

UNIVERSIDADE ESTADUAL DE CAMPINAS INSTITUTO DE QUÍMICA

ADRIANO DOS SANTOS MARQUES

STUDIES OF INTER-AND ACTIVE LAYERS WITH DIFFERENT DEPOSITION METHODS IN PEROVSKITE SOLAR CELLS

ESTUDO DAS CAMADAS INTERNAS E ATIVA COM DIFERENTES MÉTODOS DE DEPOSIÇÃO EM CÉLULAS SOLARES DE PEROVSKITA

CAMPINAS 2021

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"Todo abismo é navegável a barquinhos de papel." - Guimarães Rosa

Resumo

As células solares de perovskita apresentam um grande potencial como fonte de geração de energia elétrica no futuro. No entanto, esse tipo de tecnologia apresenta algumas dificuldades que ainda têm de ser superadas. Um desses fatores é em relação a sua fabricação: o alto custo de alguns materiais utilizados nesse tipo de célula (i) e a confecção desses dispositivos em grande área para serem futuramente aplicados (ii). Neste trabalho foram propostas alternativas a esses dois problemas distintos. Na primeira parte foram utilizados os polímeros condutores polianilina (PAni) e poli(o-metóxianilina) (PoMA) como materiais transportadores de buracos, em substituição ao Spiro-OMeTAD que apresenta alto custo devido a sua rota sintética complexa. Esses polímeros foram sintetizados, caracterizados e aplicados na forma dopada com o ácido dodecilbenzenosulfônico nas células de perovskita e seu desempenho foi comparado com um dispositivo padrão contendo o Spiro-OMeTAD. Os dispositivos com PAni tiveram uma eficiência (10,05%) similar ao alcançado pela célula padrão (10,06%), enquanto o desempenho da PoMA foi inferior (5,59%). Na segunda parte do trabalho o foco foi a deposição das camadas que compõem a célula de perovskita pela técnica de blade coating. Devido às particularidades no processo de cristalização da perovskita, nessa técnica de deposição normalmente são empregadas altas temperaturas ou outros artifícios que podem limitar a viabilidade desse processo. O estudo desenvolvido conseguiu superar essas limitações ao utilizar solventes e precursores diferenciados para a perovskita, resultando em camadas livres de defeitos e com alto recobrimento do substrato. Na melhor condição esses dispositivos obtiveram eficiência de 14,3%.

Abstract

Perovskite solar cells have a great potential to become a source of electricity generation in the future. However, this type of technology presents some difficulties that have yet to be overcome. One of these issues is regarding its fabrication: the high cost of some materials that are used in this type of cell (i) and the manufacturing of these devices in large areas to be commercially viable (ii). In the present work, alternatives to these distinct problems were proposed. In the first part, the conductive polymers polyaniline (PAni) and poly(o-methoxyaniline) (PoMA) were applied as hole transport materials in replacement of Spiro-OMeTAD, which has a high cost due to its complex synthetic route. These polymers were synthesized, characterized, and applied in their doped form with dodecylbenzenesulfonic acid, and their performance were compared to a standard device containing Spiro-OMeTAD. Devices containing PAni achieved a power conversion efficiency (10.05%) similar to the standard (10.06%), while the devices with PoMA displayed a lower efficiency (5.59%). In the second half, the focus was on the deposition of the layers that compose the perovskite solar cell through the blade coating technique. Due the peculiarities of perovskite crystallization, it is necessary to employ high temperature or other artifice to control the film formation, which can limit the application of this process. A method was developed to surpass these limitations by using different solvents and precursors to make the perovskite, resulting in a layer free of defects and with a high substrate coverage. The device assembled with this method achieved 14.3% efficiency.

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List of Abbreviations

- 2ME 2-methoxyethanol
- AM 1.5 Air Mass 1.5, correspondent to solar spectrum at ground level.
- CIGS Copper Indium Gallium Selenide
- CSA Camphorsulfonic acid
- CTZS Copper Tin Zinc Sulfide
- DBSA Dodecylbenzenesulfonic acid
- DMAC Dimethylacetamide
- DMF Dimethylformamide
- DMSO Dimethylsufoxide
- DSSC Dye Sensitized Solar Cell
- EIS Electrochemical Impedance Spectroscopy
- ETM Electron Transport Material
- FEG-SEM Field Emission Gun Scanning Electron Microscope
- FF Fill Factor
- FTIR Fourier-Transform Infrared Spectroscopy
- FTO Fluorine Tin Oxide
- GBL γ-Butyrolactone
- Ge Gerischer Element
- GIWAXS Time-resolved Grazing Incidence Wide-Angle X-Ray Scattering
- HOMO Highest Occupied Molecular Orbital
- HTM Hole Transport Material
- ICP Intrinsically Conductive Polymers
- Impp Current at the maximum power point
- Isc Short-Circuit Current
- ITO Indium Tin Oxide
- IV Plot of Current-Voltage
- J Current Density
- J_{mpp} Current Density at the maximum power point
- Jsc Short-Circuit Current Density

- JV Plot of Current Density Voltage
- LiTFSI Lithium bis(trifluoromethanesulfonyl)imid
- LUMO Lowest Unoccupied Molecular Orbital
- MAI Methylammonium Iodide
- MPP Maximum Power Point
- NHE Normal Hydrogen Electrode
- NMP N-methyl-2-pyrrolidone
- **OPV** Organic Photovoltaic
- P3HT (poly(3-hexylthiophene-2,5-diyl)
- PAni Polyaniline
- Pb(Ac)₂ Lead Acetate Pb(CH₃CO₂)₂.3H₂O
- PC61BM [6,6]-Phenyl-C61-butyric acid methyl ester
- PCE– Power Conversion Efficiency
- PEDOT:PSS Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
- Pin Power of the incident light
- PoMA Poly(o-methoxyaniline)
- PSC Perovskite Solar Cell
- PTAA Poly(triarylamine)
- R2R Roll-to-Roll
- Rs Series Resistance
- RSH Shunt Resistance
- Spiro-OMeTAD 2,2´,7,7'-tetrakis-(N,N- di-p-methoxyphenylamine)9,9´-spirobifluorene
- TSA p-toluene sulfonic acid
- TW h Terawatt-hour
- UV-Vis Ultraviolet-Visible spectroscopy
- V_{mpp} Voltage at the maximum power point
- XRD X-Ray Diffraction

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1. Introduction

1.1. Energy consumption and perspective of solar cells

In 2019, approximately 27004.7 terawatt-hour (TWh) of electrical energy was produced worldwide [1]. This energy was used to sustain the comfort of the modern lifestyle, in which smartphones, personal computers, microwaves, refrigerators, air conditioning, televisions, heaters, among others are common items existent in each home. As new things are added to this list, the outcome is that the consumption tends to rise in a yearly base; from 2018 to 2019 it increased by 1.3%. With the means of transportation changing towards electrical energy, which is expected to occur in the near future, this trend is expected to increase significantly.

The primary source of energy generation is through the use of fossil fuels in the form of either coal, oil or gas; together these fuels account for approximately 62.7% of electric generation used worldwide [1]. The reason that led to the present scenario is due to the historical use of these fuels and the fact that today they still are economical attractive when compared to other types of energy sources. Unfortunately, the use of these fuels is linked to several environmental impacts, the most known example is the global warming. Other issues associated to these fuels that cannot be overlooked are air pollution, acid rain, and environmental degradation due to leakage during their extraction and production phase.

Concern about the environmental impact is the main reason pushing towards a change in the way that electrical energy is generated. Renewable energy is often pointed as the best possible solution to this situation. Nevertheless, renewables are currently accountable to 25% of the total energy generated, which decreases to only 10% if hydro energy is left unaccounted. This value corresponds to approximately 2805.5 terawatt-hour generated, in which wind contributes with almost 51%, and solar currently generates 724.1 TWh, corresponding to 26% of the total generated by the renewable sources (Figure 1) [1].



Figure 1: Share of each energy source in the total generated electricity (left), TWh generated by renewable source (right). Reference: [1]

Despite currently having a small contribution, solar energy has the biggest resource available for use. The energy irradiated by the sun on the Earth's surface in one hour is enough to supply the world's demand for a year [2]. This huge capacity is currently underused, as the major drawback of photovoltaic (PV) technology is the price, which limits the widespread use of this energy source. The first generation of solar cell was built from monocrystalline high purity silicon, this material was obtained from silicon wafers through the Czochralski process, which requires high temperature to melt the silicon [3][4]. The combination of high energy usage and high purity is the reason why this process was so expensive and made these initial cells economical unattractive. A second type of photovoltaic using multicrystalline silicon was later developed, this solar cell has lower production cost but the efficiency that it achieves is lower than monocrystalline as well.

Despite its initial high price, solar cells based on silicon are the most common type of photovoltaic employed nowadays and have been used in domiciliary environment and in solar farms. Although the production volume of these devices has gradually reduced their price over the years (Figure 2), the cost of produced energy per watt using these solar cells is high, making the return over the investment only possible in a long period of years. To be economically viable the cost of the PV must reduce to \$0.02-0.05 per kWh [5].



Figure 2: Yearly evolution of price per watt obtained by each type of solar cell. Reference: [5]

Development of new materials led to the creation of second generation solar cells. Instead of crystalline silicon, this new generation uses thin films ranging from few nanometers to tens of microns as the photoactive layer, which allows to reduce the production costs of these devices in comparison to those of the first generation. Typical examples of this type of solar cells are copper indium gallium selenide (CIGS), cadmium telluride (CdTe), gallium arsenide (GaAs) and amorphous silicon. Although this second generation is cheaper to produce, their Power Conversion Efficiency (PCE) is lower than those achieved by first generation [6].

Third generation of solar cells aims to achieve both the low production cost of the second generation and high efficiency obtained by crystalline silicon. To fulfill this task, the third generation of solar cells retained some of the characteristics of the second generation, such as using thin films in the photoactive layer, and adopted new strategies such as decoupling light absorption and carrier transport [7]. Some examples of the third generation of solar cells are the polymer solar cells, copper tin zinc sulfide (CTZS) and dye-sensitized solar cells (DSSC). Recently, a new material has been recently added to this list of upcoming technologies, the perovskite solar cell (PSC).

1.1. General perspective of Perovskite Solar Cells

Perovskite is the name given to the calcium titanate (CaTiO₃) mineral, discovered in the Ural Mountains in 1839. The name was a tribute to the Russian mineralogist Lev Alexevich von Perovski and initially it was used to name this mineral. Later, the term came to be used to describe materials that had the same ABC₃ crystal structure as the mineral. In the perovskite structure, A correspond to the biggest cation, B is a smaller cation and C represents the anions, usually oxide or halogen ions [8].

In the perovskite structure, the B cation is coordinated by six anions forming an octahedron unit. These octahedra are connected to adjacent units through the vertex, forming a B-C-B bond; the A cation is coordinated by twelve anions and is situated in the site generated by the connection of 8 octahedron units. The high symmetry cubic phase is considered the ideal perovskite structure (Figure 3). However, deviations from the cubic phase are normally found due a mismatch between A and B cations [9].



Figure 3: Crystal structure of cubic perovskite. Adapted from [9].

The type of polymorphic structure adopted depends on the relative size of the ions that compose the perovskite. In 1926, Goldschmidt proposed a tolerance factor (t) (Equation 1) in order to predict when distortions would occur in the structure. In this equation, R_a and R_b are the radius of A and B cations and R_c the radius of C anion. The ideal cubic phase occurs in the range of 0.8-0.9 but other perovskite polymorphic structure can exist in the range between 0.75<t<1.13 [10]. Due to the ability to adapt to elements with different size, the perovskite structure can have a variety of compositions and accommodate most of the periodic table [11].

$$t = \frac{R_a + R_c}{\sqrt{2}(R_b + R_c)}$$
 (Equation 1)

In solar cells, the role of perovskite is to act as the photoactive material, responsible for light (photon) absorption. The mechanism in which light is converted in electrical energy relies in a property of semiconductors, in these materials there is a separation between the conduction and valence bands, called band gap. Depending on the material, the energy of the band gap may be within the visible part of the electromagnetic spectrum. A photon that is absorbed by this semiconductor with a higher energy than the band gap can excite an electron from valence band towards the conduction band, forming an exciton [4]. After the exciton is split, the charge carriers can be extracted from the device and used to produce electrical power (Figure 4).



Figure 4: Schematic showing the inner workings of a solar cell. Reference: [4]

The first appearance of perovskite in solar cells occurred in 2009 by Tsutomu Miyasaka and collaborators [12], describing the use of two hybrid organic-inorganic perovskite with the composition CH₃NH₃PbI₃ and CH₃NH₃PbBr₃ in replacement of the ruthenium(II) dye, which was the light absorber commonly used in DSSC. The best solar cell achieved a PCE of 3.81%, which is approximately half of

the maximum efficiency that could be achieved with ruthenium dyes in DSSC by that time. This first application of perovskite in solar cells used the parameters and materials that were optimized for the ruthenium dyes, this partially explains the low efficiency achieved.

Posterior studies with this material sought to obtain higher performance through optimization, a breakthrough was made when the ionic I⁻/I⁻₃ electrolyte used in DSSC was substituted for the organic molecule 2,2′,7,7′-tetrakis-(N,N- di-p-methoxyphenylamine)9,9′-spirobifluorene (more commonly known as Spiro-OMeTAD); the change for a solid p-type hole conductor allowed the efficiency of the solar cell surpass those obtained with ruthenium dyes and reach 10% [13]. These results allowed the perovskite solar cells to become a new type of photovoltaic device, instead of just a ramification of DSSC.

Compared to other materials used in photovoltaic devices, the perovskite has unique advantages. Differently to the case of crystalline silicon, the PSC does not require precursors with an ultra-high purity grade and the materials to make perovskite are abundant. The precursors to make the most used perovskite, the CH₃NH₃PbI₃, are the salts methylammonium iodide (MAI) and lead(II) iodide. The synthesis of MAI is easily accomplished by reacting methylamine with hydroiodic acid (Equation 2). After purification, the resultant salt can be dissolved with lead iodide in a 1:1 ratio to generate the perovskite structure (Equation 3):

CH₂NH₂ + HI → CH₃NH₃I (Equation 2)

 $CH_3NH_3I + PbI_2 \rightarrow CH_3NH_3PbI_3$ (Equation 3)

Deposition of the perovskite can be done via solutions, which in principle can facilitate the production of devices using this material and allows different deposition methods to be used. These characteristics are important to, in the future, reduce the final cost of the photovoltaic devices made from this material.

The hybrid organic inorganic perovskite has optoelectronic properties that also makes this material an interesting choice for photovoltaic applications. The band-gap can be adjusted by tailoring its composition, although CH₃NH₃PbI₃ has a band gap of 1.6 eV which is nearly ideal for a single absorber solar cell [14]. Perovskite has a high molar extinction coefficient, allowing to absorb most of light irradiated even in thin films. The exciton generated by absorption of the light in perovskite has a low exciton binding energy (30 to 50 meV), resulting in spontaneous dissociated free charges [15]. Once the charges are separated, their transport is also facilitated in perovskite due its ambipolar nature, and the charge carriers can be efficiently transferred through the material to the interfaces due to the high mobility (~60 cm² V⁻¹ s⁻¹) and long carrier lifetime (~ 100 ns) [16].

These characteristics made this material an interesting compound to explore its properties and relatively easy to work with, which contributed to the spread of perovskite solar cell research among different groups across the world. The intense interest in this material led to a unique situation in the history of photovoltaic development as PSC showed the fastest increase of PCE in the least amount of time. Currently the record for perovskite solar cells is 25.5% in laboratory scale, which is close to the performance achieved by the monocrystalline silicon solar cell (26.1%) (Figure 5) [17].



Figure 5: Chart with the efficiency record for each type of solar cell. Reference: [17]

Regarding the structure of the solar cell, the PSC are usually assembled on top of a glass substrate containing a transparent conductive oxide, generally ITO (Indium Tin Oxide) or FTO (Fluorine Tin Oxide). In addition to the photoactive layer, other charge collection layers are used to increase performance. These layers are made from the electron transport material (ETM) and hole transport material (HTM). Depending on their components and arrangement the PSC configuration is classified in two groups: normal and inverted. The former consists of ETM/Perovskite/HTM (n-i-p) layout in relation to the substrate, while the latter has the ETM and HTM reversed in a p-i-n manner (Figure 5). Mesoporous ETM, such as TiO₂ and Al₂O₃, are commonly used in PSC in the normal configuration, further subdividing this configuration into mesoporous or planar, depending on the material used.



Figure 6: Different structures of PSC: (n-i-p) normal configuration in mesoporous (A) and planar (B); inverted (p-i-n) configuration (C).

The main reason for the predominance of TiO₂ in PSC is due its heritage from DSSC, moreover it has some advantages such as: low cost, chemical stability, nontoxic, and has a suitable conduction band energy in relation to the perovskite. The mesoporous TiO₂ layer acts both to reduce the distance that the electron must migrate within the perovskite and as a scaffold in which the precursor solution can percolate and crystallize. The lack of this structure leads to reduced perovskite coverage, a common problem in planar PSC [18]. As a disadvantage, the mesoporous layer adds a further step during the deposition process and requires annealing at high temperature (>450 °C). For these reasons, the planar configuration is more desirable, especially in future industrial production of these devices.

