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FABRICATION AND CHARACTERIZATION OF NANOSTRUCTURED ORGANIC AND HYBRID SOLAR CELLS BY SPRAY COATING TECHNIQUES

PhD in Renewable energy and energy efficiency

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*A mi familia,
os quiero.*

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Abstract

Currently, due to the increase in population there is an urgent need to re-structure the energy model of the planet to maintain a sustainable system. Renewable energy are a great bet to address this. Solar energy as the most abundant and in particular, photovoltaic energy, is one of the best choices as a solution.

The organic photovoltaic (OPV), within the different photovoltaic technologies is subject to study thanks to its low manufacturing cost, its low impact to the environment and its flexibility to be manufactured by multiple methods. In this work, OPV devices have been manufactured by depositing each of the layers by means of the different printing techniques, special focus in spray coating, which allows an industrial level production and a greater reproducibility.

These results obtained in the manufacture and characterization of organic photovoltaic devices, using the spray technique for the different layers; allow checking the operating parameters. All these processes, except for the evaporation of silver in the vacuum hood, have been carried out in normal environmental conditions, without clean rooms or inert atmosphere, which leads to a more real manufacturing process and oriented the industry.

Resumen

Actualmente, debido al aumento de población existe una necesidad urgente de reestructurar el modelo energético del planeta para mantener un sistema sostenible. Las energías renovables son una gran apuesta para abordar este problema. La energía solar como la energía más abundante y, en particular, la fotovoltaica, es una de las mejores opciones como solución.

La fotovoltaica orgánica (OPV), dentro de las diferentes tecnologías fotovoltaicas está sujeta a estudio gracias a su bajo coste de fabricación, su bajo impacto al medio ambiente y su flexibilidad para ser fabricada por múltiples métodos. En este trabajo se han fabricado dispositivos OPV depositando cada una de las capas mediante las diferentes técnicas de impresión, especial foco en la técnica de spray coating, que permite una producción a nivel industrial y una mayor reproducibilidad.

Estos resultados obtenidos en la fabricación y caracterización de dispositivos fotovoltaicos orgánicos, utilizando la técnica del spray para las diferentes capas; Permiten comprobar los parámetros de funcionamiento. Todos estos procesos, a excepción de la evaporación de la plata en la campana de vacío, se han llevado a cabo en condiciones ambientales normales, sin salas blancas ni atmósfera inerte, lo que conduce a un proceso de fabricación más real y orientado a la industria.

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Nomenclature

η	Efficiency (%)
λ	Wavelength (10 ⁻⁹ meters)
C	Celsius degree
<i>AFM</i>	Atomic Force Microscopy
<i>AL</i>	Active Layer
<i>AM</i>	Air Mass
<i>AZO</i>	Aluminium Zinc Oxide
<i>BHJ</i>	Bulk Heterojunction
<i>BNEF</i>	Bloomberg New Energy Finances
c	Speed of light in vacuum (m/s)
<i>CdTe</i>	Cadmium-Tellurium
<i>CNC</i>	Computerized Numeric Control
<i>DSSC</i>	Dye-Sensitized Solar Cell
<i>EQE</i>	External Quantum Efficiency
<i>ETL</i>	Electron Transport Layer
<i>EU</i>	European Union
<i>FF</i>	Fill Factor (%)
<i>GW</i>	10 ⁹ Watts
h	Planck constant

<i>HIL</i>	Hole Injector Layer
<i>HOMO</i>	Highest Occupied Molecular Orbital
I_D	Saturation Current (I)
I_L	Photo current generated (I)
$I_{\max}$	Current in the maximum power point (I)
I_{SC}	Short-Circuit Current (I/Area)
<i>IEA</i>	International Energy Agency
<i>ITO</i>	Indium Tin Oxide
J_{SC}	Short-Circuit Density (J/Area)
kW_P	10^3 Watts Peak
<i>LUMO</i>	Lowest Unoccupied Molecular Orbital
MW_P	10^6 Watts Peak
<i>NREL</i>	National Renewable Energy Laboratory
<i>OSC</i>	Organic Solar Cell
$P_{\max}$	Power in the maximum power point (W)
<i>PCE</i>	Power Conversion Efficiency (%)
<i>PV</i>	Photovoltaic
q	Boltzmann Constant
<i>QE</i>	Quantum Efficiency (%)
<i>R2R</i>	Roll to Roll
<i>R&D</i>	Research and Development
R_{SH}	Shunt Resistance Ω /Area
R_S	Series Resistance Ω /Area
<i>REE</i>	Red Eléctrica de España
<i>SEM</i>	Scanning Electron Microscopy

UV – Vis Ultra Violet Visible

$V_{\max}$ Voltage in the maximum power point (V)

V_{OC} Open-Circuit Voltage

XRD X-Ray Diffraction

Chapter 1

Introduction

The increase in global energy demand will be progressive in the coming decades, according to the International Energy Agency (IEA), this increase could reach one third in 2040 [1] central scenario in figure 1.1. This increase is due to a growing global demand, which can be covered with both fossil fuels and renewable energies, which has allowed new emerging powers to grow. If we talk about renewable energy, we can not ignore the largest source of energy we have and receive every day, the Sun. Approximately the Earth receives a total of $1.74 \cdot 10^{17}$ W of power (about $5.49 \cdot 10^{24}$ J of total annual energy). In 2018 it is estimated that the total primary energy consumption globally was about $5.68 \cdot 10^{20}$ J, so if everything were an ideal system it would cover all the energy demand worldwide, although we know today that this is not it is like that, even taking into account the losses and that there are also other sources of energy if we have a good plan to at least reduce the consumption of fossil fuels.

Figure 1.1: World energy primary demand by fuel projected by 2040 from IEA.

1.1 Global Energy Market

On the other hand, those already known as China (one of the largest consumers of fossil fuels), the main driver of global trends, which begins to apply more regulations on the emission of gases and install more renewable energy. Thanks to this and the approval of agreements such as the COP21 (summit held in December 2015 in Paris) almost half of the new electricity generation capacity installed in 2014 was renewable [2], as can be seen in Figure 1.2. Economic growth is an important factor in the growth of electricity demand. Although there has been a decrease in this growth during 2016 compared to the last two decades, this demand continues to increase, especially among the new emerging economies. Taking into account that the electricity sector is gaining ground in many end-use sectors and this leads to an increase in demand (according to forecasts made in 2015, demand will grow strongly by more than 70% until 2040), the use of renewable energy is which is having a faster growth, with an average annual increase of 2.9% from 2012 to 2040 [1].

