause greater light intensity. [11]

The electric field has a greater influence on luminance if there is an increased amount of phosphor particles. A higher pohosphor powder concentration, increases the number of ZnS:Cu particles, which means an increased impact ionization and avalanche phenomenon. This idea is supported by the graph 3.13 where it is possible to verify that an increase on phosphor powder concentration significantly increases the luminance.

It is not accurate to compare the luminance values achieved on this work with the reported values by the Michael Wessely team since the measurements were not made accordingly to the devices specifications. However, since it is possible to observe relative luminance and the production method was identical on both works, the graph of figure 3.13 shows that the STEC enhancer presence on the electrodes increases the device luminance, it is plausible to assume that the luminance values expected for this work may be similar or greater than the values of 120 to 200 cd/m^2 achieved by Michael Wessely's team.

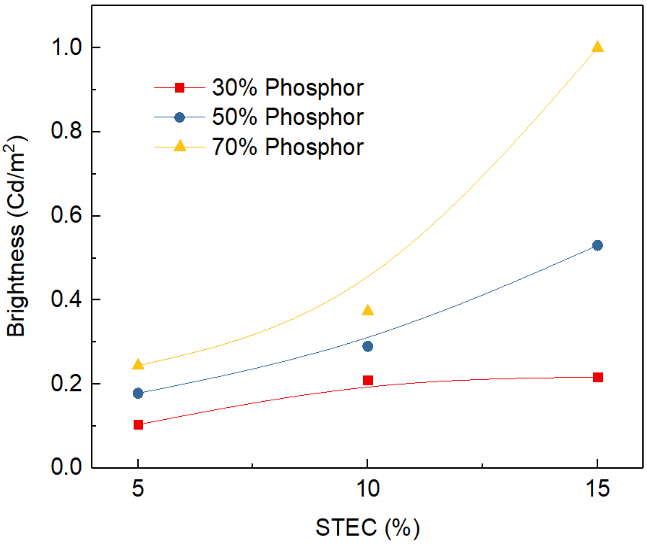


Figure 3.13: Luminance Vs STEC concentration graph to study the influence of electrode STEC concentration and emissive layer phosphor concentration on the brightness of the overall EL device.

3.4.2.2 Luminance characterization under strain

The graph of figure 3.14 show the relationship between extension and luminance. This measurement was made on a EL device with a phosphor layer of 70% phosphor powder and PEDOT:PSS electrodes with 5 screen printed layers enhanced with 15% STEC enhancer with 2 layers.

The graph 3.14 show that there is a slight increase in luminance from the 0 to 200% strain. Such was expected since with strain applied on the sample the thickness of the emissive layer diminuishes increasing the electric field which will have an impact on luminance. After that it is seen an abrupt deacrease in luminance, wich may happen since the electrodes increase resistance so significantly that it surpasses the influence of the reduced thickness in the electric field. Since the electric field is influenced by the acumulated charge on the interfaces, a higher resistance will decrease the number of charges on the dieletric interface decreasing the electric field. This influence could affect more the electric field than the lower thickness. However, further studies must be done to prove this statement, as well as to ensure the relationship between extension and luminance increase, already discussed on literature. [25] It must be taken in consideration that despite the high strains of 800% the value of luminance is higher than half of the initial value, which shows the good mechanical properties which permit so high strains on the device without a lot of degradation.