Differently to the mesoporous case, planar PSC is employed both in normal and inverted configurations. This arrangement allows a greater variety of materials to be used as ETM, ranging from n-type oxides (compact TiO₂, ZnO, SnO₂, WO₃) to fullerenes derivatives (PC₆₁BM and PC₇₁BM) [19]. Lower annealing temperatures and simpler construction process are some of the main advantages of this configuration. Although being simpler than mesoporous, this configuration does not limit the performance and high efficiency devices can be obtained with either structure.

In the early stages of PSC research, the removal of a liquid electrolyte was fundamental to enhance the performance of the device. Nowadays many compounds can be used as hole transport material, ranging from pure inorganic (Cul, NiO, CuSCN) to organic molecules and polymers; each type of material employed has its strengths and weakness. Inorganic materials displays a high hole mobility, chemical stability, and low cost [20], however the deposition of these materials is not so easily accomplished which may limit their application.

Due the disadvantages of inorganic materials, HTM from organic sources are the vast majority in PSC studies. Spiro-OMeTAD, the most used material, belongs to a class called *small molecules* which possess good hole mobility and is easier to deposit than inorganic materials, mostly due their higher solubility in organic solvents. PCE results over 20% are commonly achieved by this type of HTM, unfortunately the spirobifluorene core of these molecules is highly complex and difficult to synthetize, which makes this material expensive in comparison to the others used in PSC. Another downside is that Spiro-OMeTAD is often doped with other compounds such as lithium bis(trifluoromethanesulfonyl)imid (known as LiTFSI). Unfortunately, lithium salts are highly hygroscopic which aggravates the stability problem of PSC [21].

Conjugated polymers are another type of organic HTM, many of these materials have already been explored in other types of solar cells such as organic (OPV) DSSC. One widely photovoltaic and used is the poly(3,4ethylenedioxythiophene) polystyrene sulfonate, also known as PEDOT:PSS, this material is a mixture of two charged polymers together. Single polymers without charge can also be used as in the case of poly(triarylamine) (PTAA) and (poly(3hexylthiophene-2,5-diyl) (P3HT). Polymeric HTM are an interesting alternative as they can have qualities of both inorganic HTM and small molecules [20].

Regarding their manufacture, one of the most explored arguments in favor of perovskite solar cells is their ability to be produced using solutions from their precursors. However, most studies involving PSC still opt for the spin coating as the deposition technique to manufacture these solar cells. Spin coating's favoritism over other techniques since the beginning of PSC research is due to its qualities such as simplicity, ease of use and ability to obtain uniform films. Although this type of deposition is extremely useful in laboratory environment, future application of perovskite solar cells will need to use other type of depositions, because spin coating is unsuitable for an industrial or continuous flow production. Unfortunately, spin coating works in a very specific way which hinders the correlation of parameters to a different deposition technique. As result, a significant amount of study and optimization still need to be done to fully utilize the property of being processed by wet solutions that is often pointed as an advantage of PSC.

The unique properties of this material combined with its advantages and relatively easiness to produce, made this type of photovoltaic device a hot topic over the last few years. Despite the intense research made so far, there is still room for improvement to overcome the issues that this kind of device has. The current work will focus in two different problems of PSC, first the replacement of the high-cost Spiro-OMeTAD to a cheaper polymeric HTM alternative. On the second part the focus will shift to develop a method to produce the PSC in mild conditions using scalable methods.

1.2. General aspects of solar cells measurements

The measurement of solar cell performance is done by a current-voltage curve, commonly known as IV curve, which is the representation of the relationship between the applied voltage and the current that flows across the device. This type of measurement is useful for different applications such as batteries, resistors, and diodes.

In the case of solar devices, a few photovoltaic parameters are obtained from the IV curve and used to determinate the numeric PCE of the device. At the point where the voltage applied to the device is equal to 0, the solar cell generates the maximum current that can be harvest, known as the Short-Circuit Current (I_{sc}). Devices with divergent active area generate different current values, to avoid this issue it is common practice to divide the current obtained by the active area of the solar cell. By doing this operation, the current density (J) is obtained and is often used to build the JV curve (analogue of the IV curve) and the Short-Circuit Current Density (J_{sc}) is used to compare the performance from different devices.

During the measurement, as the potential applied by the external power source increases, it generates a counter force to the natural movement of electrons inside the device. Initially the effect of this force in the current generated is small, which can be seen by the plateau formed in the JV curve (Figure 7), at some point it drastically reduces the current extracted from the solar cell, until it reaches zero. In this point, the potential applied by the external power source has the same magnitude of the voltage generated within the cell, and the movement of current across the device ceases, this is called the Open Circuit Voltage (Voc).

The power that is generated by a solar device is the product of the voltage and the current obtained by the JV measurement. The power graph can be plotted along with the JV curve but is usually omitted. The power generated increases with the voltage applied to the cell, reaches a maximum and then decreases again (Figure 7). Its highest value is the Maximum Power Point (MPP), and a value of voltage (V_{mpp}) and current (I_{mpp} or J_{mpp}) is associated to it. These values of voltage and current obtained at the MPP are used to calculate the Fill Factor (FF) of the solar device. The FF is the ratio of power extracted from the device in relation to the maximum that could be achieved (Figure 7 and Equation 4). It also can be perceived by the squareness of the JV curve.



Figure 7: Example of a typical JV curve depicting the photovoltaic parameters.

$$FF = \frac{V_{mpp} \times J_{mpp}}{V_{oc} \times J_{sc}} = \frac{Area 1}{Area 2}$$
 (Equation 4)

With the beforementioned photovoltaic parameters it is possible to calculate the Power Conversion Efficiency (PCE) with Equation 5:

$$PCE = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}$$
(Equation 5)

Where P_{in} is the power of incident light. The samples are illuminated by a source which simulates the solar spectrum at ground level, called Air Mass 1.5 (AM 1.5) with a power of 1000 W/m². This standardization allows for devices built by different groups to be compared in terms of their performance.

Another parameter that can be obtained from the JV curves are the parasitic resistances, the series and shunt resistance (Rs and RsH, respectively). The series resistance arises from the materials, the metallic contact, and the substrate. A high Rs means that there is resistance against the current flow. The shunt resistance is related to defects within the solar device, a low shunt resistance indicates that the photogenerated current can diverge to a different path, resulting in a power loss [4]. Both resistances can be derived from the JV curve, the RsH can be obtained by the slope of the JV curve at the short-circuit point while the Rs can be estimated by the slope at the Voc.

2. Polyaniline based materials as HTM

2.1. Introduction

Polyaniline (PAni) history can be traced back to the early 1800's, although the original discovery still under debate and credited to different authors from the same period [22]. These first reports of PAni were based on 'aniline black' and refers to one state, from a total of 3, that polyaniline can assume. These states are related to the oxidation of the nitrogen atoms in the polymer backbone. When the nitrogens are fully reduced the polymer is called leucoemeraldine, on the opposite end it is called pernigraniline, if fully oxidized. The intermediary state is called emeraldine and is achieved when half of the nitrogens are oxidized (Figure 8A) [23].

PAni is a material that belongs to a class called intrinsically conductive polymers (ICP). This type of material has a conductive nature due their conjugated π system in the polymer structure [24]. PAni has some advantages when compared to other ICPs, it has superior thermal stability, the monomer is less expensive and the synthesis of PAni is easy, which helps to reduce the final cost of the polymer. Compared to other materials PAni is also chemical stable and non-hazardous, these properties make PAni one of the most studied ICP.

One of the most explored property of PAni is its conductivity, which is deeply affected by the oxidation state. The emeraldine state is the most conductive and can be further improved by doping. P-type doping occurs mainly by mixing the polymer with acids, leading to formation of positive charges (called polarons), along the backbone. The doping process can be executed either during the polymerization reaction or in a post process. When PAni materials are in their doped state they are often called in *salt* form, while the undoped state is called *base* (Figure 8B).



Figure 8: In (A) Representation of the base polyaniline structure. When Y = 1 the nitrogens are in the fully reduced state (leucoemeraldine), and when Y = 0 the nitrogens are oxidized (pernigraniline). Y = 0.5 represents the half-oxidized state of emeraldine. In (B) the structure of the salt emeraldine.

The downside of the doping process is that it affects the processability of the polymer. The base form of PAni is readily soluble in many different organic solvents, such as dimethylformamide (DMF), dimethylacetamide (DMAC), dimethyl sufoxide (DMSO), N-methyl-2-pyrrolidone (NMP), among others [24]. In contrast, the salt form has limited solubility being soluble mostly in acidic solutions or concentrated sulfuric acid. The insolubility is due to the higher coulombic forces between the polymer backbone and the counter ion than the solvent-polymer and solvent-counter ion interaction.

Doping the material after the casting of the polymer is inefficient, because the diffusion of protons within the solid is slow leading to long acid exposure and a lack of control of the doping content in the final material [25]. Increasing the processability of doped PAni is the best way to utilize this material, which can be accomplished with two modifications. The first is to use organic acids as dopant, the organic chain of the counter ion will have a better interaction with the solvent, thus improving the solubility of the polymer, in contrast to the case with smaller inorganic anions such as CI⁻. Some organic acids that have been used in this approach are the acid (CSA), sulfonic camphorsulfonic p-toluene acid (TSA) and dodecylbenzenesulfonic acid (DBSA) [26].

A second alternative is to use derivatives of PAni, substituted monomers in *para* and *meta* positions results in a material with similar properties while being more processable than the original polyaniline. An example is the poly(o-methoxy)aniline (PoMA), the o-methoxy group in the aniline monomer generates a steric effect, which reduces the Van der Waals interaction between adjacent polymer chains. A reduction of the polymer-polymer interaction will make the interaction between polymer-solvent more favorable, thus increasing the solubility of the resultant material as consequence [27]. This modification can be used in conjunction with doping using organic acids, resulting in a final material that can be easily processed.

Due to its interesting properties PAni has been used in many different applications, from protective coatings against corrosion [28], supercapacitors [29], sensors [30], electrochromic devices [31] and many others [32]. One of the applications that could fully take advantage of PAni conductive properties is as HTM in solar devices. Polyaniline has been successfully applied in this role in organic solar cells as replacement of the traditional PEDOT:PSS [33] and in dye sensitized solar cell as substitute of the liquid electrolyte [34][35].

There were similar attempts in PSC, the first being the work of Xiao *et. al.* in 2014 [36], which used PAni obtained through electropolymerization on a FTO substrate. In this attempt, the solar cell had a sandwich-like structure with the following configuration: FTO/TiO₂/Perovskite/PAni/FTO. In this case the polymer was attached to the FTO substrate at the back of the cell. The reported photovoltaic parameters obtained by this device was a Voc of 0.74V, a Jsc of 12.84 mA/cm² and a fill factor of 54%, resulting in a PCE of 5.13%. By using lithium salts as additive in PAni, the photovoltaic performance was enhanced, achieving a Voc of 0.78V, Jsc of 14.48 mA/cm² and fill factor of 65%, resulting in 7.34% of PCE.

However, this first work using PAni in PSC presented several problems, the most prominent being the adopted solar device architecture, which was heavily influenced by the old DSSC. The perovskite solution had to be injected through a hole to fill the gap between the substrates as depicted in Figure 9, and then converted to perovskite through heating. This type of process is now discontinued in favor of using a single substrate and sequential deposition, because it has an improved quality control of the deposited films. The efficiency achieved using PAni as HTM was also low compared to the standard Spiro-OMeTAD, and the use of lithium salts to increase the efficiency is undesirable due their hygroscopic nature. Later in the same year, the work of Ameen *et. al.* [37] exploring nanoparticles of PAni as HTM in PSC was published. This report presented some advances in relation to the work of Xiao, it used the standard structure with a single FTO substrate and sequential deposition of the layers (Figure 9). Compared to Xiao's work, the synthesis of PAni followed a different route, using the chemical oxidative polymerization. Although both routes can generate a similar material, the chemical oxidative polymerization allows for a higher scalability, which reduces the final cost and can make an attractive alternative for PSC future industrial production.

The work of Ameen and collaborators also presented some problems, although it is more representative of the current state of the PSC than the pioneer work of Xiao. One of the issues is that the PAni used was not doped, and similar to the first case, lithium salts were used to improve the performance of the solar device. The photovoltaic parameters achieved by the device in this work were similar to the results obtained by Xiao, the Voc was 0.87 V, Jsc of 17.97 mA/cm² and fill factor of 40%, resulting in a PCE of 6.29%.



Figure 9: Structural representations of the perovskite solar cells used in Xiao's (A) and Ameen's (B) work. References: [37][38].

Another attempt was performed by Lee and collaborators [38], which used PAni obtained through chemical polymerization route mixed with poly(styrenesulfonate), forming PAni:PSS, and applied as HTM in inverted perovskite solar cells. The best photovoltaic performance obtained in optimum condition was Voc of 0.77 V, Jsc of 15.02 mA/cm², fill factor of 57% and a PCE of 7.46%. Using the same materials but in a different concept, Lim and collaborators [39] synthetized a graft copolymer of PAni with PSS and applied as HTM in an inverted PSC. The photovoltaic parameters achieved by the device were Voc of 1.04 V, Jsc of 14.10

mA/cm², fill factor of 67.30% and a PCE of 9.70%. The latter work achieved a soluble material, unfortunately, the synthetic route to produce the graft polymer is complex to execute, which nullify one of the advantages of polyaniline.

With the exception of Ameen's work, the other studies chose to use PAni in the inverted configuration of PSC. The problem with this approach is that in inverted configuration the standard materials are changed from TiO₂ to PC₆₁BM and from Spiro-OMeTAD to PEDOT:PSS. With this change the most expensive material in inverted configuration becomes the ETM, which is the PC₆₁BM. Despite being a useful approach to test PAni effectiveness, it does not solve the problem of replacing expensive materials in PSC. Testing the beforementioned reports in normal configuration is not a realistic possibility, either due to the strategy used for polymerization or due to the solvents used for the solubilization of PAni, which degrades the perovskite.

This scenario shows that although polyaniline appears to be a viable HTM for perovskite solar cells, there are still some fabrication issues that need to be overcome to fully take advantage of what this material has to offer. To substitute the Spiro-OMeTAD, a process to produce PSC in normal configuration using a solution of PAni in doped form would be highly desirable. A direct comparation between the two types of HTM is also a factor that was overlooked in most cases in the previously cited reports.

2.2. Objectives

In this part of the current work, the objective was to synthetize and characterize polyaniline and its derivative, poly(o-methoxyaniline), in both states: undoped and doped with 4-dodecylbenzenesulfonic acid. After this initial procedure, these materials were applied as HTM in perovskite solar cells in the standard configuration. The devices were evaluated to verify how the doping process and the structural modification of the monomer would affect the photovoltaic performance and were compared to the standard device using Spiro-OMeTAD.

2.3. Methods and Procedures

2.3.1. Polyaniline and Poly(o-methoxyaniline) synthesis

The chemicals used were purchased from Sigma-Aldrich, unless stated otherwise. PAni and PoMA materials were synthetized by the oxidative polymerization method and followed the same procedure described by Gazotti et. al. [40], modifying only the monomer for each corresponding case. For the doped materials, the route began with the hydrolysis of the dopant salt, for this purpose a 70/30 (v/v)water/ethanol HCI solution containing and sodium dodecylbenzenesulfonate, both at 1.0 M, was prepared. After stirring for a 24 h period at 25 °C, the resultant solution was ready to be used as a medium to carry out the polymerization reaction. Ammonium persulfate was dissolved in 40.0 mL of this solution with a concentration of 0.375 M, forming solution A. Previously distilled aniline (or o-methoxyaniline in the case of PoMA) was diluted in 100.0 mL of the same medium solution, forming solution B with a concentration of 0.10 M. 200 µL of a saturated CoSO₄ solution was added to solution B, to act as catalyst. Solution B was kept in an ice bath with a magnetic stirrer while solution A was transferred to a dropping funnel and then added to solution B dropwise. After the addition finished, the resultant solution was left stirring and kept at 0 °C for 6 h to proceed with the polymerization. After this period, the resultant solution was vacuum filtered through a Durapore 0.22 µm membrane and the precipitate was washed with ethanol until the filtrate was colorless. The final material was a dark green solid that was left to dry for 18 h at 25 °C and then transferred to a vacuum oven at 50 °C for 6 h to finish the drying process. The final solid was grounded and stored in a close recipient.

For the polymeric materials without dopants, the procedure consisted of initially synthetizing another batch of PAni and PoMA doped with HCI and then remove the dopant. For the first reaction, the medium was changed to an aqueous solution containing 1M HCI and 3 M NaCI and then the polymerization reaction followed the same procedure described above. After the drying process, the resultant solid materials were suspended in 100 mL of an aqueous solution of 10% (v/v) NH₄OH and left stirring 24 h to completely remove the dopant from the polymers. After this period, the resultant materials were vacuum filtered and then washed with
deionized water until filtrated reached pH 7. The wet solid was then dried using the same process described for the doped polymers.