Figure 1.2: New world electricity capacity in 2014-2040 from IEA.

Even in spite of this trend, it can be seen in Figure 1.3 that the trend in oil consumption is still growing, as well as its production. In addition, oil, as well as other fossil fuels, is a finite resource that we have been exploiting for many years and it is then, in 80s approximately, when we start to consume more than we discover per year. This fact has generated a strong demand that added to its scarcity and its increasingly difficult extraction causes an

increase in the considerable price [1]. This has led during all these years to an increasingly noticeable change in the energy mix of countries, in the special case of Spain we can see in the following figure that is composed of a good amount of energy from different sources, classified in this case by REE (Red Eléctrica de España) in "Non-renewable" and "Renewable" [3].

Figure 1.3: Global oil production/consumption from IEA.

Figure 1.4: Peninsular energy mix of Spain (without the Balearic Islands and the Canary Islands) as of 2018. Source REE.

Approximately, we can see that in terms of installed power, we talk about almost 50/50 between renewable and non-renewable sources but the reality is that if we go to terms of generation this is reduced to 65/35. This does not mean that it is bad, because if we compare with Germany, which at first was said to take us a lot of advantage, they surpass us by only 3% in total production [4] as we can see in the following figure.

Figure 1.5: Energy mix of Germany as of 2018. Source AG Energiebilanzen, ZSW, BDEW.

Recall that even with these forecasts, we are still far from covering the agreements set in Paris (around cover about 2/3 of the demand through renewable sources) but that is undoubtedly a great step and evolution in this regard.

1.2 Global warming

For this cause and the agreements that were signed, intend to replace the Kyoto Protocol and which aims to maintain the annual average temperature rise below 2°C and to continue striving to limit it to 1.5°C. It is likely that between 1983 and 2012 it was the 30-year warmest period of the last 1400 years in the Northern Hemisphere [5] (Figure 1.6). This is corroborated by the increase in greenhouse gas emissions, such as CO₂, whose emissions as of 2012 at world (excluding China) is 32,814 million tons [6], Figure 1.7.

Figure 1.6: Surface global average temperature over 30 years.

Figure 1.7: Global greenhouse emissions in equivalent CO₂ ton.

In addition, this is one of the main reasons why the substitution of fossil fuels is being sought. Also and as the second main reason, we must bear in mind that these are finite, and that with the passage of time are running out. Although they have been making predictions every year warning that there really is little, this figure is changing every year, extending the term more and more, but this will not always be the case since they will stop discovering deposits or simply the cost of extraction is excessive. To all this, we must add that in addition to oil and coal, the first and most numerous sources of fossil energy is gas, which has been used since the 50s in the US 70 / 80s in Europe and since the 90s in Spain.

The following figure shows schematically the predictions made about the reserves of these three fossil fuels.

Figure 1.8: Prediction of available reserves of coal, oil and gas by CIA World Factbook.

It can be seen that although coal is the fossil fuel that has been used the longest, it is also the most numerous and the one with the greatest 'life' that it has, approximately until 2088. It is followed, although far enough, by gas and finally oil, being the scarcest with only about 25 or 30 years of life [7].

In summary, it can be observed that from these data and from some of those shown in previous points that even with their shortage these fuels are still used today and that they have even increased the use of these despite their scarcity and is mainly due to the general increase in population and the total demand for energy. Even so, this will not last forever.

The new reserves that are discovered are becoming less and more difficult to exploit and that is why, for a long time and as has been shown in these chapters, we work on alternative energy sources that are renewable and, above all, less polluting and more friendly to the environment.

1.3 Renewable Energy

Currently there is a wide variety of renewable energies in the world which today are mostly perfectly integrated into the day to day. Among all of them, we can highlight the three most used worldwide as we can see in the Figure 1.9.

Figure 1.9: Estimated Renewable Energy Share of Global Electricity Production, End-2017 by IEA.

1.3.1 Hydroelectric power

This type of energy is one of the first and oldest to be exploited, since ancient Greece used water mills to grind wheat and flour, the kinetic energy of water turned the mill and thus become mechanical energy. It is not from the 19th century when the first hydroelectric power station was built (Niagara Falls 1879).

A conventional hydroelectric power plant is composed of three parts, a power plant where electricity is produced; a dam that allows to open and close the water passage; and a reservoir to store water. The operation is simple, the dam is opened and the water circulates through turbines, which move and spin a generator to produce electricity. The amount generated depends on the kinetic and potential energy in addition to the amount of flow that passes [8].

1.3.2 Wind power

Harnessing the energy of the wind is one of the oldest things of the human being. From the first boats in antiquity, through the systems of pumping water from Babylon to the current wind turbines. In 1900 we had the first prototypes of electric wind turbines¹ and thanks to the I and II World War and its advances in aviation rotors makes it possible to investigate more in this technology. Although in the 60s his research is slowed by the overwhelming decline of oil is from the 80s when it again take impact until today, being one of the leading energies in the field of renewable energy [9].

¹modern wind power is considered to have been first developed in Denmark in 1891 and a 22.8-meter wind turbine began operation in 1897

1.3.3 Photovoltaics

Thus, the photovoltaic market has grown in the last decade at a remarkable rate (even during difficult economic times) and is becoming an important source of energy for the world. In 2019, 114.9 GW were installed worldwide reaching an accumulated capacity of 627 GW [10]. Studies carried out in different scenarios show that photovoltaic solar energy installed in countries such as Spain is 15% behind only China with 26% end of 2019 and being in the Top 10 of the countries with the most installed capacity in 2019 (Figure 1.10).