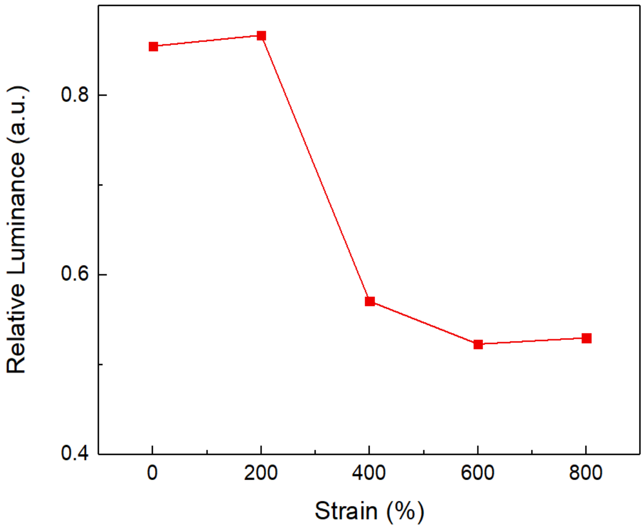
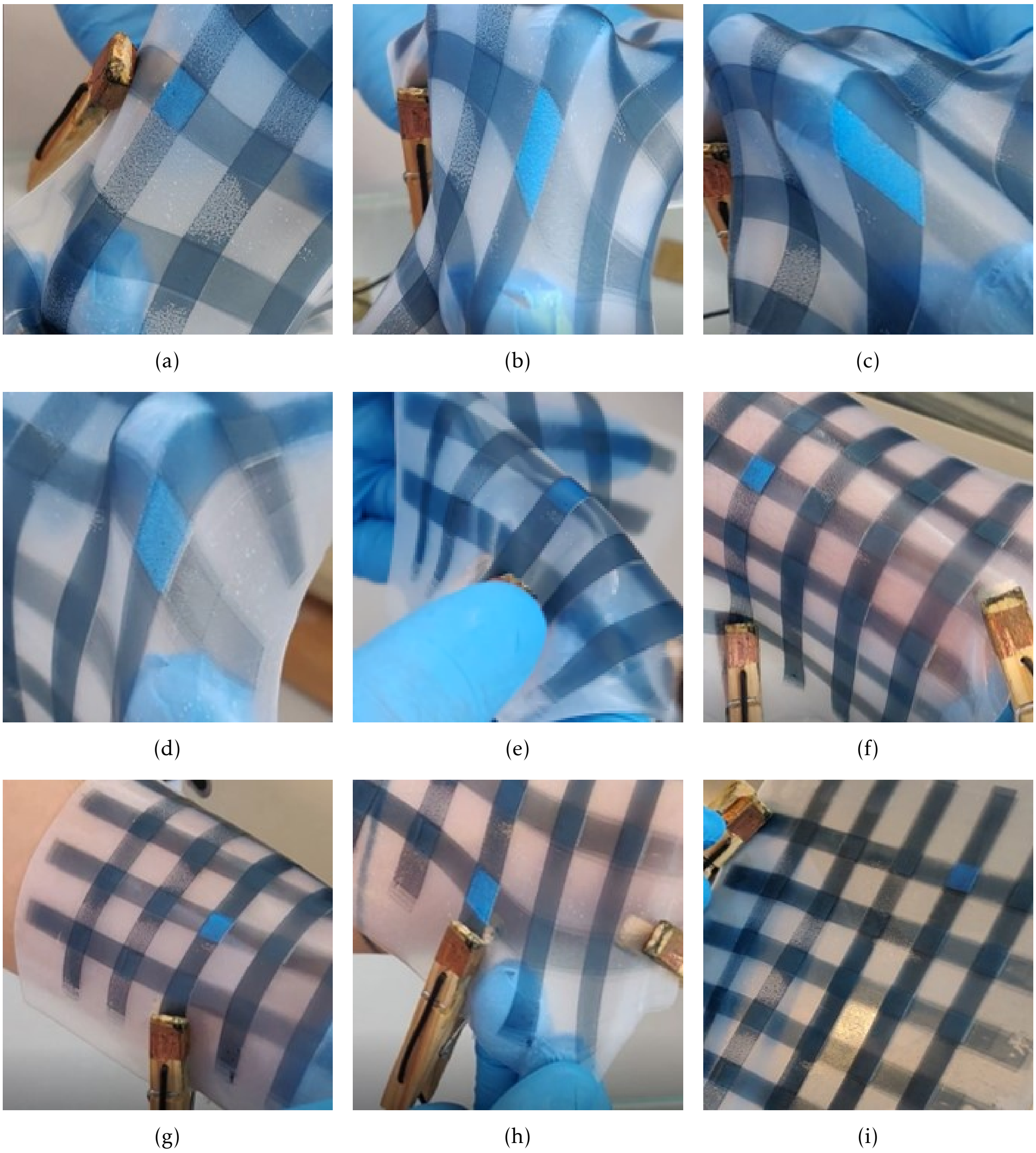


Figure 3.14: Brightness Vs Strain Graph for studying the extension influence on brightness.

3.5 EL Passive Matrix Display

Using the methods reported on this work it was produced a 5 × 5 passive matrix display, with 25 pixels. The matrix has a size of 11 × 11 cm and a pixel size of 0.8 cm. Electrodes were spaced by 1 cm to securely avoid overlapping of the electrodes causing short circuiting. Only one matrix was produced and no further characterizations were carried given the duration of the project. This matrix was produced as proof of concept and it was not connected to hard electronics (as for example a copper tape or wire) for future addressing tests using Arduino. Given the fragility of the electrodes and the lack of proper material, for the time of the project it was not possible to produce the addressing connections. Figure 3.15a, 3.15b, 3.15c and 3.15d shows this passive matrix being stretched on different situations. Figure 3.15e shows a working pixel flexed, while figure 3.15f, 3.15g and 3.15h shows the working matrix being wore on an arm with the particularity that the last one is being stretched. Figure 3.15i shows a working matrix sticked to a refrigerator, which shows that ecoflex adhesion is enough to adhere to walls, fridges, windows and the majority of the surfaces, which is a good property for future applications as programmable alert signs.



(a) (b) (c) (d) (e) (f) (g) (h) (i)

Figure 3.15: Pictures of the working passive matrix on different situations like being stretched, flexed, used on a harm and sticked to a fridge.

Chapter 4

CONCLUSIONS AND FUTURE PERSPECTIVES

This thesis compiles the work to obtain low cost easily reproducible stretchable and transparent electroluminescent device for display applications. The final goal of the thesis was to obtain a fully functional transparent EL passive matrix display. To fulfil this objective several different tasks were set:

1. Obtaining a working LiCl based hydrogel electrode;
2. Producing a small stretchable EL device;
3. Studying methods to pattern and obtain a functional passive matrix;

The first task was not accomplished given the production method being too difficult and dangerous for the conditions available. Hydrogel electrodes proved to be difficult to produce and they lacked biocompatibility due to the use of highly carcinogenic acrylamide monomers and LiCl toxicity. Moreover, the hydrogel electrodes produced showed lack of adhesion to the ecoflex substrate or encapsulation layer. Such properties hinder the devices production, making them fragile and with low brightness. Given the objective to obtain thin low cost stretchable EL devices that show robustness and good brightness, the method revealed to not be the best approach despite the literature reported results.