2.3.2. Device Fabrication

The devices were assembled by successive deposition of each layer by spin coating, using a fluorinated tin oxide glass (FTO glass, Hartford 20 Ω/sq) as substrate. The first step consisted of partially etching the substrates with zinc powder and HCI 2.0 M. Then the FTO was cleaned with detergent followed by an ultrasonic bath with water, acetone, and then isopropyl alcohol. Prior to use, the substrate was treated with UV-ozone for 30 minutes. The blocking layer was made using a 0.15 M solution of titanium diisopropoxide bis(acetylacetone) in 1-butanol. The precursor solution was spin coated on top of the substrate at 2000 rpm for 20 seconds, followed by annealing at 125 °C for 5 minutes. After the substrates were cooled down to room temperature the mesoporous layer was deposited using a 150 mg/mL 18-NRT paste (Dyesol) dispersed in ethanol and deposited at 5000 rpm for 30 seconds (Figure 10, Step 1). The substrates containing the mesoporous layer proceeded to a second annealing that consisted of two phases: at 150 °C followed by 500 °C for 30 minutes each.

The methylammonium iodide used in the perovskite precursor was synthetized by an equimolar reaction between hydriodic acid (HI, 57% in water) and methylamine (40% in water). The reaction mixture was stirred for 2 hours in an ice bath and afterwards the solvent was removed in a rotary evaporator. The resultant solid was dissolved in ethanol and recrystallized with diethyl ether, filtrated, and then dried in a vacuum oven at 50 °C for 12 hours. The precursor solution contained equimolar PbI₂ and MAI at the concentration of 1.3 M, dissolved in a DMF/NMP 7:1 (v/v) solution. The deposition of the perovskite occurred with the anti-solvent method, for this procedure the spin coating program followed two steps: the first at 1000 rpm for 15 seconds and the second at 4000 rpm for 24 seconds. 300 μ L of diethyl ether was used as the anti-solvent and was dropped onto the sample during the second step, forcing the crystallization of perovskite. After this procedure, the substrate was placed on top of a hot plate at 100 °C for 10 minutes to remove any residual solvent (Figure 9, Step 2).

Part of the proposed work is to compare the performance of devices containing the polymeric HTM with a standard using Spiro-OMeTAD. For the latter, a 1.0 mL stock solution of chlorobenzene with the following composition was prepared: 80.0 mg of Spiro-OMeTAD, 32.0 μ L of 4-tert-butylpyridine, 18.0 μ L of a LiTSFI solution (170 mg/mL in acetonitrile) and 32.6 μ L of a H₂SO₄ solution in ethanol (0.2 M). The Spiro solution was spin coated at 3000 rpm for 45 seconds. For the devices based on polymeric materials, a precursor solution containing 100 mg/mL of the polymer in each respective condition with m-cresol as solvent was used. For polymeric based HTM, the spin coating procedure consisted of 4000 rpm for 60 seconds (Figure 10, Step 3), however, in the case of PAni more material was added during the initial 30 seconds of spin coating to ensure the complete coverage of the sample (Figure 10, Step 4). After the deposition procedure, the substrates were placed on top of a hot plate at 70 °C to remove any residual solvent.



Figure 10: Illustration of the device fabrication procedure.

Post HTM deposition, the samples were transferred to a nitrogen filled glove box. A thin layer (70 nm) of gold or silver was thermal deposited on top of the samples, forming the contacts of the solar device. The active area of the solar cells was determined by the overlap of its constituting layers, being the same for all devices: 0.15 cm². A photography of a device in each condition is shown in Figure 11. After these procedures, the devices were individually transferred to a sample

holder and their performance was measured, without leaving the glovebox atmosphere.



Figure 11: Photography of a solar cell containing polymer materials as HTM.

2.3.3. Characterization Fourier-transform infrared spectroscopy (FTIR)

The polymer-based materials had their IR spectra taken in an Agilent Cary 630 spectrometer. The samples were transformed into pellets by mixing the powder with KBr and applying a 7 MPa pressure into the mixture.

Ultraviolet-visible spectroscopy (UV-Vis)

An Agilent Cary 60 was used to take the UV-Vis spectra of the polymer solutions in m-cresol, in the 1000-300 nm region.

Hall Effect

Hall effect measurement was taken in an Ecopia HMS-3000, using a Van der Pauw geometry, with a current of 200 μ A and a field of 0.55T

Cyclic Voltammetry

Cyclic Voltammetry was carried on an Autolab Potentiostat using a threecompartment cell with Ag/AgCl in ethanol saturated LiCl as the reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile was used as electrolyte and ferrocenium/ferrocene couple as standard. The samples were deposited over a bare FTO. The voltage sweep was carried at speed of 20 mV/s. After the measurements, the onset potentials were converted to Normal Hydrogen Electrode (NHE) values and used to calculate the energy levels of the bands.

X-Ray Diffraction (XRD)

X-Ray diffraction was performed in a Shimadzu XRD 6000 with Cu K α with wavelength of 0.154 nm with a step size of 0.05° and a scan rate of 2°/min.

Field Emission Gun Scanning Electron Microscope (FEG-SEM)

FEG-SEM images were taken in a FEI inspect F50 with beam acceleration of 20 kV and working distance around 9 mm.

Measurement of solar cell performance:

Solar cells were characterized using a Sciencetech class AAAcalibrated with a reference silicon solar cell with KG5 filter in AM1.5 G to 100mW/cm². The JV curves were carried out using a Keithley 2400 sourcemeter, in forward (from 0 to 1.0 V) and reverse (from 1.0 to 0 V) scan. The delay time used was 0.50 s with step of 25 mV resulting in a scan rate of 50 mV/s. The mean photovoltaic values were obtained by at least six different devices.

Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance plots were taken in an Autolab potentiostat in a frequency range of 1 MHz–0.1 Hz, under illumination at 0 bias voltage.

2.4. Results and Discussion

The polymeric materials were characterized after their synthesis to verify the oxidation state and if the doping process was successful. The structural difference between PAni and PoMA samples is noticeable in FTIR spectra of the polymers (Figure 12). A shoulder in 1450 cm⁻¹ is apparent both in doped and undoped samples of PoMA and is related to C-H vibrational modes in the methoxy group. Differentiation between the two types of polymeric materials is also evident by a band in 1011 cm⁻¹ relative to a C-O-C stretching [41][42].

Distinction between doped and undoped states of the polymer can also be observed by the FTIR spectra. In the doped samples there is an absorption band around 1114~1121 cm⁻¹, related to vibration modes of $-NH^+=$ structure. This band has a strong absorption in relation to the rest of the spectrum and is a signal of positive charges along the polymer chains, confirming the success of the doping process [43][44]. In the case of the undoped samples, two absorptions are evident in 1110 and 1164 cm⁻¹ (1121 and 1168 cm⁻¹ for undoped PoMA), related to the vibrational modes of N=Q=N (Q = quinoid structure) and B-NH-B (B = benzenoid structure), respectively [45]. A band at ~1380 cm⁻¹ in the spectra of the undoped samples can be attributed to C-N structure in Q-B-Q unit and this is a characteristic absorption band of the emeraldine base form [43][45]. Besides, in doped samples, vibrational modes of the dopants at 620~670 cm⁻¹ and 1041 cm⁻¹ are observed for PAni and PoMA and assigned to S-O stretching of DBSA backbone [46].



Figure 12: FTIR spectra of the PAni (A) and PoMA (B) based materials.

Two bands are present in every FTIR spectra of PAni and PoMA samples, regardless of its doping state, they are situated around 1560~1585 and 1470-1500 cm⁻¹ and are related to the absorption by the quinoid and benzenoid rings, respectively. Those bands arise from the vibration of -C=C- in amine and imine units. The relativity intensity of those bands (Iquinoid/Ibenzenoid) can be used to obtain the oxidation state of the polymer [46]. Since the polymer materials can contain only quinoid or benzenoid rings, the oxidation state can be obtained using the Equation 6 [27]:

$$X + X\left(\frac{I_{Quinoid}}{I_{Benzenoid}}\right) = 1$$
 (Equation 6)

Since these bands are not well defined in some of the samples, only a qualitative estimative can be draw from the FTIR spectra. Picking the point correspondent to the lower transmittance, the ratio between the absorptions of quinoid and benzenoid structures was close to 1, resulting in an oxidation degree value close to 0.50 in every sample (Table 1).

Sample	Oxidation State
PAni-DBSA	0.50
Undoped PAni	0.50
PoMA-DBSA	0.49
Undoped PoMA	0.48

 Table 1: Oxidation state of polymeric samples.

The UV-Vis spectra of the polymer samples are heavily dependent on its electronic configuration and can be affected by both the doping and oxidation states. The FTIR data shows that the polymer samples have the same oxidation state, consequently the major differentiator is the presence of the dopant. Doped polymers have more absorption bands due to a higher number of possible transitions, a consequence of the half-filled intra-band called polaron band (Figure 13). The first absorption is a π - π * transition, it occurs in all samples since it is related to the intrinsic structure of the polymer backbone. This absorption appears at 350 nm for doped materials and is blue shifted to around 322 nm (305 nm for PoMA) in undoped samples. The second band that occurs in doped samples is located around 420 nm

and is related to polaron- π^* transition, this band is exclusive to doped samples since the undoped polymers do not have the polaron band to generate this transition. There is a third band apparent in the UV-Vis spectra of the polymer samples, this absorption band originates from different sources in the doped and undoped materials. In doped PAni the third band is around 831 nm (790 nm for PoMA) and reflects the doping degree of the polymer, in doped materials this band is assigned to the π -polaron transition and is often called polaronic band [47][41]. In undoped PAni the origin for the band at 685 nm (660 nm for PoMA) is due a local charge transfer between quinoid and benzenoid rings (intramolecular charge transfer exciton) [48]. The beforementioned wavelength values are relative to their maximum absorbance, however due to the broad absorption of some of these transitions (e.g. the π -polaron in PAni) the sum of the energy of the π -polaron plus the polaron- π^* exceed that of π - π^* transition.





The results obtained from FTIR and UV-Vis spectroscopy shows that the synthetic route employed was successful in generating both PAni and PoMA materials in the emeraldine state and that the doping process occurred flawlessly in the desired samples. The next set of characterization procedures were used to determinate other properties of PAni and PoMA and correlate these properties with the photovoltaic performance of the solar cells using these polymers as HTM.

Thin films of the doped polymers were cast on a glass substrate and a Tauc-Plot was derived from the UV-Vis spectra of the thin films using the following formula:

$$\alpha h \gamma = A(h \gamma - E_{gap})^m$$
 (Equation 7)

Where, α is the absorption coefficient, A is a constant and E_{gap} is the energy of the band gap. The value of m can vary (1/2, 3/2,2...) depending on the type of the transition. In the case of a direct and allowed transition (as is the case of PAni and PoMA) the value 1/2 is used. By plotting a $(\alpha h \gamma)^2 \times h \nu$ graph, it is possible to estimate the optical band gap by doing an extrapolation of the linear portion of the absorption edge (Figure 14). For PAni, the optical band gap value is 2.5 eV while for PoMA this value was a found to be slightly higher, at 2.6 eV, these values are similar to other reports involving PAni and PoMA [49][50], they are mistakenly named as the band gap of the polymer; instead they should be interpreted as excitations involving the polaron band [51].



Figure 14: Tauc-Plot of doped PAni and PoMA films.

Cyclic voltammetry of the polymer films was used to estimate the energy of the highest occupied molecular orbital (HOMO) of the doped polymers. The voltammograms of the polymeric materials (Figure 15) had their onset oxidation potential measured, ferrocenium/ferrocene standard couple was used to minimize the errors associated to this type of measurement.



Figure 15: Cyclic voltammetry of the doped polymer films

Once the obtained oxidation potentials are converted to the normal hydrogen electrode (NHE) values, the HOMO energy can be estimated by the formula [52]:

$$E_{HOMO} = -(E_{onset,ox vs NHE} + 4,75) eV$$
 (Equation 8)

The estimated energy of the HOMO for PAni is -5.39 eV and for PoMA -4.90 eV. These values can be used in conjunction with the energy of the band gap obtained previously to estimate the energy of the Lowest Unoccupied Molecular Orbital (LUMO):

$$E_{LUMO} = E_{HOMO} + E_{GAP}$$
 (Equation 9)

With these values, it is possible to build an energy diagram of the PSC containing different materials (Figure 16).



Figure 16: Energy diagram of the materials used in the perovskite solar cells.

The estimated HOMO and LUMO of PAni and PoMA polymers indicate that the synthesized materials are compatible to the energy levels of perovskite. Injection of holes into the polymer are expected to occur flawlessly and due to the LUMO energy of the polymers being situated much higher than that of perovskite the polymers will also act as an efficient electron blocking layer. The diagram also indicates that a lower performance is expected for the case of a device using PoMA and gold as metallic contact due to their energy mismatch.

Hall effect was used to measure the conductivity of the polymer materials. Doped PAni conductivity (2.48 S cm⁻¹) is 3 orders of magnitude higher than doped PoMA (8.06 x 10⁻³ S cm⁻¹). Other interesting parameters obtained from Hall Effect is the mobility and concentration of charger carriers, for PAni these values were 3.71 × 10^{-2} cm² V⁻¹ s⁻¹ and 4.16 × 10^{20} cm⁻³ and for PoMA 2.47 × 10^{-1} cm² V⁻¹ s⁻¹ and 2.04 × 10^{17} cm⁻³, respectively. Although the mobility of the charge carriers was one order of magnitude higher for PoMA, the carrier concentration is much lower than PAni. The overall conductivity of the material is calculated by:

$\sigma = n\mu e$ (Equation 10)

Where n is the concentration of carriers, μ their mobility and e the elementary charge [53]. For comparison, in the literature the conductivity of Spiro-OMeTAD is reported to be 10^{-3} - 10^{-4} S.cm⁻¹ [54][55], which is lower than the values obtained by both doped polymers, reassuring that these materials can be promising alternatives to Spiro-OMeTAD in PSC. Regarding the undoped polymers, it was not possible to determinate the conductivity of these materials as they are below the limit of experimental setup. In the literature the value of base emeraldine PAni can be as low as 10^{-10} S.cm⁻¹ [56].

After the initial characterization, the polymeric materials were used to assemble perovskite solar cells. The adopted structure was the n-i-p configuration in order to have a platform to compare the performance of Spiro-OMeTAD to the polymeric materials. X-ray diffraction of FTO/TiO₂/CH₃NH₃Pbl₃ displayed sharp and intensive peaks due to the high crystallinity of the material (Figure 17), resultant of the anti-solvent method used to deposit the perovskite layer. The diffraction peaks at $2\theta = 14.1^{\circ}$, 28.4° and 31.9° can be assigned to the crystallographic planes (110), (220) and (310), respectively, and are related to the tetragonal perovskite phase,

which exist at room temperature [57]. Other peaks shown in the diffraction pattern can be assigned to the FTO substrate. A small peak can be spotted at 11.40°, related to Pbl₂ phase due incomplete conversion of the precursors into perovskite. Although it is undesirable, a small quantity of Pbl₂ (< 5%) is not detrimental for the performance of the photodevice [58].



Figure 17: X-ray diffraction pattern of FTO/TiO₂/CH₃NH₃PbI₃.

Perovskite deposition using the anti-solvent method was developed shortly before this work and was a breakthrough compared to the other procedures that were used before. The FEG-SEM images (Figure 18) shows that this deposition generates a dense perovskite layer, with grains having size within 100 to 400 nm and possessing edges shared with adjacent grains. With this concise formation of grains, there are only a few signs of pinholes in the perovskite film. The lower magnification image shows that the perovskite completely covered the TiO₂ mesoscopic layer.





Figure 18: FEG-SEM images of the perovskite layer.

The initial attempts to deposit doped PAni over the perovskite layer presented an issue. Although a high concentration of polymer was used in the deposition procedure, it has not effectively covered the entire surface of the perovskite. The red arrows in Figure 19 shows the pinholes in the polymeric layer where it is possible to observe the perovskite beneath. This condition is undesirable because it can lead to a performance loss, most of the devices measured in this condition had almost no photovoltaic effect and became shunt.



Figure 19: FEG-SEM image of the polyaniline layer, the red arrows highlight the voids on the polymeric layer.

A countermeasure to solve this problem was to further add PAni solution during the spin coating process, with this change the voids in the polymeric layer was mitigated, as can be seen in Figure 20. Despite the improvement, the morphology of the PAni layer visually indicated that thickness remained small. This fact is observed in high magnification FEG-SEM images, in which is possible to observe that the polymer resembles the shape of the perovskite grains that exist beneath. A cross section of the device confirms that the thickness of PAni lies within the range of 50-150 nm.



Figure 20: FEG-SEM images of the doped PAni layer in different magnifications. In (D), a cross-section of the device containing PAni as HTM.

PoMA on the contrary, did not present the same issue as PAni. A single application of the precursor solution during the spin coating was enough to generate a polymeric layer without voids (Figure 21). Direct comparison to previous case clearly shows that PoMA has a better capacity to create a good polymer layer. The morphology of the PoMA layer also differ; from above the layer seems smoother and the perovskite grains are not recognizable, which suggests that the thickness has increased in comparison to PAni. This hypothesis is proven to be correct by the cross section, which shows that PoMA can reach up to 700 nm in thickness.



Figure 21: FEG-SEM images of the doped PoMA layer in different magnifications. In (D), a cross-section of the device containing PoMA as HTM.

The strikingly change in the morphology is a consequence of the difference of each polymer at the molecular level. The o-methoxy group existent in PoMA induces a steric effect which reduces the interaction between polymer chains, increasing the polymer-solvent interaction and consequently making PoMA much more soluble than PAni. As the solvent volatilize during the spin coating the concentration of the polymer in the wet film increases, in the case of PAni since the interaction between polymers chains is more favorable this will lead to regions with agglomerate of PAni and others without any cover. A better interaction between the polymer and the solvent also lowers the surface tension of the solvent so it can spread more evenly over the substrate during the spin coating, which can also be a factor that resulted in better films obtained with PoMA.