However, the photovoltaic market evolves and photovoltaic systems move from the deployment of large floor installations (from > 100 kWp to > 100 MWp) to smaller systems (around 5 kWp up to a maximum of 300 kWp). This may be because in order to carry out large installations, there is a relationship between space and energy that sometimes involves the elimination of vegetation, the transformation of the landscape or the change in the perception of cities [11]. In addition, distributed generation not only reduces costs in infrastructures, lost in the transport or distribution of energy, but it provides other benefits such as the decrease in peak demands or the assurance of electricity supply in areas of difficult access[12–15] (Figure 1.11).

Figure 1.10: Global PV market since 2001 from Snapshot of Global PV Market Report 2020 by IEA.

Figure 1.11: Cumulative installed grid-connected PV capacity in EU 2019 by JRC.

That is why the inclusion of photovoltaic systems in sectors such as industry or construction can be an advantage not only from the environmental point of view but also technical and economic. Despite the fact that the photovoltaic market is progressing and that photovoltaic technology is experiencing rapid improvements in the power conversion performance and in the reduction of the economic cost, great R&D challenges continue to be identified, such as making these emerging technologies more efficient and competitive against the conventions of silicon or other renewable sources [16].

Within the photovoltaic it can be said that there are three large families of technologies. The first one (or first generation, 1G) is possibly the best known since it was the first one from which everything evolved (the first useful generation device was in 1954 [17] and had a 4.5% efficiency). This is the family of silicon, monocrystalline or polycrystalline and we are currently as we can see in Figure 1.12 in a 30% efficiency, practically in the theoretical limit. The second family or generation (2G) is the so-called thin layer, whose foundation is to use a very small amount of material, thanks to evaporation techniques among others. Some of the clear examples are amorphous silicon, cadmium tellurium (CdTe). In spite of using much less material and that could be said in a reduction of costs, the high price of these makes that in the end is determinant for the final price of the device. Therefore, a third generation (3G) appeared that included high efficiency (concentration) technologies, which are formed by many unions or what are called tandem cells (multiple p-n junctions in the form of a sandwich). In this way efficiencies of more than 30% can be achieved, as shown in Figure 1.12 (about 45%). Within this family has also included emerging technologies such as organic and hybrid.

In recent years, research into organic photovoltaics, has grown enormously. This is due to its low manufacturing cost (since they can be manufactured using continuous printing techniques) and can have cheaper devices with acceptable efficiencies (currently they are already around 11% compared to conventional photovoltaic technologies, see Figure 1.12), so it is expected that in the near future they can compete with these technologies in the market. One of the advantages of this type of technology due to the use of organic materials and in thin film is the possibility of being able to manufacture flexible devices, very light and semi-transparent, which can adapt to surfaces very easily[18–20].

Figure 1.12: Best efficiencies of photovoltaics technologies from NREL.

Because of this, organic solar cells (OSCs) will enter the electricity market (some companies like Infinity OPV being one of the first if not the first to enter the market) and be able to compete with other conventional technologies such as crystalline silicon and thin film technologies. In the following figure, we can see the price of kWp depending on the technology.

Figure 1.13: PV module price of different technologies from Bloomberg New Energy Finances (BNEF).

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Chapter 2

Photovoltaic energy

Until now, we have seen that Earth receives a large amount of energy by the Sun in form of radiation. In this chapter the main principles of a photovoltaic device and the most common materials used in the organic-based family will be showed.

2.1 Photovoltaic effect

Primarily the photovoltaic effect consists of the absorption of photons by a material, the generation of charges and the collection of these by the electrodes for their subsequent transport to an external circuit. In this way, a solar cell exposed to solar radiation is able to convert these photons into electrical energy. On the other hand, unlike inorganic devices where this photon energy is transferred to an electron, in an organic device the absorption of light generates electron-hole pairs, known as excitons, as indicated in the next Figure [1].

Figure 2.1: Diagram of a solar cell with p-n junction (left), and an organic heterojunction solar cell (right).

In this way, we can explain the photovoltaic effect of an organic solar cell in four stages [2]:

1. Absorption of light and generation of excitons.
2. Dissemination of excitons towards the interface between acceptor and donor.
3. Dissociation of these excitons in holes and electrons.
4. Transport to the electrodes and collection.

Figure 2.2: Diagram of operation of a solar cell [2].

It is appreciated that the semiconductor, that is to say, the conjugated polymer that forms the active layer it is located between the electrodes, which have a different work function. Thanks to this, an electric field is created. Under normal lighting conditions as has already been commented, an exciton would be generated. In order to increase this photovoltaic effect these excitons should be dissociated allowing the electrons to move towards the electrode with a smaller work function and on the other hand to the hole towards the electrode with a function of greater work. For this to happen there must be two materials with different affinities electronic, this is so because the excitons only dissociate in the interfaces between them. These materials are called donor and acceptor.

The material that acts as a donor must have levels HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) lower than the acceptor, taking as reference the level of vacuum. In addition, the donor will take care of transporting the holes and will be in contact with

the anode while the acceptor will be in charge of transporting the electrons while it is in contact with the cathode. In the following figure this process is observed [1, 2].

Figure 2.3: Band diagram of a OSC.

Taking this into account, the electric current generated in a photovoltaic cell corresponds to the number of charges collected in these electrodes. It should be added that logically each of the efficiencies of each stage will affect the final efficiency of these devices, or what is the same, by the losses associated with each process. The first of these is the absorption stage, which is linked to the absorption spectrum of the organic molecules that make up the cell and the fraction of absorbed photons. The process of diffusion of the excitons is clearly related to the distance they must travel to the heterojunction and its morphology. The dissociation depends mainly on whether the process is more or less favorable energetically and finally the collection depends both on the difficulty for the carriers to reach the electrodes and on the amount that reach them without undergoing recombination [1, 2].

That said, as almost any real process, there are losses such as in the absorption of photons can occur various situations as not all absorb because they have less energy than the gap, lost by reflection, thermal losses, etc.

2.2 Conjugated Polymers

The conductive polymers, also called synthetic metals, were discovered in 1974 and since then they have aroused great interest and rapid growth in

organic electronics. One of its main characteristics is that they present delocalized links, which makes them a priori good substitutes for silicon in the field of photovoltaics. Having delocalized links means that they have single and double links located in different orbitals of their electronic structure, the simple links would be in the orbitals σ , while the double ones are in the orbitals σ and π . Specifically these electrons of the orbital π are those that can move among the others giving place to what is called delocalization of electrons allowing the mobility of the charges along the polymer chain [3].