With the first task not completed, alternatives to obtain the electrodes were searched.The use of PEDOT:PSS 1.3 wt% in water electrodes enhanced with Bis(triflu-oromethane)sulfonimide lithium salt was the best presented solution. This approach also revealed problems with adhesion of the PEDOT:PSS watery solution to the hydrophobic ecoflex 00-30, which was solved by using an intermediate layer of AQUAPLAST. The use PEDOT:PSS 5 wt% screen printing ink instead of the PEDOT:PSS 1.3 wt% in water was more suitable since enabled more robust electrodes therefore more robust devices. The screen printing of enhanced PEDOT:PSS ink was limited to a maximum STEC enhancer concentration of 20%. Since a greater concentration of the enhancer turned the solution too watery for screen printing use. The results were promising and electrodes showed robustness, stretchability and a significant increase in conductivity when compared to electrodes produced with PEDOT:PSS ink alone.

Some of the devices produced had less than 170 µm thickness and showed promissing luminance results with and without strain, using only portable 9V AC inverter presented on figure I.8 of annex I. A proper luminance characterization it was not possible but is expected a luminance around 120 cd/m^2. Since as explainded, the work of this thesis is similar to the Michael Wessely team work.[32] Also, when compared the photographs of

Michael Wessely team to the photographs of annex III it is visible the intense brightness of the devices produced by this work even with ambient light, such photographs support the idea of similar brightness, but further studies must be carried.

The work is concluded as successful since a final EL passive matrix was obtained as it is shown on section 3.3. A low cost easily reproducible method was found to produce enhanced PEDOT:PSS electrodes with better conductivity and better overall mechanical properties than PEDOT:PSS ink electrodes. The visible resistance reduction will permit a fastest response required for application on passive matrix's or on more complex EL displays. Despite the limited time and equipment difficulties that compromised the final results, the future perspectives for this work are significant.

Access to a surface treatment would have permitted the use of the PEDOT:PSS 1.3 wt% water dispersion which will have permitted the use of a greater STEC concentration as 40%. Such will permit better conductivity and transparency on the electrodes, which if combined to inkjet printing will permit the printing of small thickness and more complex patterns as an active matrix. Furthermore, combining surface treatments with the use of AQUAPLAST-DIY may unlock device properties expected improve properties of the device. With this it is concluded that, with some more equipment, tests and time, by following the line of thought initiated on this thesis it can be achieved low cost proper working displays, ready for the design and commercialization given the easy applicability to industrial mass production.

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ANNEX

I

COMPLEMENTARY INFORMATION AND PHOTOGRAPHS TO METHODOLOGY

This Annex contains complementary information to chapter 2. Here can be found detailed descriptions of procedures explained on that chapter but also photographs that better help the understanding of the methods used and how they were used.

I.1 Complementary information to methodology

First it was acquired Acrilamide (Aam)≥ 99% Sigma Aldrich) as well as polyacrylamide (PAM) $M_W \sim 5 \times 10^6$ (92560; Sigma Aldrich). As ionic conductor it was used lithium chlorite (LiCl) (203637; Sigma Aldrich) wich was used on a solution alongside with a crosslinker (N,N'-methylenebisacrylamide; 146072; Sigma Aldrich) and a photoinitiator (Irgacure 1173- 2-Hydroxy-2-methyl-1-phenyl-propan-1-on; 405655; Sigma Aldrich). For obtaining the electrodes AAm and LiCL were dissolved in deionized water at the concentration of 1.75M and 8M, respectively. Followed by PAM at weigh ratio of 0.142 PAM:Aam.[25] This solution was mixed magnetic stirrer at 60 ± 8°C for 4 hours (this interval of temperatures it is due to the lack of a proper hot plate that could maintain a stable temperature at 60°C). After 4 hours a crosslinker was added alongside with the photoinitiator at weight ratio off 0.01 and 0.016: Aam, respectively. The solution was mixed for additional 2 hours and then Ultra Violet (UV) cured (Vilber UV Hand LAMP with UV emission at 365 nm)for 15 seconds. To obtain the thin films it was used a manual film applicator, which casted the films while the hydrogel was uncured. For bulkier films only a blade was used to spread the uncured hydrogel.

I.2 Detailed procedure of screen printed devices production

In order to obtain the final EL Device achieved on this work you must:

1. Clean the substrate with acetone;
2. Spray the substrate with Ease Release;
3. Prepare the ecoflex 00-30;
4. Take the prepared ecoflex 00-30 two minutes to low vacuum;
5. Cast a ecoflex 00-30 thin film of around 100 µm
6. Cure the ecoflex for 10 mins at 100°C;
7. Let the ecoflex cool down;

8. Screen print the AQUAPLAST-DIY in the desired shape;
9. Cure the AQUAPLAST-DIY using the blow drier as described on chapter 2;
10. Cool down the sample;
11. Prepare a solution of PEDOT:PSS 5 wt% ink and STEC (with 10 to 15% STEC);
12. Mix the solution for 15 mins;
13. Screen print the enhanced ink on the desired shape;
14. Cure the electrode with the blow drier and let the sample cool down;
15. Repeat point 13 and 14 for a minimum of 3 layers;
16. Screen print an ecoflex 00-30 layer larger than the deposited electrode, taking in consideration the contact needed for power supply;
17. Cure using the blow drier and let cool down;
18. Screen print the AQUAPLAST-DIY with the size of the ecoflex 00-30 layer, cure and let cool down;
19. Repeat the step 13 and 14, for 3 layer of the top electrode;
20. Screen print ecoflex 00-30 layer to encapsulate, taking in consideration the contact needed for power supply;

I.3 Complementary photographs to methodology

Figure I.1: Illustrative layer schematic of the layers required to obtain the PEDOT:PSS enhanced electrode.