A device with FTO/TiO₂/CH₃NH₃PbI₃/Spiro-OMeTAD/Au configuration was assembled to serve as standard, for posterior comparison against the devices containing the polymeric materials. At the time that this work was performed, the standard device produced in our laboratory could achieve a Voc up to 0.96 V and a Jsc that reached 21~22 mA/cm², resulting in a PCE around 10% (Figure 22). The hysteresis between forward and reverse scans was also more prominent in the research done in the early days of PSC.



Figure 22: JV curve of the standard device.

Table 2: Photovoltaic parameters of the standard device.

	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)
Forward	0.96	19.65	43.36	8.18
Reverse	0.95	18.90	56.01	10.06

For the polymeric materials, the first adopted structure used silver as the metallic contact, a choice based in Ameen's previously published work [37]. In this condition, devices containing PAni achieved 3.34% PCE while PoMA displayed a superior performance, reaching up to 5.69% (Figure 23). From the photovoltaic parameters, the superior performance displayed by PoMA is a consequence of its higher Jsc and Fill factor in comparison to devices with PAni.



Figure 23: JV curve of doped polymers as HTM and Ag as metallic contact.

	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)
PAni Forward	0.78	9.86	38.33	2.93
PAni Reverse	0.72	10.19	45.23	3.34
PoMA Forward	0.82	15.28	38.59	4.86
PoMA Reverse	0.82	16.52	41.71	5.69

Table 3: JV parameters of the devices using doped polymers and Ag as metallic contact.

Devices with the undoped polymers were assembled in the same condition used above to observe the influence of the dopant in the device performance. Once again, devices containing PoMA performed better than those with PAni, showing that under this set of parameters the PoMA outperforms PAni as HTM (Figure 24). Comparing both doped and undoped conditions, it is clear that the absence of the dopant in the polymer negatively affects the performance of the solar device. The current density of the devices containing undoped polymer is the photovoltaic parameter that is most affected by this change, going from 16 to 10 mA/cm² in the case of PoMA (from 10 to 6 mA/cm² in the case of PAni). This behavior is direct consequence of the lower conductivity of these undoped materials.



Figure 24: JV curves of the devices containing the undoped polymers as HTM.

	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)
PAni Forward	0.60	4.77	27.89	0.80
PAni Reverse	0.65	5.44	36.56	1.29
PoMA Forward	0.82	8.44	34.24	2.38
PoMA Reverse	0.82	9.52	40.81	3.20

Table 4: JV parameters of the devices using undoped polymers and Ag as metallic contact.

The PCE values obtained by the devices using doped polymeric materials are far lower than those using the standard configuration. The low current density obtained by these devices in comparison to the standard is the main culprit for their low performance. This situation motived the change of the top metallic contact to check if it could have any influence in the performance of the solar device. This modification resulted in a performance far different from what was observed so far. The device containing PAni had a better performance than PoMA and could achieved 10% PCE in the reverse measurement (Figure 25), which shows that this material has the potential to match the performance of the device with Spiro-OMeTAD.



Figure 25: JV curve of doped polymers as HTM and Au as metallic contact.

	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)
PAni Forward	0.70	18.81	37.18	4.90
PAni Reverse	0.88	17.73	64.42	10.05
PoMA Forward	0.82	10.14	37.52	3.14
PoMA Reverse	0.80	11.50	41.24	3.79

Table 5: JV parameters of the devices using undoped polymers and Au as metallic contact.

Some observations can be drawn from the results presented above. Firstly, it is noticeable a high degree of hysteresis in all conditions, especially in the device with PAni as HTM and gold as metallic contact. This effect can be associated to an increase in the capacitance in the perovskite/polymer interface, cause by the presence of the ionic dopant in the HTM. Under the effect of an external electrical field the ions can migrate and accumulate at the interface, modifying the energy levels and creating an energy barrier to the injection of electronic carriers [59]. The observed underperformance of PoMA in this condition was also expected, as discussed earlier, and is a direct consequence of the energy barrier created by the mismatch of the energy levels between PoMA and Au, as seen in the energy level diagram of Figure 16.

Electrochemical impedance spectroscopy of the solar devices containing doped polymers was conducted in order to obtain a better understanding of their functionality. A comparison can be made within the devices with the same set of metallic contact, in this case the HTM will be the sole differentiator of their performance. The Nyquist plots from the devices shows two distinct charge transport regimes, characterized by the two semicircles (Figure 26). The impedance associated with the first semicircle situated in the high frequency region located near the origin is related to the charge transfer at the electrode interface [60]. On mid frequencies the impedance is relative to interface of the perovskite layer and the TiO₂/HTM, it is possible to observe only half of the second semicircle, the slope at its beginning is close to 45°, which suggests that some process involved with diffusion is also occurring.

By using an equivalent circuit to fit the experimental data to the model it is possible to obtain certain parameters and have a better insight of the device operation. From the first semicircle, it is possible to obtain the series resistance (R_s) which accounts for the ohmic contribution of contacts and wires. The fitting of the first semicircle is also adjusted with a resistive element (R_r) and a capacitive element in parallel, represented by a constant phase element (CPE), as shown in the inset of Figure 26. The linear part of the second circle can be adjusted by a Gerischer element (Ge), the physical meaning of this element is that the perovskite layer can be considered a reservoir of electrochemically inactive species with infinite dimensions and the region from which it is possible to collect charges is thinner than thickness of the sample. The consequence of the Gerischer element appearance is that the transport resistance (R_{tr}) and recombination resistance (R_{rec}) cannot be distinguished and only a resultant resistance, the Gerisher resistance (R_G), can be obtained. According to Bisquert *et. al.* [61] the transport resistance has a major role in the resultant resistance as R_{tr} > R_{rec} and is given by:

$$R_{tr} = \frac{L}{\sigma A}$$
 (Equation 11)

Where L is the thickness of the layer, A is the area and σ is the conductivity.



Figure 26: Impedance spectra of PSC using Spiro-OMeTAD, DBSA-doped PAni and PoMA as HTM. The dots represent the experimental data, and the full line is the fitting model. The inset shows the equivalent circuit used.

	R _s /Ω	R _r /Ω	CPE			R_G / 10 ³ Ω
			Y₀ / nFs ⁿ⁻¹	n	С	1
Spiro Au	4.41	23.55	52.0	0.889	100.33	1.11
Pani Au	3.95	24.00	27.6	0.919	41.18	2.01
PoMA Au	4.02	34.05	154.0	0.787	851.11	3.56
Pani Ag	4.63	25.65	49.3	0.871	107.52	4.57
PoMA Ag	3.86	26.55	182.0	0.788	1023.44	1.93

 Table 6: Resistance values (R) obtained by electrochemical impedance spectroscopy (EIS) of the PSC using different HTM materials.

The series resistance obtained from the EIS fitting does not show much variance across devices with different compositions, as is expected due its main contribution coming from the wires and contacts. The R_r presents a small variation across the samples in different conditions, except for PoMA with gold as electrode, in this case the R_r presents a deviation from the rest of the devices. This parameter is obtained by the fitting of the first semicircle and is relative to the resistance at the back electrode and its high value is correlated to the energy barrier created by the energy mismatch between PoMA and gold. The capacitance associated with the charge transfer was estimated from the admittance obtained from CPE element using the formula:

 $C = Y_o^{\frac{1}{n}} (Rs^{-1} + Rr^{-1})^{\frac{n-1}{n}}$ (Equation 12) Reference: [62]

Devices made with PoMA as HTM had higher capacitance compared to those with PAni, showing that that there is a greater charge accumulation at the interfaces between the layers of the devices made with the former. This result is a consequence of the lower conductivity displayed by PoMA in comparison to PAni.

From table 6, the parameter that has the best correlation between its values and the performance found for the devices is the Gerischer resistance. The lowest Gerischer resistance is obtained for the device with Spiro, followed by cells containing polymers that showed best efficiency in each situation, PAni-DBSA-Au and PoMA-DBSA-Ag. By the reasons explained before, the device with PoMA and Au cannot present a high performance, this fact is also reflected in its R_G value that is situated higher than the conditions with Spiro, PAni-Au and PoMA-Ag. Surprisingly,

the device with PAni and silver as electrode presented the highest R_G of all cases. This result shows that there is another factor for which PAni could not achieve a high performance with silver as electrode.

Unlike the case of PoMA with Au, the low efficiency of the device containing PAni as HTM and Ag as electrode does not seem to be linked to an energy barrier created between the two materials, nor it is caused by a poor charge transport performance of PAni, since the polymer presented a good result with Au. Based on these points, the deviation observed in this configuration may be linked to a different reason, which can be speculated based on the collection of results obtained so far. As seen in FEG-SEM images, the PAni layer can become thin in some places and it is more prone to the appearance of pinholes, which facilitates the contact between the perovskite and Ag. The iodine existent in the perovskite can react with silver forming AgI, this reaction promotes the degradation of the photoactive layer and leads to a loss of performance, mostly due a drop of Voc [63][64], as observed in the JV curve of doped PAni with Ag as electrode (Figure 23). It seems that that the further addition of PAni during the deposition was not enough to completely avoid this problem, as this phenomenon is also evident when comparing samples containing undoped PAni and PoMA with silver as electrode (Figure 24). This process also explain the high R_G found for this configuration: with the perovskite degradation the resistance would increase due the contribution of transport resistance within the cell (Rtr).

These analyses led to a better understanding of the operation of these solar devices, making possible to draw some conclusions on the viability of these polymers as HTM in PSC. Although the solar device with PAni as HTM and gold as electrode achieved similar performance to the one containing Spiro-OMeTAD in its best result, the Spiro has a higher average PCE. This is due to the slightly higher Voc that can be achieved by Spiro in comparison to PAni; with the former the Voc is usually above 0.90 V while with the latter it stays below this value. The Voc obtained in this experiment seems to be the limit for this type of polymer, from the studies using PAni cited previously, 3 out of 4 displayed the same behavior with the device possessing a Voc below 0.90 V, the exception is the work of Lim [39] which used a grafted copolymer of PAni and PSS. In this regard, Spiro-OMeTAD seems to have an advantage over PAni due to the higher limit of Voc that can be achieved. The

conclusions discussed previously are aligned to the statistical results displayed in tables S1, S2, S3 and S4 in appendix.

From the results demonstated above PAni based materials are viable to be used as hole transport materials in n-i-p configuration, despite their simplicity. In order to achieve a high performance, these materials must be in the doped form and optimization of the film deposition must be carried on. One last advantage of these materials is that they can also be used as a base platform for further development; with different monomers or using dopants containing other type of chains, different properties could be obtained. This could be a viable strategy to produce PAni derivatives that could both function as HTM and enhance other properties of the device, for example, increase of the stability by protecting the perovskite layer from the outside water.

2.5. Conclusions

In the present work it was shown the viability of the PAni based materials as HTM in perovskite solar cells with n-i-p configuration. The use of dodecylbenzenesulfonic acid as dopant in both PAni and PoMA increased their conductivity while allowed for the resultant material to partially retain their processability. With m-cresol as solvent, the polymeric materials could be deposited over the perovskite without noticeable degradation.

The doping process is a crucial step for these materials to be applied as HTM as the base materials does not possess enough conductivity, devices with undoped materials achieved only 1.2% and 3.2% for PAni and PoMA, respectively. The devices built with doped polymer materials as HTM achieved low efficiencies of 3.3% for PAni and 5.6 % for PoMA. These results motivated the investigation and posterior change of the metallic contact to gold. After this change, the devices could reach up to 3.7% with PoMA and 10.0% with PAni, the latter performing at similar level of the standard device using Spiro-OMeTAD.

The results also emphasize that, in relation to new materials and their properties, multiple factors are determinant for a device to be able to perform reasonably well or not. This observation is evident by the fact that PAni had a higher conductivity and yet was outperformed by PoMA with silver as electrode, due to the better film formation of the latter. On the other hand, despite the higher quality of PoMA films, it could not have a good performance with gold as electrode due the energy mismatch, while PAni had the highest performance of all conditions tested.

The efficiency achieved in perovskite solar cells using Spiro-OMeTAD is outstanding, this is one of the reasons of why it still a standard material in high performing perovskite solar cells with n-i-p configuration up to this day. Nevertheless, the results shows that polymeric materials can be used as hole transport layer in PSC and still performs at similar level of the Spiro-OMeTAD despite being simpler and costing a fraction of its price. Among the possible polymers, polyaniline-based material may be one of the most promising due the low production cost and the possibility of being modified in order to obtain enhanced properties, which can result in devices with high performance.

3. Production of perovskite solar cells through blade coating

3.1. Introduction to scalable methods

The research of perovskite solar cells is heavily based on the use of the spin coating as the method of choice to deposit each layer that compose the device. This trend began in the early days of PSC research and has not changed much, thankfully to the advantages of this technique such as simplicity and low cost combined with the capability of producing uniform films.

In spin coating, the substrate is hold on its place by vacuum or by using a sample holder, then a solution is spread over the substrate and the sample is submitted to a high-speed rotation, expelling the excess of solution from the substrate by the centrifugal force. Shortly after the rotation begins, a thin wet film is formed and starts to dry due to the evaporation of the solvent [65]. The conversion of the wet film into the dry film depends both on the volatility of the solvent and the speed of the substrate rotation, higher rotational speeds promote a faster evaporation due to the effect of the air on top of the substrate.

Despite being the most used method to assemble PSC, this technique however has several limitations. Spin coating only allows production in batches since only one sample can be loaded in the equipment at a time, other constrain is that the size of the sample is limited, usually up to 5x5 cm. The last disadvantage is that most of the solution used in spin coating is wasted during the substrate rotation. Most of these disadvantages does not have a big impact in a laboratory environment, however these characteristics make the spin coating deposition an unrealistic option in future production and commercialization of these devices.

To make this technology a reality in the future, it is imperative for these devices to be built with a technique that allows scalability: deposition in a large area and preferentially in a continuous flow production. There is a group of methods that can fulfill those requirements taking advantage from perovskite ability of being produced from solutions. These methods rely on the formation of a meniscus to coat the solution (also called as *ink* in these methods) over the substrate to form a wet film. These methods can be referred as *'meniscus-guided'* deposition due their

unique way of functioning. Some of the methods that can be fitted in this group is the dip coating, blade coating, slot-die and roll-to-roll [66].



Figure 27: Illustration of the meniscus guided deposition techniques: dip coating (A), blade coating (B) and slot-die (C). Reference: [66]

Dip coating is the most peculiar process from the beforementioned group, the unique way that it operates generates the same issue as the spin coating: only one sample is produced per batch and so this process is also impractical for mass production of perovskite solar cells. Blade coating and slot-die have many similarities between them, both can produce a film over a large area due the meniscus being carried over the substrate by the '*printing head*' (slot-die) or '*knife*' (blade coating). In blade coating the meniscus is formed between the substrate and the knife before the deposition while in slot-die the solution is continuously fed into the printing head.

While blade coating and slot-die are usually employed in substrates that can be centimeters long, the roll-to-roll (abbreviated R2R) technique is more suitable to produce lengthy substrates that can be meters long and in a continuous flow regime. In R2R a flexible substrate is used, generally made of PET covered by a layer of ITO, that is pulled across the machine with a constant speed. The R2R can be multi stationary; numerous materials can be deposited at the same time by multiple slot-dies placed along the machine, it is also possible for the substrate pass through several ovens to undergo different types of annealing [67].



Figure 28: Scheme of a roll-to-roll machine deposition. Adapted from [67].

The methods employing meniscus guided deposition have been successfully applied to produce an older type of solar cells, the organic photovoltaics (OPV) [68]. Nowadays the OPV technology can be bought on the market, showing that the manufacturing and commercialization of the PSC using the same process is feasible. However, for perovskite solar cells to achieve the same level of technology maturity displayed today by OPV it will be a more difficult task than it was in the past with OPV. That is because the process of formation of a perovskite film involves not only the deposition of the wet film followed by subsequently removal of the solvent, but also the crystallization of the perovskite itself, which is a critical step in the film formation.

Control of the perovskite crystallization process in spin coating took several years to achieve the level that is observed today with the anti-solvent method [69]. Unfortunately, due the big difference between the mechanics governing the spin coating deposition and the methods using a meniscus, most of the knowledge about film formation cannot be direct translated from spin coating to roll-to-roll [70]. This means that for the methods employing a meniscus, the deposition of the perovskite must be optimized from the beginning.

The task of optimizing the film deposition usually involves testing multiple compositions and physical parameters that needs to be extensively changed. With this type of experiment which has a lot of variability, both slot-die and roll-to-roll are not the most suitable techniques to obtain the initial deposition parameters. This is because they need a considerable amount of solution to fill the reservoir, the pipes and the printing head of the slot-die, this dead volume makes the job of testing different compositions an inefficient task, since most of the solution goes to waste. In blade coating this type of experiment is done more easily: there is no dead volume to fill, and to test another ink composition during the experiment is as simple as cleaning the knife and changing the substrate to a new one.