As happens in an inorganic device, here there is also a structure in bands, but with a slight difference, since in this case there is no band of valence and driving if not energy levels known as HOMO and LUMO, separated both by the banned energy band, called band gap. The HOMO would correspond to the last energy level occupied by the electrons (analogous to the valence band) and the LUMO to the first energetic vacuum level of electrons (analogous to the conduction band). Band gap is the space between these energy levels and varies between 1 and 4 eV for this type of polymers, it is usually slightly higher than conventional silicon which is around 1.4 eV [4].

The main difference between conventional semiconductors and conjugated polymers is that in the former, the excited electron and the hole migrate freely towards the opposite electrodes (see Figure 2.4) while in the latter, an electron-hole pair is generated after the impact of a photon, what we know as exciton [5].

Figure 2.4: In a conventional semiconductor, the absorption of light generates an electric field that separates the photoinduced charges. E_C and E_V are the conduction and valence bands respectively.

2.3 Organic solar devices

Within this large group of devices, we can distinguish in two large families for this work:

- Solar cells sensitized by dye (Dye-Sensitized Solar Cells, DSSCs).
- Organic solar cells (OSCs).

Within this work, we are only going to focus on OSCs. The DSSC are based on capturing light in a liquid electrolyte or gel and currently it has also been tested with solids and the generation is carried out by means of a dye; the electrode is nanostructured. The transfer of charges happens between an organic and an inorganic material. On the other hand, in OSCs this transfer happens between organic materials. Among the active layers most used today are those formed by a polymer and a fullerene derivative, being donor and acceptor respectively [1, 3, 5, 6]. In the group of OSCs, devices have been historically manufactured in a bilayer configuration, but this geometry has been superseded by dispersed heterojunction.

1. Bilayer devices:

These devices are formed by a semiconductor type p (donor) and another type n (acceptor) separated by a flat interface. In this interface is where exciton separation occurs due to the difference of ionization potential and electronic affinity between them (see Figure 2.5). In these devices the distance to which these excitons have been created is significantly influenced with respect to where it is dissociated since the diffusion length of the exciton is approximately 10 nm, bearing in mind that it is clearly visible that only the excitons formed at a sufficient distance for that can reach the heterojunction without undergoing recombination can dissociate and continue their way to the electrodes [2], so in this configuration much of the active layer is wasted for photo generation.

Figure 2.5: Diagram of a bilayer configuration (Lynn, 2010).

2. Dispersed heterojunction devices:

In the dispersion heterojunction devices both materials p and n are mixed forming two interconnected percolation networks, one type p and another type n. In this way, we increase the contact surface and favour the separation of charges. Similarly, we also reduce the distance between materials and thus the exciton makes a shorter travel, thus avoiding its possible recombination [2, 7–9].

Figure 2.6: Diagram of a dispersed heterojunction configuration [10].

The materials ¹ most used today (see Figure 2.7) for this type of configuration are:

- The conjugated poly-3-hexylthiophene polymer known as P3HT whose function is that of electron donor.
- The fullerene derivative [6, 6] -phenyl-C61-butyric acid methyl ester also known as PCBM which acts as an electron acceptor.

Figure 2.7: Chemical structure of two molecules used in the manufacture of OSCs. P3HT and PCBM [2].

¹the materials will be detailed in section 3.3

2.4 Characteristics of a solar cell

So far the operation of an organic photovoltaic cell has been shown (the physical and chemical principles that are produced), as well as its configuration and some of the most common materials used, but it has not been explained how it is applied in practice and, how to obtain an external electric current. For this, as in the case of a battery, a resistance is connected to its electrodes.

2.4.1 Equivalent circuit of the solar cell:

The electrical model that best suits a solar cell is composed of a current source that represents the photo generated current, a diode in parallel, and two resistors, one in series and one in parallel. Each of these resistors represent losses in the circuit inside the cell, the series resistance symbolizes the losses due to the low conductivity of semiconductors or electrodes (lost by heat or Joule effect) and the parallel resistance represents the possible leaks in the system (due to impurities near the union and to the same p-n junction). In the following figure, an outline of this circuit is observed [2].

Figure 2.8: Equivalent circuit of a solar cell.

Once the scheme is known, the equation of the solar cell can be displayed.

$$I = I_L - I_D \left(e^{\frac{q(V - IR_s)}{nk_B T}} - 1 \right) - \frac{V - IR_s}{R_{SH}} \quad (2.1)$$

Where I_L is the photo generated current, I_D is the saturation current of the diode, q is the charge of the electron, V is the potential at the terminals, n is the suitability factor, k is the Boltzmann constant, T is the temperature

at Kelvin, and R_S and R_{SH} are the series and shunt resistances, respectively. In the next figure, you can see the curves IV of a solar cell in darkness and in lighting conditions, and in turn the point of maximum power under given conditions. It is clearly seen that the incidence of light tends to move the IV curve to the fourth quadrant [4].

Figure 2.9: a) Curve IV of a solar cell in darkness (black) and in illumination (red). b) Point of maximum power in a curve IV defined by I_{max} and V_{max} .

As observed in (2.1), the second term (see (2.2)) is what is called dark current, I_{dark} , this current appears in the opposite direction to the photocurrent when a load occurs and a potential difference is generated.

$$I_{dark} = I_D \left(e^{\frac{q(V+IR_S)}{nk_B T}} - 1 \right) \quad (2.2)$$

The series and parallel resistance negatively affect the electrical behavior of the system, although in a very different way. The series resistance mainly affects high current densities, on the surface of the contacts. On the other hand, the parallel resistance is more related to current leakage at the ends of the device. That is why, as will be seen later, they reduce the fill factor.

2.4.2 Characteristic parameters of a solar cell:

In the previous section, we have shown the equation of the equivalent circuit, from it we can extract different important parameters that will allow us to interpret the functioning of a solar cell. The IV curves shown in Figure 2.9 (up), of which in addition to the maximum power point, values such as I_{SC} (short circuit current), V_{OC} (open circuit voltage), FF (fill factor) can be extracted and the η (power conversion efficiency) [10].