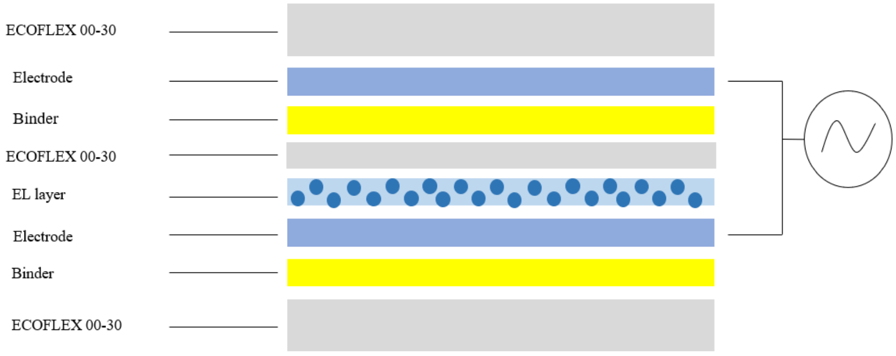
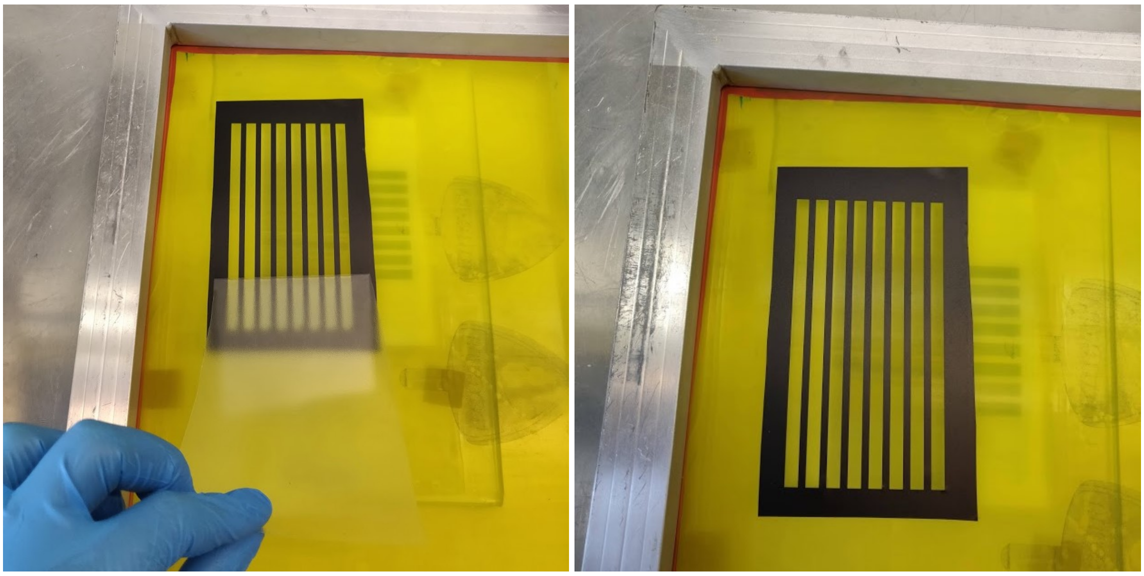


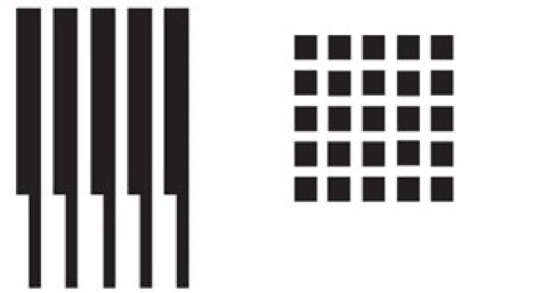
Figure I.2: Illustrative layer schematic of the EL device produced on this work.



(a)

(b)

Figure I.3: (a) Sticking of Vinyl mask on the mesh for matrix electrode paternization(b) Vinyl mask stuck the mesh for matrix electrode paternization.



(a) (b)

Figure I.4: 5 × 5cm passive matrix Vinyl designs. (a) electrodes designs; (b) Pixels designs with 0.8 × 0.8cm (emissive layer).