The blade coating technique is useful to understand the working mechanism of the meniscus guided deposition methods and to find the first set of parameters that can be used to build a process to assemble perovskite solar cells. Important parameters such as gap between the knife and the substrate, concentration, composition of the precursor solution (also referred as *ink*) and speed of the knife can be fine-tuned before being applied in other scalable methods.

While the effect of concentration and composition of the ink in the final film is straightforward, the influence of the gap and the blade speed is not, at first, clearly evident. The blade height generates a wet film that is approximately half of the gap between the knife and the substrate (Figure 29-A) [71]. However, this relation is only true in high-speed deposition regimes (>200 mm/s) which is far higher than the usually employed in laboratorial experiments. In lower speeds the effect of the blade height diminishes, and the thickness of the film is better tuned by the other parameters.

The knife sweep speed also affects the film formation. In evaporation regime, the knife moves at extremely low speeds (~10 μ m/s), in this condition the solvent has enough time to evaporate right after the meniscus moves to the adjacent unit length (Figure 29-B) [66]. The evaporation of the solvent governs the film formation and in this regime the thickness is inversely proportional to the speed of the blade. However, this regime is impractical for PSC fabrication due its extreme slow speed. By increasing the meniscus sweep velocity, the Landau-Levich regime govern the film formation. In this mode, the blade speed is much faster than the evaporation and the coated film is still wet after the meniscus is swept (Figure 29-C) [72].



Figure 29: In A, the influence of the blade height into the wet film thickness. In B, the film formation in the evaporation regime and in C the wet film formed in the Landau-Levich mode. Adapted from: [61][66].

From the topics discussed before, it is clear that blade coating can be a very useful technique to study the assembly of perovskite solar cell through meniscus guided deposition. Important parameters can be studied and fine-tuned and then transferred to the other meniscus guided deposition (slot-die and R2R).

3.2. Blade coated perovskite solar cells

Production of PSC through scalable methods have the challenge of controlling the crystallization of the perovskite during the transition from wet film to dry film. The crystallization of the perovskite film is often explained using a LaMer model of particle nucleation and growth [73]. In Figure 30-A the graph is representing an isothermal evaporation of the wet film over time. As the solution begins to evaporate, the concentration of the solutes increases, until the saturation point is reached (Cs on graph). As the solvent continues to evaporate the wet film reaches the critical concentration (Cc), while the concentration is above this point, crystallization nuclei are constantly generated and grow over time. As more solvent is removed from the wet solution the concentration of the resulting wet film rises continuously, increasing the rate of nucleation. As time passes, the generation and grow of crystals consume the solute present in the wet film, decreasing the overall concentration. When the consumption of the solutes decreases the concentration to the critical point (Cc) the generation of new nuclei ceases, and the growth of the crystals remains as long the solution stays above the saturation point (Cs).

From the LaMer model, two regimes for crystal nucleation and growth can be defined depending on the ratio of solvent evaporation. Under the slow evaporation regime, the nuclei that are initially formed will start to grow and consume the solute present in the wet film, a concentration gradient is formed around the growing crystal, represented by the blue region in Figure 30-B. Inside this gradient region, the solute stays below the Cc and above Cs, favoring a continuous growth of the crystal. As result these crystals become too big in an inhomogeneous way, forming needle like crystals that are called dendritic structures [74]. This type of film is unsuited for a photovoltaic application, because of the big voids existent in the perovskite layer that can be percolated by the other materials, which can be a route of performance loss due recombination of photogenerated charges.

In the fast evaporation regime, the generation and growth of the crystals in the wet film occurs concomitantly and have a competitive relation to consume the solutes. As the solvent is swiftly removed from the wet film the concentration of the solution always stay above the Cc and the concentration gradient around the crystals is minimal. The consequence of this evaporation regime is that there is an increase in the formation of new nucleation crystals and a decrease in the grain growth. As result, the perovskite film becomes more uniform but composed of smaller grains.



Figure 30: A) LaMer model of concentration of solution over time. In (B) and (C), the two regimes of solvent evaporation and the representation of film outcome. Reference: [73].

Unfortunately, the fast evaporation regime that governs in the spin coating differs from the methods involving a meniscus. In spin coating, the solvent drying rate is accelerated by the air that is surrounding the substrate rotating at high speeds. This effect is so significative that the anti-solvent method, which is the most used nowadays, rely on the use of additives (DMSO, NMP) into the DMF solution to slow down the crystallization of the perovskite during the formation of the wet film, until the anti-solvent is poured onto the sample [75]. In the case of methods involving a meniscus guided deposition there is an absence of external factors to act upon the

substrate and affect the evaporation of the solvent. The result is that the wet film tends to dry based on the properties of the solvents. In the case of the perovskite solution, which is mainly constituted of DMF, the rate of evaporation is slow due to its high boiling point (153 °C).

Several attempts have been made to try to control the morphology and formation of the perovskite film by altering the deposition parameters. Despite some of these studies being successful to produce a PSC through blade coating, most of the modifications proposed by these studies cannot be direct replicated or have undesirable steps to be applied in an industrial environment. As example, Jen's group explored in two of the early work involving blade coating the use of 1,8-diiodooctane (DIO) as additive in the perovskite solution [76][77]. The role of DIO was to modulate the morphology of the perovskite film, preventing it to form the dendric structure. While it accomplished the objective of producing a PSC in the slow evaporation regime, the PCE achieved was only 10.71% and the film required 2 hours to dry. Despite the effort, the perovskite film still exhibited voids on its surface as result of the problematic crystallization.

Because of the long drying time required and the difficult to control the morphology in the slow evaporation regime, most attempts focus on accelerating the evaporation of the solvent in order to move to the fast evaporation regime. Parvazian and collaborators employed a vacuum chamber to remove the excess solvent before the perovskite annealing [78]. The best performance achieved by this method was 10.1%, while the devices without the vacuum process could attain only 2.3% PCE. Another methodology was employed by Yang and collaborators, they pursued the anti-solvent method developed in the spin coating and applied the same principle in blade coating [79]. After the solution deposition and formation of the wet film, they submerged the substrate in a diethyl ether bath to promote the perovskite crystallization. The device assembled through this route displayed an astounding PCE of 18.5%, which is close to the best results displayed in spin coating. Although this work shows that it is possible to achieve a high performance through meniscus guided deposition, the procedure necessary in the perovskite processing was not scalable.

There are other works focusing on different strategies to accelerate the solvent removal while maintaining the scalable aspect of the whole process. Cotella and collaborators employed a gas assisted process to promote the crystallization of the perovskite in a slot-die deposition. They preheated the substrate and applied the pressurized gas through an air knife over the sample to force the solvent removal. In its best condition, the assembled device could reach a 9.2% PCE [80]. Su and collaborators further improved the technique by heating the air knife and by changing the delay before the gas quenching [81]. In their best conditions they could achieve a PCE of 11.12%. Their improved result is also due to the presence of chlorine in the perovskite composition, which can improve the electrical properties of this material [82].

By far the most used procedure to accelerate the evaporation of the solvent is by heating the substrate while the perovskite is deposited. Several works adopted this strategy to regulate the perovskite crystallization and study their deposition with blade coating. Zhong and collaborators assembled a device through this route that could achieve a PCE of 17.5% [83], while Li and co-workers increased this mark to 18.7% [84] by changing the solvent from DMF to γ -Butyrolactone (GBL) /DMSO. Besides the high efficiencies, the common point in these works is that they used in situ time-resolved grazing incidence wide-angle X-ray scattering (GIWAXS) to study their samples during crystallization. Their results show that at low temperatures the crystallized material stays in an intermediary solvated phase for a prolonged time due the high boiling point of the commonly used solvents in perovskite solutions (Figure 31). In those conditions, in order to accelerate the rate of solvent evaporation a high temperature is needed, 135 °C at minimum. However, to achieve such high efficiency in both studies the applied temperature was 150 °C.



Figure 31: GIWAXS intensity maps of the perovskite blade coated films in different temperatures. Reference: [83]

While this temperature is not so high that would make this method unfeasible it can severely limit the type of substrate employed and consequently the methods that could be used. For a rigid substrate like FTO the 150 °C temperature would not pose a problem, even higher temperatures are used with this substrate during the TiO₂ annealing, consequently this method can be applied to deposit perovskite over a rigid substrate through blade coating or slot-die. However, the R2R process uses flexible PET based substrates, which in high temperatures can bend, deform and shrink during the process [85]. For this kind of application, a process that can be performed in lower temperatures would be more desirable, not only because it would allow the use of R2R but also because it would reduce the energy waste.

From an industrial point of view, many of the processes discussed above are not viable, either because of the difficulty of their implementation (e.g. vacuum chamber and long evaporation time) or due potential environmental and health hazards (e.g. anti-solvent bath). While the high temperature deposition could be scalable it may restrict the substrates and the deposition methods that can be used. There are other possibilities that were not described above such as a two-step deposition [86], with this method it could be possible to obtain a film with good coverage, however this method introduces new problems such as incomplete conversion of Pbl₂ into perovskite and the addition of an extra step in the manufacturing process.

These topics demonstrate that the difficulty to produce PSC can quickly escalate when a set of parameters that can be applied in real conditions are considered. Most of the reports related to a scalable production of PSC only consider the deposition of the active layer through this method to avoid problems with the other layers. Moreover, the research of the perovskite deposition in mild conditions is of utmost importance and the assembly of a complete device using only scalable methods to deposit its layers would be a better representation of the difficulties and challenges that would be observed in real-world conditions.

3.3. Objectives

In this part of the work, the objective is to develop and optimize a route to assemble perovskite solar cells entirely through blade coating. The control of the crystallization of the perovskite layer in this route must utilize steps that can be applied in the scale-up process while staying relevant for future industrial applications.

3.4. Methods and Procedures

3.4.1. Device Fabrication

This experimental part was carried on in the physics institute of USP – São Carlos (IFSC) in collaboration with the Polymer Group Prof. Bernhard Gross.

Most of the materials were purchased from Sigma-Aldrich unless stated otherwise. ITO substrates (Delta Technologies, 8-12 Ω /sq) were patterned by photolithography before use. Previous to the deposition, the substrates were cleaned by sequential sonication in detergent solution, distilled water, acetone, isopropanol, and then submitted to O₂ plasma treatment for 10 minutes. The deposition of the materials was performed on a ZAA 2300 Zehntner blade coater with a heating mantle placed inside a dry box with humidity control (15-20 % relative humidity, dry air atmosphere).

PEDOT:PSS (Clevious) was used as the HTM, the pristine solution was diluted on isopropanol in a 1:3 ratio. The resultant solution was stirred for about an hour and then filtered through a 0.45 μ m PTFE filter prior to use. This solution was deposited with a blade height of 30 μ m and a blade sweep speed of 15 mm/s at 60 °C. Sequentially the films were annealed for 10 minutes at 100 °C.

The perovskite precursors were dissolved in the corresponding solvent and stirred for 3 hours before use to assure complete dissolution. With Pbl₂ as a lead source it was used a 1:1 ratio Pbl₂:MAI, while for Pb(CH₃CO₂)₂.3H₂O (abbreviated Pb(Ac)₂) and PbCl₂ a molar ratio of 1 Pb²⁺ to 3 MAI was employed to ensure the formation of CH₃NH₃Pbl₃. The concentration of the perovskite precursor solution was varied between 0.5 to 0.2 M. The deposition was carried out under a humidity between 10-20 %. The deposition parameters used in the deposition were 50 µm of blade height, 10 mm/s of blade speed and the temperature was adjusted accordingly as described in the text. A dry airflow outlet was suspended over the sample at heights of 5 or 15 centimeters above the substrate. The films were annealed over a heating plate, with Pbl₂ as the lead source the heating treatment was optimized for 1 hour at 100 °C, while for compositions containing Pb(Ac)₂ the duration could be reduced to just 15 minutes at the same temperature, without loss of performance. $PC_{61}BM$ (American Dye Source) was used as the ETM, first it was dissolved in chlorobenzene with a concentration of 15 mg/mL and the resultant solution was coated over the perovskite layer by using a blade height of 100 µm and a speed of 20 mm/s. Then the substrate was annealed at 100 °C for 5 minutes after the coating, to ensure the complete removal of any residual solvent. After the deposition of the ETM, the sample was transferred to a glovebox and the metallic contacts, 40 nm of calcium and 70 nm of aluminum, were deposited by thermal evaporation. The active area of each solar cell was defined by the overlap of the deposited layers and the thermo-evaporated contacts, the resultant area has a value of 0.045 cm².

3.4.2. Characterization

<u>Ultraviolet-visible spectroscopy (UV-Vis)</u>

A Hitachi U2900 was used to take the UV-Vis spectra of perovskite films in the 400-900 nm region.

Optical microscopy

An Olympus optical microscope model BX41 was used to investigate the surface of the perovskite films.

Profilometry

A Veeco Dektak 150 Surface Profiler was used to measure the thickness of the films that compose the solar device.

X-Ray Diffraction

X-ray diffractions were obtained on a Rigaku RU200B with Cu Kα with a scan rate of 2°/min and operation conditions of 40 kV and 40 mA.

Field Emission Gun Scanning Electron Microscope (FEG-SEM)

FEG-SEM images were obtained with a ∑igma microscope from Zeiss, with beam acceleration of 4 kV and working distance around 6 mm.

Atomic Force Microscopy (AFM)
AFM images were obtained in a Nanoscope III from Digital Instruments.

Measurement of solar cell performance

JV scans were performed in an inert atmosphere with a 100 mV/s scan rate using a 2400 Keithley Sourcemeter and an Oriel AAA class simulator with an AM 1.5 G filter as the light source. Statistical distributions were obtained by measuring over 15 different devices in each condition.

3.5. Results and Discussion

In this part of the work the adopted structure for the perovskite solar cell was the p-i-n configuration. This configuration has some advantages over the n-i-p that was explored earlier: its layers require lower annealing temperatures, the hysteresis during the measurement tends to be lower or non-existent and some of the materials were already explored in OPV technology, meaning that the transition from laboratory to large scale production may be easier due the previous acquired knowledge. To avoid the process being influenced by external environmental factors, especially during the deposition of the perovskite layer that is sensible to ambient conditions, the blade coating equipment was placed inside a box with dry air atmosphere (Figure 32) with 15-20% relative humidity.



Figure 32: Photography of the blade coated used inside the dry box (A), illustration of the blade coating process during the deposition (B).

As the first layer in the p-i-n structure, PEDOT:PSS was selected as the HTM. This material is already well stablished in the OPV market and were already proven in meniscus guided deposition [71]. The commercial PEDOT:PSS solution was diluted in isopropanol to improve its wettability and enhance the quality of the deposited film. After annealing, the deposited film was analyzed with atomic force microscopy. Comparison of the images of the bare ITO substrate and the one with PEDOT:PSS (Figure 33) shows that the morphology of the two samples is completely different and that the PEDOT:PSS layer presented a good coverage of the substrate, without significant defects on the surface.



Figure 33: AFM images of the bare ITO substrate (A) and ITO/PEDOT:PSS (B).

With a profilometer, the thickness of the PEDOT:PSS layer was determined to be within the range of 30-40 nm, in agreement with results from other reports using this type of architecture [76]. Compared to the bare ITO, the root mean squared roughness (Rq) of the substrate estimated through AFM was reduced from 2.84 nm to 1.94 after the deposition of the PEDOT:PSS layer. This value is close to the optimum value (1.84 nm) found by Chen *et. al.* [87] for devices using multication perovskites. Lower roughness values may hinder the subsequent crystallization of perovskite since there are no anchoring points in which perovskite grains can start to grow cohesively.

At low temperatures, blade coating the perovskite layer from a precursor ink containing DMF generates the dendritic structures that possess needle-like appearance (Figure 34-A). To improve the quality of the deposited perovskite layer and obtain a homogeneous film it is imperative to accelerate the solvent removal. A higher rate of solvent evaporation will promote the generation of new nucleation sites by maintaining the concentration of the solutes in the wet film above the critical point. Introducing a dry air flow briefly after the solution is swept over the substrate can accelerate the drying rate of the excessive solvent content, partially mimicking the dynamics that occurs in the spin coater. This modification improves the morphology of the perovskite film to some extent (Figure 34-C) and can be easily transferred to other scalable methods. Despite the improvement of the film morphology, the perovskite layer obtained from precursor inks based on low vapor pressure solvent still possess many defects. Large voids are formed due the 3D network that is created during the crystallization. The films obtained by this process were kept for future performance comparison.



Figure 34: In (A) and (B), FEG-SEM images of the dendritic structures formed during the perovskite crystallization at ambient temperature. In (C) and (D) FEG-SEM images of the perovskite layer obtained using a precursor ink containing DMF and with dry airflow application during the deposition.

To further improve the morphology of the perovskite film in these mild conditions the drying rate of the solvent must increase. To achieve this task without resourcing to the methods discussed before, the solvent itself must be changed to one with a higher vapor pressure. Unfortunately, the Pbl₂ used in the perovskite composition is not soluble in many solvents and usually strong polar aprotic solvents such as DMF, DMSO, NMP and GBL are employed to dissolve this material. These solvents however possess lower vapor pressure than DMF (Table 7), consequently they are harder to remove from the wet film and thus will not improve the morphology.