- The short-circuit current (I_{SC}) is the one that circulates through the device when the potential between the terminals is zero. This current occurs due to the created charge carriers [7].
- The open circuit voltage (V_{OC}) is the maximum voltage that can be produced in the solar cell.

The filling factor (FF) is a parameter that together with the I_{SC} and the V_{OC} allows to determine the maximum power of a solar cell as shown in (2.3), where the FF is shown as the quotient between the maximum available power and the product of I_{SC} and V_{OC} (maximum theoretical power). In turn, the maximum power is represented as the product of I_{max} by V_{max} , which determine the point of maximum power in the IV curve. This point is obtained by making a maximum in the function of the product $I * V$ with respect to V as shown in (2.4). It is a measure of the quality of the union and the series resistance of the cell. The higher this factor is, the closer to one, the characteristic IV with illumination is closer to the rectangle of maximum theoretical power and, therefore, the cell is of higher quality.

$$FF = \frac{P_{max}}{V_{OC}I_{SC}} = \frac{V_{max}I_{max}}{V_{OC}I_{SC}} \quad (2.3)$$

$$\frac{d(IV)}{dV} = 0 \quad (2.4)$$

- Power conversion efficiency (PCE) is the most common parameter to compare cells, since it is an indicator of the performance of this. It relates the amount of power produced and the amount received by the sun, that is, the amount of power produced by the total received. In (2.5) it is represented.

$$\eta = \frac{P_{max}}{P_{in}} = \frac{FFV_{OC}I_{SC}}{P_{in}} \quad (2.5)$$

- In addition, a parameter to take into account is quantum efficiency (QE), which is defined as the number of electrons moving from the valence band to the conduction by incident photon [11]. Then:

$$J_{SC} = q \int b_s(E)QE(E) \cdot dE \quad (2.6)$$

Where J_{SC} is the photocurrent density, $b_s(E)$ is the incident spectral photon flux density, the number of photons of energy in the range E to

$E+dE$ which are incident on unit area in unit time and q is the electronic charge. Because energy is a more suitable parameter for this field, QE can be given as a function of photon energy and wavelength. The relationship is as follows [12]:

$$E = \frac{hc}{\lambda} \quad (2.7)$$

Where h is Planck's constant and c the light's speed in vacuum. A conversion between electron-Volts and wavelengths is $E(\text{eV}) = 1240/(\lambda(\text{nm}))$.

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Chapter 3

Polymeric solar cells

As we have seen in section 2.3 the different organic devices that we can find, in this chapter we will deal in depth with those that are the main object of study in this work, polymeric solar cells.

3.1 Geometry of organic solar cells

When we talk about polymeric solar cells, we mainly talk about two architectures or ways of depositing the layers (this type of cells has a sandwich type arrangement, stacking one layer on top of the other). The first one, as seen in figure 3.1 (left), called standard architecture and the second, figure 3.1 (right), inverted architecture.

Figure 3.1: Standard architecture (left); Inverted architecture (right).

In the standard structure, the semitransparent electrode acts as an anode (usually indium tin oxide, ITO) is deposited on a transparent substrate,

after a hole injector layer (HIL) is deposited (usually PEDOT:PSS), followed by what is known as the active layer (a solution of P3HT:PCBM as most common), where the photovoltaic effect is produced. Finally, as the simplest standard configuration, the metallic non-transparent electrode is deposited (more conductive layers can also be added to favor electrons transport to this electrode), which acts as a cathode (aluminum).

On the other hand, if a metal with a higher work function to the ITO as a back electrode is used (the metal in this case as an anode and the flow of electrons going towards the cathode instead of the anode) the architecture is called inverted[1, 2].

This architecture has certain advantages if we talk about stability issues, since it is less reactive to humidity thanks to silver but they are showing less stability to oxygen[3]. In addition, it allows replacing other layers such as the PEDOT: PSS with more transparent ones, improving the absorption of light from the active layer. These devices can be manufactured in industrial processes compatible with serial production (thanks the use of silver), using printing techniques on flexible substrates and low weight (plastic materials in small quantities, with solar cell thicknesses up to 200 times lower than in silicon). That will affect a very competitive economic cost in addition to having a lower environmental impact in the manufacturing process (lower temperatures, absence of vacuum requirements especially if we talk about techniques such as spray coating, etc.). Actually, the main disadvantage is its low stability and useful life as mentioned above.

3.2 Manufacture Techniques

Currently there is a wide variety of technologies for manufacturing organic solar cells, most are well known printing techniques, and have been improved or adapted for this type of systems, some of them can be implemented in R2R systems in series ¹. We can group in printing techniques and coating techniques. The most important and currently used ones will be mentioned below:

¹a roll-to-roll is a manufacturing process in a roll of flexible plastic or aluminum

3.2.1 Printing techniques

- **Flexography:**

A cylinder, partially immersed in a tank where the ink is continuously transferred to it, and it is retained in figures previously engraved on the outside of said cylinder. This allows the ink to be deposited and thus be able to print it or deposit it towards a 3D mirror image in another cylinder, which allows the final transfer, as shown in figure 3.2. Through this technique devices have been manufactured obtaining an efficiency around 3%[2].

Figure 3.2: R2R flexography technique.

- **Gravure:**

The engraving technique is the most used in mass printing, as in the printing of magazines or newspapers, and its operation is simple. A main roller, called engraving cylinder is semi-submerged in an ink bath, in this cylinder there is a series of engraved cavities, whose depth is what fixes the thickness that will finally have the impression. A metal plate called doctor blading is responsible for removing excess ink, making sure that only the one that fills the cavity, as shown in figure 3.3. With this technique have reported results between 1.55% and 1.8% efficiency[4].

Figure 3.3: Gravure technique.

- **Screen Printing:**

In this process a screen is used, which has been stuck in a frame under tension, and over it a brush is responsible for extending and pushing the paste through it, on the substrate, as shown in Figure 3.4. Since it allows the formation of very thick layers, with high viscosity, it is very suitable for the printing of the electrodes in the OSC, but it has also been tested for the deposition of the active layers. It is also a quick technique for mass production and the technology is well developed. With this technique, efficiencies between 2.5 and 4.5% have been obtained[5].