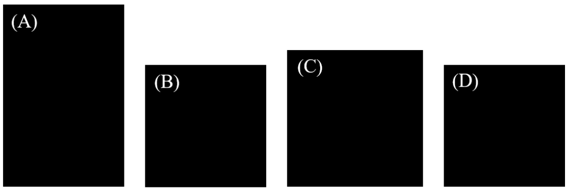


Figure I.5: Device Vinyl designs. (A) bottom electrode3 × 4cm; (B) 3 × 3cm emissive layer; (C) 3.3 × 3.3cm ecoflex dielectric layer; (D) 3 × 3cm top electrode and AQUAPLAST-DIY layer.

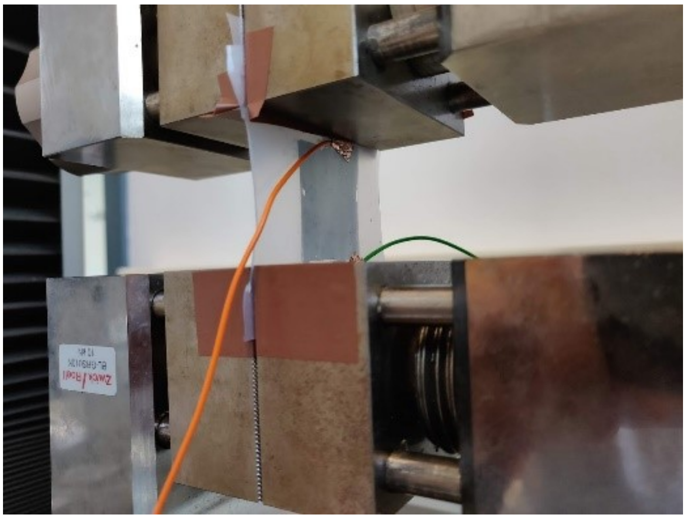


Figure I.6: Close up on an electrical characterization upon strain characterisation using the equipment by ZWICK/Roell and a data logger by Squirrel

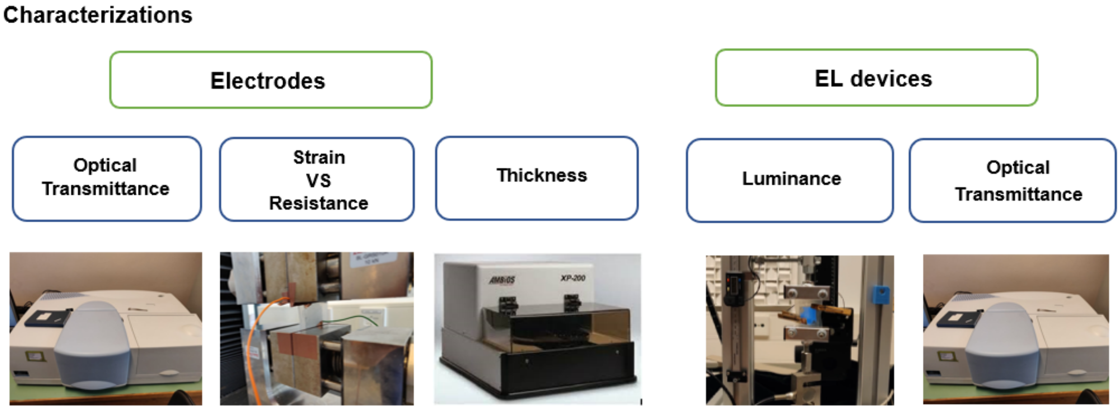


Figure I.7: Illustrative schematic of the characterizations carried on this work

(a) (b) (c)

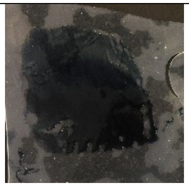
Figure I.8: Required equipment and setup for Brightness characterization. (a) General setup for brightness characterization; (b) Inverter used to power the EL devices; (c) Homemade automated extensor used on brightness characterization

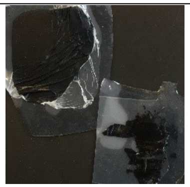
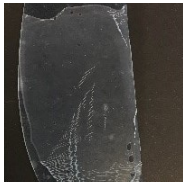
ANNEX II

RESULTS ON THE STUDY OF ENHANCED ELECTRODE PRODUCTION

This annex contains information regarding the samples produced during the study of the enhanced electrodes composition. During this study it was varied the concentration of PEDOT:PSS/STEC/AQUAPLAST and also on where it was deposited, or either ecoflex 00-30 or Aquaplast. On this table is also shown photographs of the samples in study and useful informations regarding the observable properties of the electrodes obtained.

Table II.1: Photos and information on various tests realized during the ratios experimentation for electrodes production.

Sample n º	Photo	Type of PEDOT:PSS	Sample ratio PEDOT:PSS/ STEC/AQUAP. (%)	Stretchability	Conductor	Observations	Extra info
1		PEDOT:PSS 1.3 wt%	Ratio 40/40/20	-	Yes	no film is formed; completely liquid	Sample casted on ECOFLEX 00-30
2		PEDOT:PSS 1.3 wt%	Ratio 35/35/40	it is stretchable	Yes	A film is formed but the sample is liquid	Sample casted on ECOFLEX 00-30
3		PEDOT:PSS 5 wt%	Ratio 40/40/20	it is not stretchable	Yes	A film is formed but it's too brite and doesn't adhere to Ecoflex	Sample casted on ECOFLEX 00-30
4		PEDOT:PSS 5 wt%	Ratio 20/20/40	it is stretchable	Yes	Easly pealed off wich shows that adhesion is not good; Casting defects and marks done by the conectors	Sample casted on ECOFLEX 00-30
5		PEDOT:PSS 1.3 wt%	Ratio 35/45/40	it is stretchable	Yes	The adhesion is better from the films before, it is not so easly peeled off; But with time the electrode accumulates humidity on the surface, making the sample fragile	Sample casted on Aquaplast DIY