One solvent that can be used to prepare the perovskite solution and has not been much explored is the 2-methoxyethanol (2ME). The first report using this solvent is by Hendriks *et. al.*[88] and was used to deposit the perovskite with spin coating technique. 2-methoxyethanol has a higher vapor pressure than DMF and consequently can be more easily removed from the wet film that is formed during the blade coating. This solvent seems to dissolve the Pbl₂ with more difficulty than the others, and complete dissolution is observed when the methylammonium iodide is added to the same solution (Figure 35). This property may be helpful in the perovskite film formation as a lower interaction between solvent-solute will reach more easily the super saturation point while the solvent is evaporating and nucleation sites will be generated.

Solvent	Vapor Pressure at 20 °C	Boiling Temperature (°C)
	(mm Hg)	
DMF	2.7	153
DMSO	0.42	189
NMP	0.29	202
GBL	1.5	204
2-methoxyethanol	6.17	124

Table 7: Properties of the solvents usually used in perovskite solutions.



Figure 35: Photo comparing the perovskite inks using 2-methoxyethanol (left) and DMF (right) as the solvent.

After blade coating the solution containing the 2-methoxyethanol as the main solvent the yellow wet film immediately changes to a dark reflexive brown as soon as the air flow sweeps the substrate. A reflexive aspect of the perovskite film is an indicator that a compact layer with low roughness was formed. AFM and FEG-

SEM images (Figure 36) prove that these initial observations were correct, the perovskite ink containing 2-methoxyethanol formed a layer that is compact, composed of small grains and that completely covers the substrate without apparent presence of pinholes.



Figure 36: FEG-SEM and AFM image of the perovskite layer obtained from a solution containing 2-methoxyethanol.

X-Ray diffraction was used to verify if the blade coated film obtained from the 2ME ink indeed corresponded to the perovskite material. The as-deposited film presented the same diffraction pattern as the post annealed perovskite film made from blade coating and the standard spin coating, both using precursor solutions containing DMF (Figure 37). This result shows that with 2-methoxyethanol the crystallization of the perovskite layer is almost finished during the deposition process. The annealing process of the samples obtained from the 2-methoxyethanol ink results in a film that possess a higher crystallinity, as observed by the more intense and better-defined peaks (narrower full width half maximum). The diffractograms also reveal that the crystalline grains of the perovskite layer does not have a preferred growth orientation.

A small diffraction peak in 12.7 degrees, related to the (001) diffraction plane of hexagonal Pbl₂, is present in the diffractogram of the 2ME sample after the annealing. This peak can be a result of either an increase in the crystallinity of the lead iodide, a small trace of this peak can be spotted in the as-deposited sample, or due to a small degradation during the annealing process, result of MAI removal. Regardless of the reason that originated this peak, from the diffractogram it is noticeable that the amount of Pbl₂ in the same is very low. The presence of a small quantity of the PbI₂ (usually <5%) is not harmful to the device, it might even be beneficial and increase the photovoltaic performance due passivation of defects [89].



Figure 37: Diffractogram of blade coated perovskite films produced from inks at different conditions.

Fullerene based materials are the most employed ETM in p-i-n configurations. However, the pure C60 fullerene has low solubility in most solvents, as consequence this material is mostly used in evaporated form. A fullerene derivative, the PC₆₁BM, is functionalized with solubilizing groups and can be deposited from solutions. Similar to the case of PEDOT:PSS, the PC₆₁BM is a good choice for the ETM because is a proven material that has been used in the OPV market before. The PC₆₁BM solution was blade coated on top of the perovskite film obtained from the 2ME solution and on the perovskite from DMF based ink. AFM and FEG-SEM images (Figure 38) shows that the quality of the PC₆₁BM layer is strongly dependent on the perovskite layer, as the fullerene material does not form a thick layer and only follows the pattern of the layer below, copying its imperfections. In the case of the PC₆₁BM layer over the perovskite obtained from the DMF ink, the voids could not be completely covered and pinholes across the sample are present. In comparison, the PC₆₁BM layer had a great improvement when deposited on top of

the perovskite obtained from the 2ME solution. The fullerene layer showed a complete coverage and originated a smooth film, with the profilometer the thickness of this fullerene layer was estimated between 50 to 60 nm.



Figure 38: AFM images of PC61BM deposited on top of the perovskite layer obtained through DMF ink (A) or 2-methoxyethanol ink (B). In (C), the corresponding SEM-FEG of PC₆₁BM over perovskite obtained using 2-methoxyethanol.

After the deposition of the ETM the samples are transferred to a thermal evaporator to evaporate calcium and aluminum, finalizing the metallic contacts and the assembly of the solar cell. Observation of the energy level correspondent to the assembled solar cell (Figure 39) may leave the impression that this device will encounter the same issue faced by PoMA in the first part, due to the apparent mismatch of the energy level of calcium. However, in p-i-n configurations it is common practice to use materials that possess high energy level. These materials are called the *buffer* or *interfacial* layer, and act by effectively blocking the holes (positive charges) and to provide an ohmic contact between the fullerene and the metallic contact [90]. To prevent performance loss these interfacial layers are made very thin, so the electrons can easily tunnel through them.



Figure 39: Energy diagram for the p-i-n assembled device.

The assembled devices were measured to verify how the samples obtained in ambient temperature would perform. As expected, devices with the perovskite made from the DMF based ink delivered a low performance, mostly because the open circuit voltage and the short circuit current displayed by these samples (Figure 40). These values are lower than what can be achieved by devices using the same materials and structure [91], showing that the defects existent in the perovskite layer made from DMF are indeed deleterious to the performance of the photovoltaic devices. Despite possessing a better morphology, the samples containing the perovskite layer made from the 2ME based ink showed an overall lower photovoltaic performance than those based on the DMF ink (Figure 40).

Comparison of photovoltaic performance of devices obtained by both methods shows that devices made from the 2ME route have a higher Voc than those made from DMF based ink. This result is a consequence of the improved coverage that the perovskite made from the 2ME ink possess. A perovskite layer without pinholes promotes a better separation and will prevent that the material deposited above percolate the perovskite layer, inhibiting the recombination of the photogenerated charges that would be in the vicinity of both charge transport layers. Regarding the short circuit current density and the fill factor, the parameters of the devices based in the 2ME ink was far lower than those made from the DMF. This unexpected result shows the perovskite made from DMF ink has some characteristic that makes it outperform the devices from 2-methoxyethanol, regardless of the pinholes.



Figure 40: JV curves of the photovoltaic devices assembled using inks based on DMF (Left) and 2ME (right). Dashed lines represent the forward scan.

Sample	Voc (V)	Jsc (mA/cm²)	FF (%)	n (%)
DMF D1 Forward	0.78	7.86	54.10	3.33
DMF D1 Reverse	0.78	7.78	56.32	3.40
DMF D2 Forward	0.80	7.41	61.94	3.66
DMF D2 Reverse	0.79	7.43	63.94	3.73
DMF D3 Forward	0.78	8.15	58.65	3.75
DMF D3 Reverse	0.77	8.24	62.28	3.96
2ME D1 Forward	0.88	3.27	39.82	1.15
2ME D1 Reverse	0.91	3.18	39.30	1.13
2ME D2 Forward	0.93	3.44	36.53	1.16
2ME D2 Reverse	0.93	3.38	36.39	1.14
2ME D3 Forward	0.88	3.27	39.92	1.15
2ME D3 Reverse	0.91	3.18	39.03	1.13

Table 8: Photovoltaic parameters of the devices based in DMF and 2-methoxyethanol inks.

For the device based in the 2ME, other conditions were tested to try to find the reason for its low performance. One of these tests was to change the concentration of the perovskite precursors in the solution. Changing this parameter while leaving the others unaltered reveals an inverse linear correlation between the concentration and the thickness of the dry film (Figure 41-A). The correlation shows that, at least within the tested range, the blade coating technique has a good degree of consistency, which allows to predict the outcome of the film based on the initial parameters. As the concentration of the perovskite precursor based on 2ME was reduced, and consequently the films became thinner, the photovoltaic performance of the resultant devices increased (Figure 41-B).

The improvement in performance can be attributed mainly due the short-circuit current density and the fill factor. Compared to the previous result, the current density achieved by the thinner cells at least doubled, in the best case it tripled, while the fill factor was greatly improved achieving almost 60% in the best case. A qualitatively analysis of the JV curves reveals that the shunt resistance increased concomitantly to the reduction of the thickness, as consequence the JV curves of thinner samples adopted the traditional expected shape which enhanced

the fill factor achieved by the device. This trend suggests that with reduction of the thickness of perovskite layers the charge collection and transport was enhanced.



Figure 41: Plot of concentration of perovskite ink vs thickness of the dry film (A). JV curves of solar cells containing perovskite layers with different thicknesses (B). Dashed lines represent the forward scan.

Sample	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)
2ME 280 nm Forward	0.84	9.22	45.61	3.52
2ME 280 nm Reverse	0.83	9.06	45.62	3.44
2ME 200 nm Forward	0.88	10.68	42.90	4.05
2ME 200 nm Reverse	0.87	10.65	43.42	4.03
2ME 160 nm Forward	0.91	11.86	58.73	6.35
2ME 160 nm Reverse	0.90	11.85	59.14	6.29

Table 9: Photovoltaic parameters of the devices with different perovskite thickness

With reduction of the perovskite layer thickness from the 400 to 280 nm the device made from 2ME could match the performance of those obtained from DMF and eventually surpass it. To try to find the reason for this discrepancy the FEG-SEM images of both samples were again compared. A closer inspection reveal that the perovskite based on DMF have grains that seems to be bigger and more homogeneous in relation to their size than those existent in the layer from 2ME. This observation is in accordance with the LaMer model of nucleation and growth of particles explained before and would be a direct consequence of the slower evaporation of DMF in comparison to the 2ME, which would favor the growth of the grains. According to Correa-Baena et. al. [92], a perovskite layer composed of small crystals has an increased surface area and consequently more surface defects.

These defects at the grain boundaries can act as a trap to the photogenerated charge carriers. When filled, those traps may act as potential barriers for electrons, hampering its transport from one crystallite to another, affecting their mobility. The traps at the boundaries can also act as recombination centers for electrons and holes recombine nonradiatively [93].

The morphological difference could explain the initial better performance displayed by the DMF samples; bigger grains would reflect in a better charge transport of the photogenerated charges. Compared to the DMF case, for a perovskite film with the same thickness the photogenerated charges in the samples made from 2ME would have to go across more grains until they reach the charge collection layers (Figure 42). Each one of these crossings at the grain boundaries increases the probability of recombination, reducing the performance of the device. By lowering the thickness of the perovskite layer, the photogenerated charges have fewer grains to cross before being collected by the ETM or HTM, therefore the chance of recombination is diminished and consequently the performance increase. However, the performance of the solar cells is also dependent on the amount of light that is absorbed by the active layer, with thinner films there is less absorption of light and therefore the device loses performance. For the perovskite layer made from the 2ME solution the tradeoff point seems to be around the 160 nm. At this point the PCE achieved its highest value, with thinner films the performance decreased due reduction of Jsc.



Figure 42: Representation of the photogenerated charges migration in films with different thickness.

The experimental results indicates that the size of the grains was indeed the reason for the initial poor performance of the devices with perovskite based on the 2ME ink. At these conditions, a tradeoff point is reached in which perovskite films produced by DMF route have better electronic properties while films based on 2ME have a better coverage of the substrate but do not perform as well as the former. To surpass the performance limitation imposed by the small grains, the effect of the temperature of the blade coater during the deposition of the perovskite was studied, but always keeping it below 100 °C in order to develop a low-temperature process.

The films obtained at different temperatures were characterized by AFM. The images (Figure 43) shows that the morphology profile of the perovskite film slightly changes upon the variation of temperature. The application of heat during the deposition allowed the perovskite based on 2ME to grow into larger grains and the grain size distribution became broader as can be seen on the histogram in Figure 44. The effect of the temperature upon the sample can be divided in two regimes, one from ambient temperature up to 60 °C and another above 70 °C. The former originates a perovskite film that is composed of grains sharing borders with the neighboring units, forming a continuous layer. Low magnification AFM images (Figure S 2 in Appendix) reveals that morphology of the perovskite progressively becomes more homogeneous as the temperature rises in the range between 30 to 60 °C. In the second regime, the perovskite grains form agglomerates that are spaced apart, generating large voids between them. The temperature also influences the superficial roughness of the films, Rq was estimated to be 19.1, 18.1, 11.8, 13.0, and 20.6 nm for films deposited at 30, 40, 50, 60, and 70 °C. A lower surface roughness is expected to improve the interface between the perovskite and the ETM.



Figure 43: AFM images of perovskite layers deposited at varying temperatures, from the 2-methoxyethanol ink. The scale bars represent 500 nm.



Figure 44: Histogram of the particles area vs temperature, estimated from AFM images.

Solar cells were assembled using perovskite films deposited at different temperatures, later they were measured to investigate their performance after this modification. The JV curves (Figure 45) shows that within 30 °C to 50 °C range the PCE increased with the temperature, peaking at 50 °C, and then from 60 °C on the performance decreased. The growth in performance can be attributed to the higher current density that is achieved by devices assembled above 40 °C, which could surpass the mark of 15.0 mA/cm². A decrease in the series resistance can be qualitatively observed in the JV curves above 40 °C, probably a direct consequence of the enhancement of the morphology observed in the low magnification AFM

images. A better charge transport within the perovskite layer in conjunction to a reduction of the surface roughness, and consequently improvement of perovskite/ETM interface, may be the key factors which led to the increase Jsc observed for devices assembled above 30 °C.

The open circuit voltage presented a different trend, being inversely proportional to the increase of temperature. Comparing the AFM images of the perovskite films at both high and low magnification (Figure 43 and S2), it appears that the presence of black spots on the perovskite surface increases with the temperature. These black spots are associated to pinholes formed during the crystallization, generating a layer with an inhomogeneous morphology. Presence of pinholes not only facilitates the permeation of the ETM into the perovskite layer but also increase the recombination process due the open grain boundaries with high trap densities [93].



Figure 45: JV curves of the best devices in each temperature, dashed lines represent the forward scan.

Table 10: JV parameters of the best device at each deposition tempera	ature
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Condition	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)	Rs (Ω.cm²)	Rsh (Ω.cm²)
30 °C	0.96	12.66	53.04	6.46	17.27	526.50
40 °C	0.93	16.59	55.61	8.54	7.30	408.90
50 °C	0.91	17.67	58.34	9.33	6.08	450.35
60 °C	0.87	17.77	55.38	8.57	7.76	354.82
70 °C	0.88	15.54	55.73	7.58	7.78	519.12

The conclusions draw from the JV curves of the best cells displayed at Figure 45 are replicated in a statistical analysis obtained from measurement of 15 devices at each condition. From the box plot, the inverse relation between the Voc and the temperature becomes easily observed (Figure 46). It can also be noticed the increase in the current density above 40 °C; while the fill factor achieved its best values between 40 to 60 °C, at 70 °C it displayed a high variance, probably due the many defects existent in the perovskite film deposited at this temperature. The power conversion efficiency has an upward trend up to 50 °C and then it decays due to the reduction of Voc, and FF.





The performance peak found at 50 °C was an unexpected result since an increase in efficiency is usually observed when the perovskite grains become larger. Up until 60 °C there is not much variance between the deposition of the perovskite layers at different temperatures. However, at 70 °C and above it was observed that the drying dynamics of the perovskite films differed from those at lower temperatures. The conversion of the wet film into the dry film occurred much faster, before the gas flow could reach the sample. The uncontrollable crystallization process led to the

formation of perovskite films with large voids as seen in the AFM images shown previously. These films also appeared more translucid, an UV-Vis spectrum of the films (Figure 47) confirms that those made at higher temperatures absorbs less light, mostly due their lower thickness which could be as low as 100 nm. Considering those factors, solar cells with perovskite films deposited in temperatures above 70 °C were not assembled.



Figure 47: UV-Vis spectrum of perovskite films deposited at different conditions.

The temperature of 50 °C seems to be the best compromise between the improvement that heating the substrate during the deposition may offer and the performance achieved by the solar device. At this condition, the devices could reach a Voc around 0.90V, a short-circuit current density close to 20 mA/cm² and a fill factor above 50%, giving an overall efficiency close to 10%, which is an encouraging result. Along to the study of temperature modification, other experimental parameter that was explored was the height of the gas flow in relation to the sample. The objective was to analyze if by placing the gas outlet farther it could positively influence the growth of the perovskite grains while maintaining good coverage of the substrate. The perovskite film was characterized by AFM, the image at high magnification (Figure 48) shows that the grains had a small increasement and resemble those from the film obtained at 90 °C. However, the reduced effect of the gas onto the sample during the crystallization also led to perovskite grains growing less cohesively, with many grains separated from the others, without sharing corners.



Figure 48: AFM image of the perovskite film obtained with the gas outlet in far position.

Compared to the devices prepared previously, the samples assembled in this condition had an intermediary performance (Figure 49). The current density was slightly below 15 mA/cm² and the Voc around 0.87 V. The fill factor is the parameter that was most affected by this change, its values were around 36%, much lower than any condition previously studied. The low fill factor had a negative impact in the power conversion efficiency achieved, around 4.6%, which is close to the performance of the devices obtained during the thickness optimization.



Figure 49: JV curves of devices obtained using different gas outlet positions.

These results shown previously indicates that the efficiency seems to be limited by the small grains obtained so far with this method. The physical parameters that could be modified (temperature, application of a gas flow and its height, velocity of the knife, blade gap) seems to be at their optimum conditions, nevertheless the performance of the device could not be improved any further. A change in the perovskite ink was performed to investigate if the size of the grains were the true limitation of this method and to verify how the method would perform with different precursors.