Figure 3.4: Screen printing technique.

- **Inkjet printing:**

It is a technique in which a mobile print head drops tiny drops of ink on a well-defined position of the surface to be printed. The injection can be continuous or discontinuous, in the continuous a continuous jet is injected, which is divided into drops by an acoustic wave generated by a piezoelectric device, as shown in figure 3.5. This method is used mainly in high-frequency applications. speed. In the discontinuous method or also called "drop-on-demand", drops are injected separated by a piezoelectric device or thermally. This method has more precision since the drops generated are smaller and firmer, although if they are generated thermally they may have certain problems with some soluble polymers, since water is used in that method. The viscosity should be a critical factor since low viscosities are needed, but not too much since it would increase the speed so that tails would form although this method is believed and expected to be an important candidate in the future for the processing of OSCs. With this technique have been reported efficiencies around 2%[6].

Figure 3.5: Inkjet printing technique.

3.2.2 Coating techniques

- **Slot die coating:**

If we have to talk about the most used and proved R2R technique, slot die probably be the first one. The ink is introduced inside a head (figure 3.6) who have a pattern like a stripe. The ink is pumped through this and form a meniscus. You can control the wet thickness adjusting some parameters like speed, or ink supply, temperature but all of this depends of the properties of the ink and the web surface. Thanks of this, the easiness of controlling and of course the uniformity of the layers

deposited is one of the best up-scaling techniques for OSCs. Efficiencies of 7% have been reported[7].

Figure 3.6: Slot die technique.

- **Spin coating:**

By this technique, very smooth thin layers can be grown on a substrate. The material to be deposited is dropped in drops on a platform that is rotating, as shown in figure 3.7. The speed of rotation is a determining factor in this type of technique, to control the thickness of the thin film. This technique is widely used in the manufacture of organic solar cells, with demonstrated efficiencies around 7.4% but it has no up-scale capability[8].

Figure 3.7: Spin coating technique.

- **Spray coating:**

It is a technique that has been studied in recent years as a main alternative to "spin coating". Mainly responsible for depositing, through a airbrush, the material on the substrate, usually with the help of a mask, as shown in Figure 3.8. As an advantage, the expense of material and ease of deposit is reduced. Efficiencies have been reported around 2-3%. There a lot of kind of commercial spray coating stations from conventional to plasma and ultrasonic spray[9].

Figure 3.8: Spray coating technique.

- **Doctor blading:**

In it, a blade is responsible both for removing excess ink and for distributing it in a more efficient and uniform way, as shown in figure 3.9. This is why it is compatible with most coating techniques and R2R. The efficiencies reported in this case vary, depending on what type of method the doctor blade is introduced, but we find values of 5% to 10%. Knife die coating and slot die are a variant of this, more scalable[10].

Figure 3.9: Doctor blading technique.

Of all of them, the slot die (in combination with flexography system) and spray coating are the most promising in the field of OSCs, because they are perfectly integrated into an industrial-scale processing and manufacturing series, which would allow them to compete with those that are called "Traditional technologies"².

The technology of OSC is very wide and there are completely organic devices to hybrids based on perovskites with an efficiency of up to 22.1%[11] although its useful life hardly reaches the year. Based on previous studies of inverted OSCs using the spray coating technique, the experiment consists of a sequential replacement of the layers deposited by the spin coating technique and thermal evaporation by layers deposited via spray. In the first place, only the active layer is deposited by spray and only in this step have efficiencies close to 4.1%[12] been reported. Next, it is intended to perform the same steps to deposit the ZnO layer and, finally, the tests with the silver electrode would be carried out, which, as has been demonstrated in previous investigations, have achieved efficiencies of up to 2.3%[13] working at temperatures of 150°C, which are compatible with flexible substrates. In flexible substrates, jobs have already been reported where organic solar cells are produced with an efficiency between 4% and 6% and with values of filling factor close to 70%[14]. Today we can already find that there are already companies like "OPV Infinity" that manufacture completely flexible organic solar panels or modules using "Roll to Roll" techniques. Due to the high cost of a scarce material such as the Indian and the high energy cost of manufacturing this layer, work is also being done on replacing the semi-transparent ITO electrode[15] ($<100 \Omega\text{cm}^{-1}$) with other materials such as PEDOT:PSS ($\approx 500 \Omega\text{cm}^{-1}$) where efficiencies were obtained around 2%. Materials such as carbon nanotubes[16] are also in the spotlight when talking about flexible substrates and ITO substitution due to their high conductivity, recording data of 3% efficiency, very similar to organic solar cells manufactured with ITO.

²conventional silicon technologies and thin film family

Figure 3.10: PV foil from Infinity OPV.

Therefore, organic photovoltaic technology is beginning to be considered as one of the main alternatives to conventional technologies due to its low manufacturing cost and its great capacity to adapt to other systems and be fully integrated. The systems of organic solar cells are also complemented with other conventional technologies such as silicon, which added to elements such as graphene allow manufacturing solar cells with an efficiency close to 12% and improving their conductivity. In addition, this layer of graphene oxide can act as an anti-reflective layer and improve the transport of cargo[17].

Within this group of OSCs, we also find tandem cells in which it is intended to integrate layers of other organic materials or even organic molecules in order to increase the absorption of light[18] and thus significantly increase the efficiency of the devices reaching values also close to 12% like the hybrid devices with perovskites. The main advantage compared to these is the same as any other completely organic device, mass manufacturing in a roll-to-roll process, costs, flexibility... Consolidating these concepts and taking advantage of the advantages of this new technology could be carried out a wide range of applications, where we could print solar cells in bulk, paint virtually any surface and produce with them or even coat buildings and surfaces in any way and size because they can be semi-transparent. There is therefore a large space for innovative scientific contributions in the study of the manufacture of organic solar cells through this type of techniques for both, the scientific and academic community in the field of solar energy and for companies. The final objective is could be produced on an industrial scale and lower costs with a high reproducibility, becoming competitive with the rest of conventional technologies.