Sample n º	Photo	Type of PEDOT:PSS	Sample ratio PEDOT:PSS/ STEC/Binder (%)	Stretchability	Conductor	Observations	Extra info
6		PEDOT:PSS 5 wt%	Ratio 50/50/0	it is stretchable	No	The film is robust however the adheasion to the ecoflex is still not good, peeling off the Aquaplast with the film; Completely opaque;	Sample casted on Aquaplast DIY
7		PEDOT:PSS 5 wt%	Ratio 40/20/40	it is stretchable	Yes	There is a good ratio between robustness of the film and conductivity, which shows that a less thick will offer a good combination off conductivity, transparency and stretchability;	Sample casted on Aquaplast DIY
8		PEDOT:PSS 5 wt%	Ratio 100/0/0	it is stretchable	No	The sample is transparent, it can be seen the presence of a PEDOT:PSS layer, given the dark blue color of the film; Only one layer of PEDOT:PSS was screen printed;	Screen printed on Aquaplast DIY
9		PEDOT:PSS 1.3 wt%	Ratio 40/60/0	it is stretchable	Highly Conductive	The thin film as a watery/viscous appearance it is easily pealed off after cooling down out of vacuum, this behaviour is atributed to the increase surface moisture in the film; On the other hand coming out of the oven/vacuum the overall aspect is consistent;	Sample casted on Aquaplast DIY

Annex III

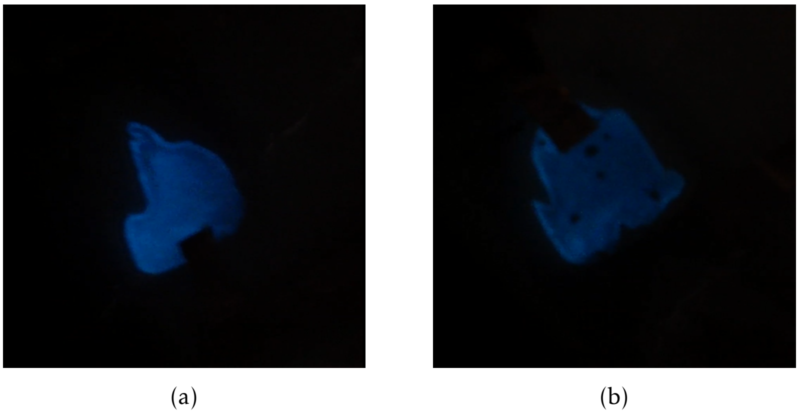
Complementary photographs of working samples

This Annex contains complementary photographs of devices working, being stretched and on different surfaces like the skin. The objective of this annex is give a more illustrated idea of the devices produced on this work. It can be seen samples produced before the final EL devices and there is also pictures pictures of the final EL devices produced by screen printing with the electrodes of PEDOT:PSS enhanced ink. This pictures have the intent to show in more detail some problems referred on this work.

First it is shown EL devices produced with enhanced electrodes of PEDOT:PSS 1.3 wt% in water by thin film casting. On the figure III.4 is is observable the humidity adsorbed on the PEDOT:PSS thin films after some atmosphere exposure, where figure III.1a shows the sample right after coming out of the oven and III.1b shows the sample after some time exposed to the atmosphere. On figure III.2 is shown the sample emitting on a dark room where it is visible the low light achieved.

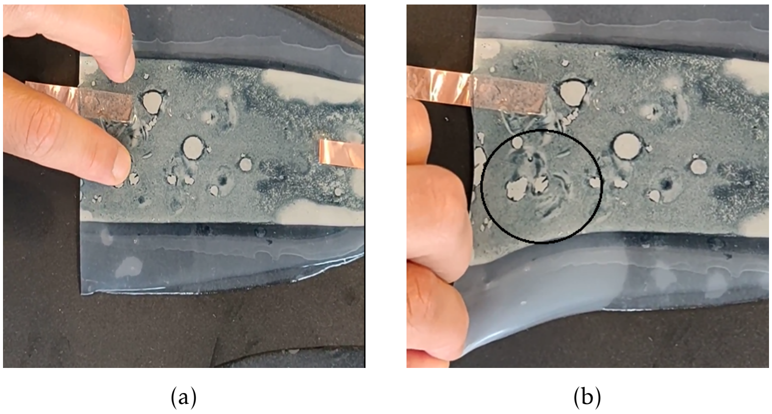
(a) (b) (c)

Figure III.1: Pictures of a PEDOT:PSS 1.3 wt% in water electrode device produced with a manual thin film applicator.(a) Bottom electrode before leaving the oven; (b) Bottom electrode after leaving the oven; (b) Top electrode of 3 cm width; (c) Top electrode of 3 cm width.