To study the modification of the precursors, lead iodide was exchanged by lead acetate and lead chloride in the perovskite precursor and 2-methoxyethanol was maintained as the solvent. These materials possess distinct characteristics which enables a fine tuning of the crystallization process. As precursor, lead acetate has a high rate of crystallization which promotes the formation of many crystallization nuclei covering the substrate, resulting in a perovskite layer without pinholes. The crystallization is accelerated due the reaction of methylammonium iodide and the Pb(Ac)₂ forming methylammonium acetate (CH₃NH₃Ac) which quickly evaporates from the wet film [94]. From LaMer model exhibited before, with a fast crystallization a good coverage of the substrate can be obtained, however the grains of the perovskite obtained by this method are expected to be small.

From the optimization process described before, a device containing a perovskite layer composed of small grains will perform just as bad as one with pinholes in the active later. To avoid this problem, PbCl₂ is used as the other lead precursor in this mixed perovskite ink. Materials containing chlorine (PbCl₂, MACl) can enhance the crystal growth of the perovskite during the film formation. In these compositions, after formation of the wet film the intermediate MAPbCl₃ is spontaneously generated first and serves as a template in which iodide anion diffuse and forms the MAPbl₃ perovskite due an anion exchange reaction [95]. The residual chlorine existent in the wet film rapidly reacts with the methylamine ion generating MACl, which is easily removed from the sample during the annealing.

Although the resulting material could be classified as a mixed perovskite (CH₃NH₃PbI_{3-x}Cl_x) because the use of a double anion, the amount of residual chlorine in the final film is negligible [96]. Its impact on the properties of the perovskite film however is longstanding, not only the crystal growth is enhanced during the film formation but also the CH₃NH₃PbI_{3-x}Cl_x films possess improved carrier

transport with the diffusion length of both electron and hole exceeding 1 μ m [97]. This value is one order of magnitude higher than that displayed by MAPbI₃ perovskite obtained from pure PbI₂.

Introduction of two new materials in the precursor solution allows a new degree of freedom in relation to the composition of the perovskite ink, allowing a fine tuning of the desired properties based on the ratio of lead chloride and lead acetate. Precursor inks with different proportions ranging from pure lead acetate to a 1:1 ratio Pb(Ac)₂:PbCl₂ were used to verify if it could solve the problems observed before and consequently obtain devices with higher efficiency. The previously optimized parameters were not modified because they worked well towards the formation of the perovskite film, despite the change in the formulation. Therefore, the temperature of 50 °C, height of the airflow, deposition speed and blade gap remained the same.

Similar to the previous precursor solution using PbI₂, the dissolution of the materials that compose this new ink occurred only when MAI was added to the solution. Lead chloride is known to be less soluble than PbI₂, however no particulate was observed even in PbCl₂ rich solutions with 2-methoxyethanol as solvent. Differently to the previous case, when using these iodine-free lead precursors a 3:1 molar ratio of MAI:Pb is necessary to ensure the necessary iodine concentration in the ink and formation of the MAPbI₃ perovskite. Compared to the deposition of the previous inks containing PbI₂, with these mixed compositions the transition from the yellow wet film to the dark brown perovskite was less abrupt, especially with a higher ratio of Pb(Ac)₂.

The films prepared with different ratio compositions were analyzed by X-Ray diffractometry (Figure 50). The most evident difference in the diffractogram of these new samples in relation to the previous shown is the sharpness of the diffraction peaks. The peaks at 14.1°, 28.5°, and 43.3° related to the (110), (220), and (330) planes have a high intensity in relation to the baseline, indicating that the perovskite crystals are highly oriented with the long axis parallel to the substrate. These high-oriented crystals occur both with mixed precursor solution and with pure Pb(Ac)₂, suggesting that this phenomenon is an effect of the lead acetate and is not related to the presence of chlorine in the composition. A small peak in 15.6° would indicate the presence of CH₃NH₃PbCl₃ [96], however since there is no indication of

this peak in the diffraction pattern obtained by these samples, regardless of the ratio composition, the deposited films are related to a pure CH₃NH₃PbI₃ perovskite. This observation reassures that the chlorine content is removed during the annealing.



Figure 50: Diffractograms of perovskite films obtained from inks with different compositions.

Although every film obtained in this condition has crystals with a high degree of orientation, comparing the results it is possible to correlate the addition of chlorine into the precursor solution to the increase of crystallinity observed in the diffractograms of the perovskite films. The peaks at 14.1° and 28.5°, referent to (110) and (220) diffraction planes, increase their intensities with crescent addition of chlorine content in the precursor mix, reaching the maximum at 4:1 Pb(Ac)₂:PbCl₂ ratio. Further addition of chlorine lead to a decrease in the intensity of the diffraction

peaks, reaching similar levels of the film prepared from pure Pb(Ac)₂. This result indicates that there is an optimum content of chlorine in the perovskite solution that can enhance its properties and that surpassing this threshold will be harmful to the device.

Sequentially, the perovskite films from each precursor composition were characterized with AFM (Figure 51). Compared to the films obtained previously with Pbl₂, the morphology changed drastically and is dependent on the composition of the precursor ink. From the LaMer model, it seems that the concentration of the solutes in the ink containing pure Pb(Ac)₂ is always above the critical point, helped by the rapid removal of the CH₃NH₃Ac generated in the wet film. In this film, the generation of new crystallization nuclei is much more favored than the growth of the already formed crystals, resulting in a film without pinholes but with the smallest grains. Addition of only a small amount of chlorine in the precursor is enough to stimulate the growth of the grains. The perovskite layer made from 8:1 composition has grains that are slightly smaller than those obtained from Pbl₂ in 2-methoxyethanol. However, in the mixed composition the grains seem more cohesive, sharing their boundaries with neighboring grains, generating a compact layer.

The impact of the chlorine in the perovskite film becomes more evident with further addition of PbCl₂ in the precursor ink (6:1 and 4:1 ratios). The perovskite layer made with these inks display vastly superior grain sizes in comparison to the previously studied compositions (Figures 51 and 52). The addition of chlorine was mainly beneficial at these ratio compositions since the perovskite grains could grow and still maintain a cohesive aspect at the grain boundaries, forming a homogeneous layer. With a higher PbCl₂ concentration (1-1 ratio) the perovskite layer is comprised of grains with an elongated shape that can be larger than 2 µm and smaller grains in the sub-micron range. Due the heterogeneity, both in size and shape, the coverage of the substrate is impaired and large defects are present in the active layer.



Figure 51: AFM image of perovskite film obtained from mixed compositions inks. The scale bar represents 2 μ m, except for high magnification images (pure Pb(Ac)₂ and 8:1 ratios); in these cases the scale bar is 500 nm.



Figure 52: Histogram of perovskite grain area at each condition.

The PbCl₂ rich composition (1-1) has another downside besides the pinholes on the layer: this film seems to suffer from degradation during the annealing process. The as-deposited films looked just like the others containing Pb(Ac)₂, but shortly after annealing these films changed from shiny reflexive dark brown perovskite to a hazy dark gray film. This behavior seems to be related to the crystals continuously growing during the heat treatment, eventually forming a rough

perovskite layer, which explains the hazy gray aspect. The massive crystal growth during the annealing also generates mechanical stress which induces generation of cracks in the film [98]. If these films were kept in annealing treatment, the covered area would gradually shrink and eventually they would deteriorate (Figure 53).



Figure 53: Photographs of 1:1 Pb(Ac)₂ :PbCl₂ ratio films: as-prepared (A), during (B), and post-annealing (C).

Solar cells were assembled containing perovskite films with each mixed composition demonstrated above, using the optimized conditions found previously for the 2-methoxyethanol solvent. With these precursors the active layer was slightly thicker, about 250 nm. However, compared to the results of the Pbl₂ there was no observable performance loss. The change of the precursors in the perovskite solution also allowed for a reduction of the annealing time to just 15 minutes, due the facilitated removal of CH₃NH₃Ac from the film.

Solar cells assembled using pure Pb(Ac)₂ as precursor ink presented the worst performance of this new batch of experiments. The solar cells in this condition achieved a good Voc (0.95 V) and a high fill factor (61.80%), those photovoltaic parameters can be direct result of the improved morphology that the pure Pb(Ac)₂ has shown. However, the short circuit current achieved in this condition was around 10 mA/cm², which is lower than the devices with Pbl₂ made at 30 and 40 °C. This result reinforces the issue of low performance due to the small grains in PSC, as the pure lead acetate originate a perovskite layer with grains smaller than those obtained with Pbl₂ at 30 and 40 °C.

Devices made with the 8:1 ratio achieved similar Voc and FF of those made from pure lead acetate, the difference was the short circuit current which improved in comparison to the cells with pure lead acetate and could reach values higher than 15 mA/cm². Despite being a small concentration, the small addition of chlorine into the 8:1 ratio induced a slightly increase in the size of the perovskite

grains as exhibited in the AFM images, the improved morphology led to an increase of the short-circuit current circuit of the devices assembled with active layers made from this composition. Due the increase in the short circuit current, the 8:1 ratio could reach a PCE up to 9% in comparison to the 5% achieved with pure lead acetate inks.

The devices assembled with the perovskite layer made from precursor solutions containing higher amount of PbCl₂ (6:1 and 4:1 ratios) showed a large improvement compared to all conditions investigated previously. From the statistical analysis of the photovoltaic devices, the fill factor remained nearly the same across all the compositions, however the PbCl₂ rich compositions reached Voc above the normally observed for devices using PEDOT:PSS, which is around 0.90V. The increase of the Voc is linked to the higher amount of the PbCl₂ in the precursor ink, however, chlorine is removed during the annealing by the volatilization of CH₃NH₃Cl, and there is no indication of its presence in the DRX. Following the same line of thought, reports in the literature state that the small amount of chlorine present in this kind of perovskite is not enough to change the HOMO and LUMO of the material and that both CH₃NH₃PbI₃ and CH₃NH₃PbI_{3-x}Cl_x have nearly identical absorption spectra [99]. Thus, the observed enhancement of Voc may be explained by these films having lower electron-hole recombination, a side effect of the enhanced charge carrier mobility.

The 6:1 and 4:1 ratio allowed a great improvement in the quality of the material, as observed by their higher crystallinity in the DRX compared to other compositions, as well as in the perovskite grain size. The 6:1 ratio represents the minimum amount of PbCl₂ in the precursor ink needed to obtain the charge transport qualities of the CH₃NH₃PbI_{3-x}Cl_x perovskite, as can be seen by the great improvement in the photovoltaic parameters (Voc and Jsc) observed for devices made from the 6-1 in comparison to the 8-1 ratio. The current density followed the observed trend of grain sizes increasement, highlighting how this feature is important for the performance of the device.



Figure 54: JV curves of the best devices in each condition. Dashed lines represent the forward scan.

Mix Ratio	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE(%)	Rs (Ω.cm²)	Rsh (Ω.cm²)
Pb(Ac) ₂	0.95	11.42	61.80	6.69	6,95	658.23
8:1	0.96	14.08	60.56	8.17	6,51	638.65
6:1	1.03	20.51	62.61	13.09	5.08	505.91
4:1	1.06	22.86	58.82	14.30	6.48	335.07

Table 11: JV parameters of the best device in each condition.

The 6:1 and 4:1 ratio were the compositions that achieved the higher efficiencies. Statistically, many of the photovoltaic parameters were similar between these two conditions, although the 4:1 ratio had a slightly higher and narrower Jsc distribution which resulted in a higher PCE (Figure 56). The champion cell of the 4:1 composition achieved a Jsc of 22.86 mA/cm² and a Voc of 1.06 V, resulting in a PCE of 14.30%.



Figure 56: Statistical distribution of the photovoltaic parameters obtained with each condition.

The observed trend of performance increase due chlorine incorporation is maintained until the 4:1 ratio. As shown previously, the films with higher chlorine content (1:1 ratio) possess many structural defects. The large voids existent in the photoactive layer made from this composition makes the devices prone to being shunt. A few devices were good enough to be measured after several attempts, the photovoltaic performance however was way below the devices assembled in previous conditions and the 1:1 ratio could achieve a PCE of only ~4%. Interestingly this device can be used to create a last analogy of the relation between performance and the morphology of the perovskite later. Since the perovskite layer made from 1:1 mix ratio possess large pinholes, the Voc and fill factor is largely affected by recombination of charges in the open grain boundaries. This phenomenon also affects the short-circuit current density to some extent, however the values achieved by this device is still higher than the value obtained by the devices with pure $Pb(Ac)_2$ layer. The explanation for this behavior is that although the perovskite layer made in this condition has morphological issues, the charges generated by the absorption of light can still travel efficiently within the grain towards the charge collecting layers. Due the size of the grains formed in this composition, there would not be many grain

boundaries to act as a trap to the photogenerated charges, and so the current density is less affected in comparison to the case of pure lead acetate.



Figure 57: JV curves of devices made of 1:1 $Pb(Ac)_2$:PbCl₂ ratio. Dashed lines represent the forward scan.

		Voc (V)	Jsc (mA/cm²)	FF(%)	n (%)
	1 Forward	0.75	16.41	33.21	4.11
	1 Reverse	0.77	16.48	35.07	4.45
	2 Forward	0.70	15.10	32.68	3.47
	2 Reverse	0.72	15.04	33.9	3.68

Table 12: JV parameters of the devices built from 1:1 ratio mix.

To verify the importance of the solvent modification, that is the core of the current process, a perovskite ink with the 4:1 Pb(Ac)₂:PbCl₂ ratio was prepared in DMF and used to deposit perovskite layers following the most optimized parameters previously described. AFM images (Figure 58) shows that the perovskite ink deposited using this precursor ink is composed of elongated grains and has many pinholes, similar to the one obtained with Pbl₂ in DMF.



Figure 58: AFM of perovskite layer made from a 4:1 ratio in DMF.

The photovoltaic parameters of the devices assembled in this condition suffered from the same problem of the devices made from the 1:1 ratio with 2ME. The Voc dropped to just 0.8V and the fill factor was around 45% due the pinholes existent in the perovskite layer. Similarly, the short circuit current stayed above 15 mA/cm² in the measured devices, which can be attributed once again to the better charge transport within the perovskite comprised of bigger grains.



Figure 59: JV curves of the devices assembled with a perovskite layer made from 4:1 ratio ink in DMF. Dashed lines represent the forward scan.

	Voc (V)	Jsc (mA/cm²)	FF(%)	n (%)
1 Forward	0.84	16.8	41.85	5.91
1 Reverse	0.83	17.79	44.86	6.63
2 Forward	0.8	19.14	33	5.03
2 Reverse	0.81	20.17	43.05	7.04
3 Forward	0.82	16.69	42.76	5.85
3 Reverse	0.82	17.18	47.36	6.65

The results obtained with lead chloride and lead acetate proves that the small grains were the main culprit for the low performance of the devices made with Pbl₂. The formation of small grains seems to be a counterpart of this type of deposition at mild conditions. The solvent has a major role in allowing the deposition to happen in low-temperature, it must evaporate quickly so the super saturation of the wet film can occur and generate a lot of nucleation sites, which will cover the substrate. However, once the process has started, the growth of these new crystals is unfavorable, which means that to obtain good results the use of solvents with high vapor must be combined with materials that enhance the crystal growth, such as PbCl₂.

3.6. Conclusions

The knowledge acquired along the years using spin coating as deposition technique cannot be readily transferred to the meniscus guided deposition methods. Several optimization steps are required in order to control the perovskite crystallization and film formation. The development of a deposition method becomes a burdensome task if only the modifications that are feasible to be used in an industrial environment are selected to control the perovskite formation. However, the development of a route that is compatible with these requirements and with the premise of assemble these devices in mild conditions is highly desirable. The blade coater was used as a test platform to execute a systematic investigation for the development and optimization of such route.

Early in the development it was observed that the commonly used solvents for the perovskite ink would not be a suitable choice for a deposition occurring at low temperatures, hence the solvent was changed for 2-methoxyethanol which has a lower boiling point. The new solvent allowed the deposition of the perovskite layer to occur even at ambient temperature, however these devices had a poor photovoltaic performance. AFM characterization revealed that the small size of the perovskite grains achieved in this condition could be the culprit behind the low performance of the solar device.

After a series of optimization steps involving fine tuning the thickness of the perovskite layer and increasing the temperature to 50 °C during the deposition the efficiency increased to just 9.3%. To further enhance the performance, the lead precursor was changed from Pbl₂ to a mixture of lead acetate and lead chloride. This exchange allowed to retain the coverage of the perovskite layer and improve the size of the perovskite grains. The step-by-step analysis during this part of the optimization showed that the morphology of the perovskite film was intrinsically related to the performance of the device.

By fine tuning the precursor ratio in the perovskite ink a composition of 4:1 Pb(Ac)₂:PbCl₂ allowed to obtain advantages of both materials. With the perovskite layer deposited from this ink, and using the optimized process developed along the study, a p-i-n photovoltaic device with 14.3% efficiency was obtained. This result is

comparable to other reports in the literature that adopted similar cell structure and used blade coating to deposit the perovskite layer [100][101]. However, the outstanding feature described in this work is that this result was obtained in low-temperature conditions and with all layers (except the electrodes) prepared by blade coating and using processes that can be applied in an industrial environment.