3.3 Materials

As seen in the previous section, an OSC is formed by a superposition of layers of different materials, each with a specific function such as transporting electrons, injecting holes, acting as electrodes and contact or extracting the current generated by the photovoltaic effect. In the next section we will describe the most used materials in each of the layers.

3.3.1 Substrates

One of the main characteristics that the substrate must have is transparency, as well as a low permeability, in order to act as an insulating medium to the exterior and also to withstand high temperatures around 150-200°C. If we look for one that meets all these parameters, we find glass and therefore it is the most widely used in the field of polymeric solar cells.

Within the range of glass we can find all possible sizes. Thanks to this and all the properties mentioned above, it is capable of being used in numerous manufacturing techniques such as those already described in the section. On the contrary, if we talk about manufacturing techniques R2R we find the problem that glass is not flexible, therefore, we must resort to transparent plastics, being the case of PET the most widespread[3].

3.3.2 Electrodes

It has already been seen in the previous section that according to what type of architecture we are using these electrodes can be front or rear and therefore be used as cathodes (electron collector) or anodes (hole collector) and although both must have conductive properties that there are certain differences. The front electrode must be as transparent as possible in order to capture the light, a high transparency in the visible spectrum (approximately 80%) is sufficient, a conductivity around 10 Ω/sq must also be added. Indium tin oxide (ITO) has these characteristics and is the most used (although its use is increasingly being reduced). The range of qualities and ways to find the ITO is wide, being the most usual way to find it is already printed on the substrate, be it glass or plastic.

But this electrode has a main drawback, that the Indian is scarce, as well as other rare metals (hence its name). Due to this, it is subject to numerous geopolitical conditions, as well as its scarce and concentrated distribution throughout the planet make it that each time, as it was said before, less is used. For this reason, it has been some years now that some substitutes are being studied. One of the first and that is also semitransparent is aluminum zinc oxide (AZO)[14, 19] along with others such as carbon nanotubes[20], graphene[21] or silver nanowires[22].

Another type of substitutes also tested are non-transparent like the PEDOT: PSS but as its name suggests, the main drawback is that they are not transparent, even so we can find efficiencies around 2%[15] and the ease of using it in almost any kind of technique mentioned.

Although in this work ITO will mainly be used for the manufacture of OSCs, all this must be taken into account since the way forward is the complete elimination of this material as an electrode, which is why the use of new materials will be explored.

On the other hand, we have the back electrode, with metals such as aluminum or silver being the most used. These metals for laboratory-scale manufacturing are usually deposited by vacuum, but we know that this process consumes a large amount of energy and also does not allow to be scaled to a mass production process. We have already seen when we talk about the front electrodes that silver in various ways is a very viable candidate and speaking as a back electrode it could be said that silver is currently the only and real candidate because it is capable of being deposited by the great most of the available techniques, either R2R[23] or by spray printing techniques[13]. Today a wide range of silver inks and pastes are sold and companies such as DuPont sell it or even prepare them on demand.

3.3.3 Active Layer

The layer that produces the photovoltaic effect is the active layer. This layer is between the gap injector layer (HIL) and the electron transport layer (ETL) as if it were a sandwich. As has been studied in previous chapters, the most common structure in which we find it is a bulk heterojunction (BHJ), a mixture of two materials, one type P (electron donor) and another type N (electron acceptor). The heterodisperse junction is a junction in which the two materials penetrate one another creating a percolated network of a few to hundreds of nanometers as shown in section 2.3. The objective as it was said is to achieve the exciton formation and its subsequent separation in

charge carriers.

- **Donor materials:** Within the materials that can be considered as donors, there must be a series of properties that comply, among them, electrical conductivity, nonlinear optical properties and crystallinity, in addition we must add that the HOMO levels are in a range between -4.7 and -5.8 eV approximately[24]. But the real discovery came in the 90s when a way to work with the P3AT polymer was discovered and to obtain a different region (HT). This region has improved properties of those already mentioned[25]. As a result, the resulting polymer is P3HT (-5.1 eV), poly-3-hexyl-thiophene, which currently has become the most used and as a safe option for the manufacture of OSCs.

Figure 3.11: Poly-3-hexyl-thiophene (P3HT) by Scharber et al.

- **Acceptor materials:** On the other hand, we have that as a maximum level LUMO for this type of materials is around 1.4 eV, since if we exceed the figure of 2 there is a fall in efficiency of 30% approximately. Despite this, the compound most used until relatively recently is the PCBM. This comes from derived from more simple called fullerenes, a carbon-based molecules with the shape of a ball. The simplest of them is the C60. Fullerenes can not be dissolved, which is why a chain called phenyl-C61-butyric acid methyl ester, or PCBM, is added after being purified, hence the name[26]. This supposes a quite expensive process of energy, that added to that in addition owns high levels of LUMO and always thinking about a profitable series manufacture has taken in the last years to a search of new BHJ³ free of fullerenes and of non-hazardous solvents.

³until the moment the most used is P3HT:PCBM

Figure 3.12: Molecular structures of commonly fullerene-based used as electron-acceptor materials.

One of the most promising is IDTBR, which is a result of sintering indacenodithiophene (IDT) with *n*-octhyl (O-IDTBR)[27]. With this new material, we are around LUMO values of 1.6 eV, which are quite better than those of the PCBM, with the addition of using non-harmful solvents and with a lower manufacturing cost. Regarding the manufacture of OSCs with this new BHJ (formed by P3HT: O-IDTBR) it is relatively new but efficiencies of approximately 5% have already been reported at module level[28]. Additionally, this type of materials, as well as the non-chlorinated solvents used for solution processing enable a serial manufacturing techniques known as roll-to-roll (R2R) allowing organic solar cells to be scaled up to an industrial process with low environmental impacts[29].

Figure 3.13: Molecular structures of O-IDTBR by Sigma Aldrich.

3.3.4 Intermediate layers

In section 3.1 we have seen that an organic solar cell can be composed of a series of layers, each one with a purpose. The intermediate layers could be said to be the layers that are included to help and favor the operation of the entire photovoltaic process (among other functions), which can be grouped mainly into two large groups, the hole injector layers (HIL) or the electron

transport layers (ETL). Although it has been seen that depending on the configuration one or the other is used, this is not entirely true since there can be both in the two configurations. These layers are usually surrounding the active layer.