(a) (b)

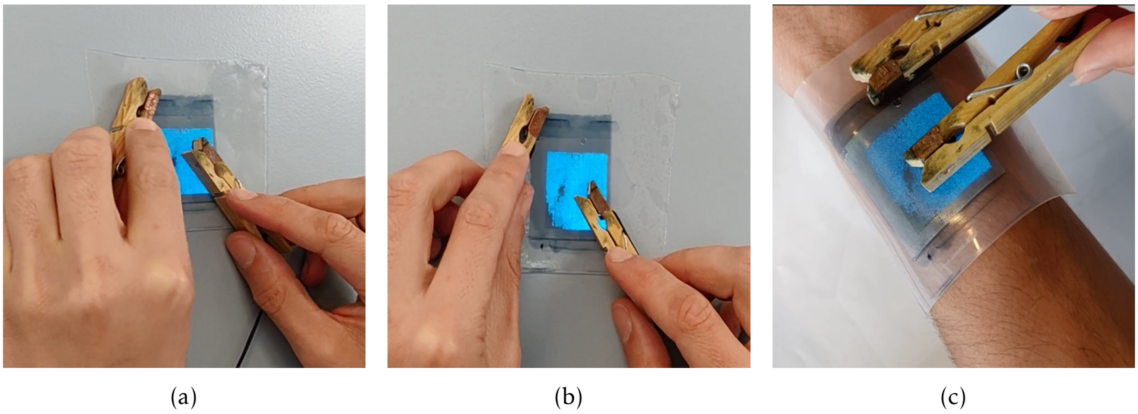
Figure III.2: (a) Thin film device working on dark room;(b) Another thin film device working on dark room.



(a) (b)

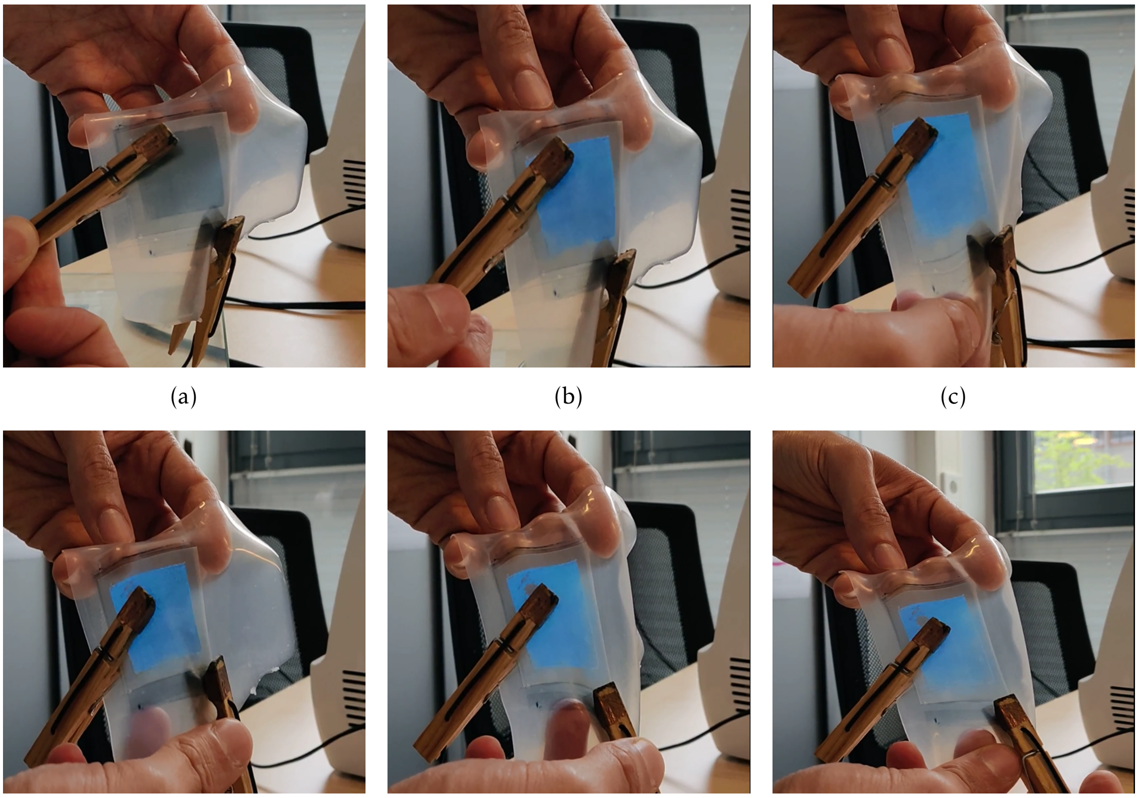
Figure III.3: Encapsulated sample produced with the manual film applicator. (a) a finger is pressed against the device; (b) The marks of the finger caused by the pressing are visible inside de black circle;

Now it is presented the devices produced by screen printing with electrodes of PEDOT:PSS enhanced ink. This samples were tested attached to walls and on skin, they were stretched and folded as pictures show, with this use it is visible sometimes the peeling of of the samples described on this work.