4. Closure and Final Remarks

The first half of the present work was dedicated to synthetize, characterize and apply polyaniline and its counterpart poly(o-methoxy)aniline as a hole transport material in perovskite solar cells in a n-i-p structure. The study successfully accomplished its goal of depositing a previously synthetized polymeric material over the perovskite layer through spin coating. Perovskite solar cells containing those materials were assembled and had their performance evaluated under different circumstances and compared to the standard material used in this configuration, the Spiro-OMeTAD.

In the second part of the work, the main objective was to study and develop a scale-up process to assemble the perovskite solar cells in mild conditions and using procedures that could be easily applied in an industrial environment. Blade coating was chosen as the technique to study the conditions necessary to carry on the upscaling process of the PSC and a p-i-n cell structure was adopted for this part of the work. A method to assemble perovskite solar cells only through blade coating in low-temperature conditions was successfully obtained.

Each part had a distinct objective, cell structure and method of deposition. A final query is if these two disparate parts could converge into a single topic. Up to date, there is no report of polyaniline deposited by blade coating to be applied in solar cells. The polymer solutions (5 mg/mL) were blade coated to create a thin film over the bare ITO substrate. After a brief annealing to ensure the solvent removal, the films were analyzed by AFM (Figure 60). The images show that similar to the case observed in FTO/TiO₂/PVK/PAni cell, the polymeric layers still adopt the rough aspect observed previously, even on top of a bare ITO substrate. For PoMA however, the morphology of the film resembles stretched fibers, which covers the whole substrate.



Figure 60: AFM images of doped PAni (left) and PoMA (right) films deposited by blade coating.

After the deposition of the polymeric layers, the remaining of the photovoltaic device was assembled using the blade coating procedure described in the second part with the 4:1 Pb(Ac)₂:PbCl₂ ratio as the precursor ink for the perovskite layer, and afterwards the finalized devices had their photovoltaic performance measured. Since this experiment was meant to be a quick test these devices did not go through a deep optimization, consequently they displayed a bad photovoltaic performance.

From a few tries to assemble these devices, only one containing PAni could be measured (Figure 61), while there was no issue when PoMA was used as HTM. The poor reproducibility observed in the case of PAni is probably related to the high roughness of this polymeric film (Rq of 103 nm), which hinders its total coverage by the perovskite layer. The devices containing PoMA as HTM did not present the same issue due to the polymeric film being smoother (Rq of 13 nm). A superior film morphology led to a better interaction between the perovskite and the HTM beneath, as result PoMA devices displayed a higher open circuit voltage and fill factor. Despite showing a worse morphology and reproducibility, the device containing PAni presented a higher short-circuit current density, which may be attributed to its higher conductivity in comparison to PoMA.



Figure 61: JV curves of the photovoltaic devices assembled in the blade coater containing doped PAni and PoMA as HTM. Dashed lines represent the forward scan.

Table 14: JV parameters of devices assembled through blade coating with PAni and PoMA as HT

	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)
Pani Forward	0.34	6.33	44.34	0.94
Pani Reverse	0.36	7.19	45.03	1.17
PoMA 1 Forward	0.7	4.19	47.64	1.39
PoMA 1 Reverse	0.68	5.05	51.06	1.76
PoMA 2 Forward	0.67	3.95	46.28	1.22
PoMA 2 Reverse	0.68	4.51	51.06	1.56
PoMA 3 Forward	0.62	3.90	36.15	0.88
PoMA 3 Reverse	0.61	4.62	41.77	1.17

The performance results obtained with these brief tests were much lower than those obtained in each half of the work. However, for the purpose of bringing both topics together, a n-i-p structure made by blade coating would be more suitable for these materials for several reasons. First, both polymeric materials have a high absorbance in the visible region, consequently the HTM layer in p-i-n structure would have to be very thin to enable enough light pass through and reach the perovskite layer. Another benefit would be that in n-i-p configuration these polymeric materials would be replacing the Spiro-OMeTAD, the most expensive material.

A final advantage that the n-i-p configuration would present in this case is that these polymeric materials could be modified and introduce interesting new properties that could be transferred to the final device. The current test however, proved that both polymeric materials could be deposited through blade coating and that a fully working photovoltaic device could be assembled. With further optimization and development, a high performing device could be achieved while using the polymeric material as HTM and blade coating as the deposition method to assemble the cell.
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6. Appendix

	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)
Forward	0.94 ± 0.09	18.3 ± 2.6	41.2 ± 4.5	7.5 ± 0.8
Reverse	0.94 ± 0.03	19.1 ± 2.2	52.0 ± 3.7	9.1 ± 1.2

Table S 1: Average photovoltaic parameters of the standard cell using Spiro-OMeTAD.

Table S 2: Average photovoltaic parameters of the cells using doped PAni and PoMA with silver as electrode.

	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
PAni Forward	0.75 ± 0.04	10.6 ± 2.1	31.7 ± 7.4	2.5 ± 0.4
PAni Reverse	0.67 ± 0.11	9.96 ± 2.0	41.7 ± 9.6	2.7 ± 0.4
PoMA Forward	0.76 ± 0.08	13.0 ± 2.2	36.7 ± 3.3	3.8 ± 1.3
PoMA Reverse	0.80 ± 0.04	15.1 ± 1.3	47.3 ± 8.8	5.2 ±0.4

 Table S 3: Average photovoltaic parameters of the cells using undoped PAni and PoMA with silver as electrode.

	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)	
PAni Forward	0.54 ± 0.08	4.4 ± 1.1	26.8 ± 1.7	0.64 ± 0.09	
PAni Reverse	0.63 ± 0.07	5.4 ± 1.3	34.9 ± 3.1	1.2 ± 0.2	
PoMA Forward	0.72 ± 0.07	7.37 ± 2.8	31.0 ± 4.2	1.7 ± 0.8	
PoMA Reverse	0.73 ± 0.09	7.71 ± 2.6	38.5 ± 4.2	2.17 ± 0.8	

Table S 4: Average photovoltaic parameters of the cells using doped PAni and PoMA with gold as electrode.

	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)
PAni Forward	0.76 ±0.09	18.2 ± 2.9	34.8 ±10.4	4.9 ± 2.1
PAni Reverse	0.83 ±0.06	17.6 ± 1.3	53.9 ± 7.4	7.9 ±1.1
PoMA Forward	0.82 ±0.04	10.1 ± 3.7	37.5 ± 3.4	2.2 ±1.0
PoMA Reverse	0.80 ±0.11	11.5 ± 3.3	41.2 ± 3.6	2.3 ±1.0



Figure S 1: Photos of blade coated perovskite films made from different ink compositions.



Figure S 2: Low magnification AFM images of the perovskite layers deposited at different temperatures.

Condition	Scan Bias	Voc (V)	Jsc (mA/cm²)	FF(%)	n(%)	Rs (Ω.cm⁻²)	Rshunt (Ω.cm ⁻ 2)
30 ° C	Forward	0.93 ± 0.03	14.26 ± 1.95	46.88 ± 5.33	6.14 ± 0.50	17.16	426.54
	Reverse	0.92 ± 0.03	14.06 ± 1.91	46.16 ± 4.59	5.87 ± 0.41	19.91	429.03
40 °C	Forward	0.92 ± 0.01	14.41 ± 1.63	54.15 ± 3.10	7.16 ± 0.84	8.49	469.03
	Reverse	0.90 ± 0.01	14.17 ± 1.55	52.70 ± 3.23	6.71 ± 0.69	9.99	520.68
50 °C	Forward	0.89 ± 0.02	17.89 ± 1.97	51.38 ± 5.78	8.17 ± 1.20	8.15	297.93
	Reverse	0.88 ± 0.01	17.50 ± 2.18	51.18 ± 5.26	7.86 ± 1.14	8.69	321.71
60 °C	Forward	0.87 ± 0.03	17.43 ± 2.40	51.48 ± 4.41	7.77 ± 0.69	8.52	332.93
	Reverse	0.87 ± 0.02	16.95 ± 2.32	50.77 ± 4.37	7.39 ± 0.63	9.36	302.73
70 °C	Forward	0.83 ± 0.04	16.32 ± 1.59	47.09 ± 7.43	6.37 ± 0.98	10.31	234.88
	Reverse	0.84 ± 0.02	15.89 ± 1.65	48.89 ± 6.95	6.52 ± 0.90	10.15	300.62

 Table S 5: Statistical Photovoltaic parameters of blade coated devices made in different conditions.

Table S 6: Statistical Photovoltaic parameters of blade coated devices obtained with different compositions.

Pb(Ac)2:PbCl2 Ratio	Scan	Voc (V)	Jsc (mA/cm²)	FF (%)	n (%)	Rs (Ω.cm⁻²)	Rshunt (Ω.cm ⁻ 2)
Pb(Ac) ₂	Forward	0.92 ± 0.03	9.27 ± 2.48	52.67 ± 7.59	4.48 ± 1.28	10.45	372.74
	Reverse	0.91 ± 0.02	9.69 ± 2.59	58.61 ± 5.83	5.19 ± 1.40	8.11	439.62
8:1	Forward	0.94 ± 0.04	15.47 ± 3.11	53.46 ± 5.29	7.88 ± 1.92	8.61	404.69
	Reverse	0.94 ± 0.04	16.00 ± 3.25	57.62 ± 5.17	8.69 ± 1.92	7.57	485.48
6:1	Forward	0.99 ± 0.04	20.52 ± 2.40	55.47 ± 4.65	11.25 ± 1.23	7.80	363.62
	Reverse	0.98 ± 0.03	20.37 ± 2.06	58.16 ± 5.25	11.57 ± 1.27	7.51	476.58
4:1	Forward	0.97 ± 0.03	21.75 ± 1.56	56.84 ± 4.74	12.11 ± 1.03	6.78	339.38
	Reverse	0.95 ± 0.03	21.50 ± 1.42	58.52 ± 4.79	12.02 ± 0.79	6.62	457.54

The following program was developed during the thesis to be used in python in conjunction to an Arduino controlling a relay and a Keithley source meter to automatize the measurement of the solar cells. The source code is pasted here in case of need in the future. Only the forward scan of a single cell is displayed due the size of the code:

#Programa de medidas de celulas fotovoltaicas utilizando Keithley

#Nome da amostra a ser analisada nome amostra = 'Dispositivo 1 - claro' #diretorio geral para salvar os dados analisados diretorio= 'C:/ ' #potencial inicial Vinicio = -1.5#potencial final Vfinal = 1.5#Area Ativa da célula fotovoltaica em cm^2 Area_ativa = 0.045#Porta USB que o arduino está ligado porta = 'COM4' #------ Main enter de la parâmetros abaixo não são modificados normalmente------- Os parâmetros abaixo não são #Potência da fonte luminosa em mW/cm^2 Pot luz = 100#definir o passo entre os potenciais, em volts passo = 0.010#Delay após a medida para ajuste de velocidade (0.1 = 100 mv/s ; 0.2 = 50 mV/s ; 1 = 10 mV/s) delay = 0.05#delay entre a aplicação do potencial e a medida (em segundo) delaym = 0.02#tempo de estabilização, em segundos estab = 5#importando bibliotecas necessarias import visa import time import datetime import os import os.path import numpy as np import matplotlib.pyplot as plt from matplotlib.pyplot import plot, ion, show import sys import serial import pyfirmata from pyfirmata import Arduino, util vfinal = float(Vfinal) vinicio = float (Vinicio) passo2 = float (passo) #calculo do numero de pontos a serem medidos e a velocidade pontos = ((vfinal) - (vinicio)) / (passo2) pontos2 = (pontos + 1)veloscan = (passo/delay)*1000 #conexão com o Keithley -----rm = visa.ResourceManager() rm.list_resources()

Keithley = rm.open_resource('GPIB0::24::INSTR') Keithley.write("*RST") Keithley.timeout = 2500000 #preparação do keithley para a leitura Keithley.write(":SENS:FUNC:CONC OFF") Keithley.write(":SOUR:FUNC VOLT") Keithley.write(":SENS:FUNC 'CURR:DC' ") Keithley.write(":SYST:RCM MULT") Keithley.write(":SOUR:SOAK ", str(estab)) #----- conexão com o arduino ----arduino = pyfirmata.Arduino(porta) #desligar todos os contatos do arduino arduino.digital[2].write(1) #rele celula 1 arduino.digital[3].write(1) #rele celula 2 arduino.digital[4].write(1) #rele celula 3 arduino.digital[5].write(1) #rele celula 4 arduino.digital[6].write(1) #rele celula 5 arduino.digital[7].write(1) #rele celula 6 arduino.digital[8].write(1) #rele Contra eletrodo A arduino.digital[9].write(1) #rele Contra eletrodo B ----- Medida Forward C1-----#----#ligar arduino arduino.digital[2].write(0) arduino.digital[8].write(0) # Voltagem de inicio, final e passo da leitura Keithley.write(":SOUR:VOLT:STAR ", str(Vinicio)) Keithley.write(":SOUR:VOLT:STOP ", str(Vfinal)) Keithley.write(":SOUR:VOLT:STEP ", str(passo)) Keithley.write(":SOUR:SWE:RANG AUTO") #determinação do limite da corrente, direção da varredura e numero de pontos Keithley.write(":SENS:CURR:PROT 100E-3") Keithley.write(":SOUR:SWE:SPAC LIN") Keithley.write(":SOUR:SWE:POIN ", str(int(pontos2))) Keithley.write(":SOUR:SWE:DIR UP") Keithley.write(":TRIG:DEL ", str(delay)) Keithley.write(":TRIG:COUN ", str(int(pontos))) Keithley.write(":FORM:ELEM CURR") #inicio da varredura Keithley.write(":SOUR:VOLT:MODE SWE") Keithley.write(":SOUR:DEL ", str(delaym)) Keithley.write(":OUTP ON") #obtencao dos resultados do keithley result = Keithley.query(":READ?") yvalues = Keithley.query_ascii_values(":FETC?") Keithley.write(":OUTP OFF") Keithley.write(":SOUR:VOLT 0") #criar uma lista com os valores obtidos xvalues = np.arange(vinicio,vfinal,passo2) #transformar para Jsc xvalues2 = np.array(xvalues) #os valores de potencial aplicado yvalues2 = np.array(yvalues)*1000 #para transformar A em mA yvaluesj = (yvalues2/Area_ativa)*-1 #transforma a corrente em densidade de corrente já invertida #Plotar o grafico JV plt.plot(xvalues,yvaluesj, color = 'blue', label = 'Forward') plt.xlabel('Voltage (V)') plt.ylabel('Current Density (mA/cm^2)') plt.title('IV Curve') plt.xlim(0,1.1)plt.ylim(0,25) plt.legend() plt.show(block=False) plt.pause(5)

```
#calculo dos parametros fotovoltaicos
zip(xvalues2,yvaluesj)
voc = np.interp(0, -yvaluesj, xvalues2)
jsc = np.interp(0, xvalues2, yvaluesj)
potencia = np.array(xvalues2 * yvaluesj)
maxpot = (max(potencia))
#maxpotx = xvalues2[potencia.argmax()]
FF = (maxpot/(voc*jsc))
FF2= FF*100
eficiencia = ((jsc*voc*FF)/Pot luz)*100
voc_ar=round(voc,2)
jsc_ar=round(jsc,2)
FF_ar =round(FF2,2)
eficiencia_ar= round(eficiencia,2)
print(nome_amostra+"\n")
print("Célula 1 Forward \n")

print("Voc= ", str(voc_ar), " V \n")

print("Jsc= ", str(jsc_ar), " mA/cm<sup>2</sup> \n")

print("FF= ", str(FF_ar), " % \n")

print("n = ", str(eficiencia_ar), " % \n")
print("\n")
#gravando os dados
#primeiro a tabela de dados
diretorio2= diretorio + time.strftime('%d-%b-%Y')
relatorio= os.path.join(diretorio2, time.strftime('%d-%b-%Y')+ '-' + nome_amostra + ".txt")
if not os.path.exists(diretorio2):
         os.makedirs(diretorio2)
tabela = zip(xvalues2, yvaluesi, yvalues2) #transformando os valores de voltagem, densidade de corrente e
corrente em tabela, respectivamente
dir_tabela= os.path.join(diretorio2, time.strftime('%d-%b-%Y')+'-JV-F-'+ nome_amostra + "-C1.txt")
with open(dir_tabela, 'w') as tabelaf:
          np.savetxt(dir_tabela, list(tabela), fmt='%.4e %.12e %.12e', delimiter=' ',newline='\r\n')
tabelaf.close()
#relatorio dos dados
arquivo = open(relatorio,'a')
arquivo.write(nome_amostra+"\n")
arquivo.write("Parâmetros de interesse:\n")
arquivo.write("\n")
arquivo.write("Célula 1 Forward \n")
arquivo.write("Voc= "+ str(voc_ar) + " V \n")
arquivo.write("Jsc= "+ str(jsc_ar) + " mA/cm<sup>2</sup> \n")
arquivo.write("FF= " + str(FF_ar) + " % \n")
arquivo.write("n = " + str(eficiencia_ar) + " % \n")
arquivo.write("\n")
arquivo.close()
#-Apagar todas as variáveis-----
del xvalues
del xvalues2
del yvalues
del yvalues2
del yvaluesj
del voc
del jsc
del FF
del FF2
del eficiencia
del voc_ar
del jsc_ar
del FF_ar
del eficiencia ar
del tabela
```