(a) (b) (c)

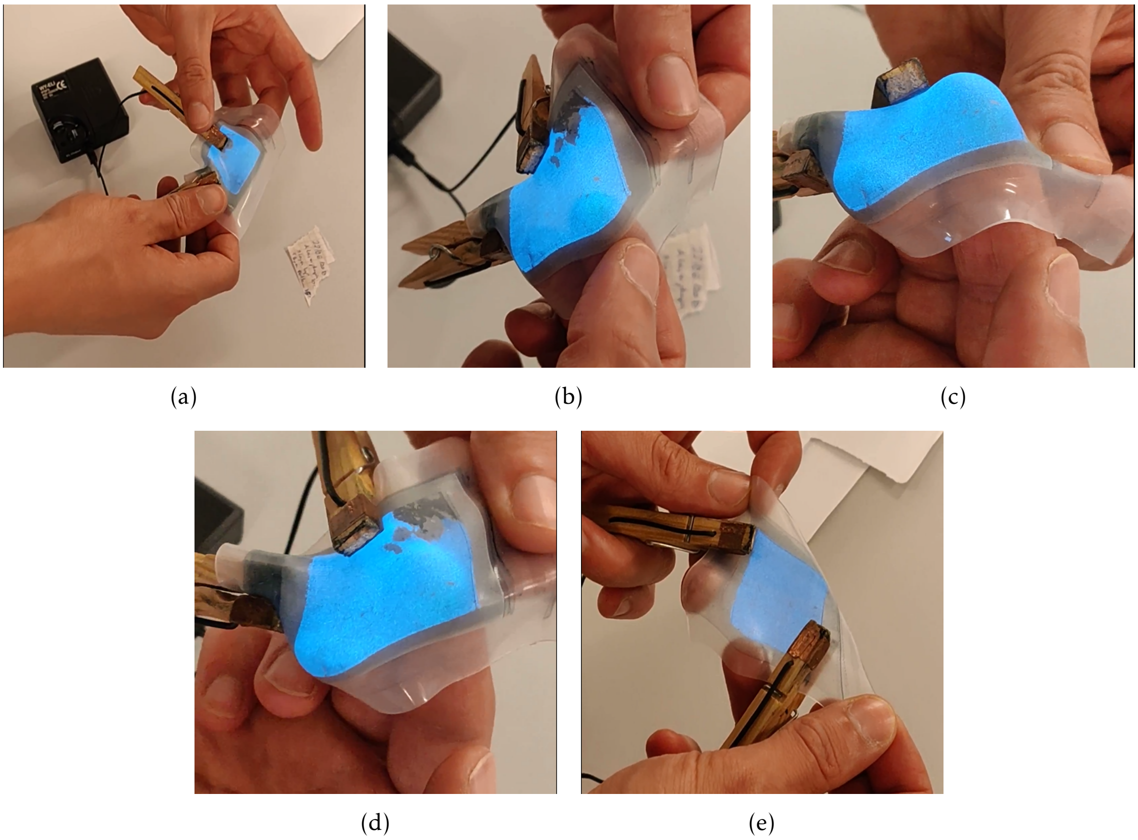
Figure III.4: EL working device stuck to a wall and on a skin surface. Device produced with 5 layer electrode enhanced with 10% STEC, 2 layers and 50% phosphor powder.



(a) (b) (c)

(d) (e) (f)

Figure III.5: Sequence of photographs from (a) to (f) stretching a device produced with a 5 layer electrode enhanced with 10% STEC and 2 layers emissive layer with 50% phosphor powder.


(a) (b) (c)

(d) (e)

Figure III.6: Sequence of pictures of an working electrode being handled sequence from (a) to (e), device produced with 5 layer electrode enhanced with 10% STEC, 2 layers and 70% phosphor powder.

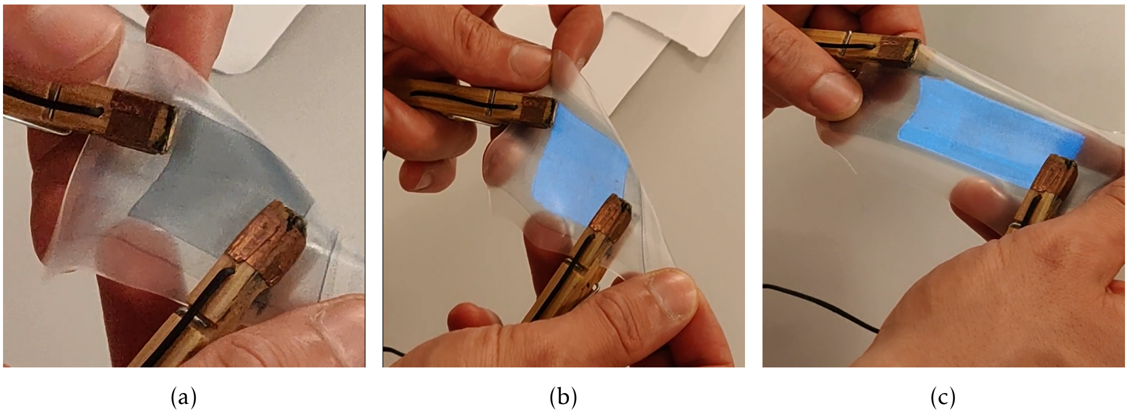

(a) (b) (c)

Figure III.7: EL device being first folded and then stretched on a sequence from (a) to (d).

2018 **Low cost stretchable thin film electroluminescentdevices for display applications** **Sérgio Gomes**