- **Hole injector layer:** Because it is a common layer in standard configuration in OSCs, the materials used in it have been studied for a long time and many advances have been made. PEDOT: PSS is the most studied and thanks to it, the most used nowadays. Today, with the new formulations, it provides good conductivity, transparency and make uniform the surface of the ITO electrode[30]. However, it has a very important defect, it has affinity for water (hygroscopic) which makes it very difficult to work outside a glove box, in where the ambient conditions humidity is present. In addition due the surface tension and the hydrophobic capacity of the active layer is difficult to deposit with uniformity above it. For this reason, in many inverted configurations it has stopped working with it and it is beginning to use other materials such as molybdenum trioxide[31] and vanadium pentaoxide[32]. Currently, most of these materials can be deposited by printing techniques, either in aqueous solution or in alcohols, as will be seen later in this work.
- **Electron transport layer:** As main materials that are used in the ETL we have the metal oxides being the Zinc oxide (ZnO) and the Titanium oxide (TiO_x) as the most widely used. In particular ZnO is non-toxic and has good stability, in addition to its high mobility of electrons, which is up to 4 times better than that of TiO_2 [33]. If we add it to its ability to be deposited by techniques such as spray or screen printing depending on the solvent used we have one of the most used materials today. If we talk about TiO_x has been for many years the main material used in the ETL, this is due to all the properties mentioned above, although its charge carrier is lower than ZnO there are the reported efficiencies superior from ZnO based this is because the slow electron-injection rate from an excited dye and its instability in an acidic dye[34, 35]. Similarly, ZnO remains one of the most promising substitutes for TiO_x .

3.3.5 Solvents

Solvents are a very important element in the inks, are those that act as a link between the different materials and allow us among other things to adjust

the viscosity and other properties in order to use them in different deposition techniques. In addition, the use of one type of solvent or another allows us to change the morphology of the compounds[36].

If we talk about the active layer, in the most widespread system of P3HT: PCBM chlorine benzene is the most used because it has a low boiling temperature and low evaporation compared to Toluene, for example. This allows a post-annealing to increase the operation and efficiency thanks to a better phase separation and crystallization of the P3HT. For the PEDOT: PSS, aqueous solutions are used. The ETL is supported by organic solutions and alcohol (such as ethanol, or methanol) and as shown and in most articles, chlorinated solvents (chlorine benzene, di chlorine benzene, toluene, etc.) are used in the active layer[37]. However, the choice of one and the other is of vital importance because it can degrade the adjacent layers.

3.4 New materials

Currently there is an emerging activity in the field of OSCs if we talk about the materials used, where graphene and perovskite play an important role. If we speak of graphene this is an allotropic form of carbon, as is graphite and diamond and is formed by hexagonal rings of carbon atoms (see figure 3.14. However, the real interest that is taking in the last years is in its utility for the technology for its important properties being some of them: high thermal, electrical conductivity, elasticity, hardness, resistance...

If we focus on the field of OSCs, the most outstanding characteristics are that it is practically transparent, with a high conductivity[38]. Thanks to this its most common use is as semi-transparent electrode[39], trying in this way to replace the ITO, which is expensive and scarce (as it showed in the last section).

Figure 3.14: Graphene structure.

On the other hand, the perovskite can be found in a multitude of devices, not only in OSCs. As such, perovskite is a mineral and it is used in combination with other materials to end up forming what is known as MAPI (methyl ammonium lead iodide) in its most common use. If we focus on the issue that happens to us, these devices are known as hybrids (inorganic-organic) and are currently obtaining the greatest efficiencies in this technology (about 22% of PCE[40]), being stability still a challenge to overcome. The importance of this and its good results lies in the properties it has and the versatility to combine with other materials[41], so that it can be used without lead, thus eliminating toxicity and complexity in its use. In addition to the stability presents other problems such as the need to work in a glove box because it degrades very quickly in its contact with humidity and at temperatures above 80-90°C.

Figure 3.15: A 10x10 cm module of perovskite made by Simone Meroni in the Swansea Institute.

Today it is used in many different ways and in many configurations[42–44]. Also in recent years but especially in the last two are starting to manufacture devices in ambient conditions (without glove box) obtaining a very varied efficiencies ranging from 4-5% to 15% in the best case[45–47].

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Chapter 4

Research methodology

In this chapter, we will describe the methodology followed throughout the work, from the start-up to the implementations and optimizations carried out. In addition, a monitoring system has been introduced to know the environmental conditions of the manufacturing laboratory. The work can be divided in different blocks: A first block focused on the preparation of the machine and writing the different programs (with different parameters). A second block, the manufacture of photovoltaic devices, as well as its optimization of manufacturing parameters. A third block, which includes all the characterization, degradation, measures of the devices and a monitoring system of the manufacturing conditions inside the lab. And a last block of data treatment.

4.1 Computerized Numeric Control

For this work, a computerized numerical control (CNC) machine has been used, in this case, a 3-axis milling machine for the spray coating technique. A CNC machine is a machine that can perform processes automatically from a programming. This programming can be given from a integred computer or an external computer. Usually these machines are used in the industrial for the various machining processes and a series production and we can find many types, from the simplest as lathes to complex stations that can perform almost all known machining processes.

A milling machine is a machine with which chip removal processes are carried out with a multi-edged tool. It consists of a head that houses the cutting tool, a bench and support where the piece or material to be worked is placed (the bench can be moved, only the head or both combinations).

Thanks to the advance and incorporation of the numerical control, it is one of the most flexible and used machines in the industry. Due to the variety of processes that can be carried out (with different speed and cut parameters) and the materials used (as well as the necessary refrigerants), it must be used by qualified personnel.

Figure 4.1: Conventional milling machine.

Figure 4.2: Schematic milling process.

In this study a CNC 3-axis milling machine (HEIZ, CNC HIGH-Z S400/T) has been adapted for the deposition by the spray technique. For this, the cutting head has been replaced by a commercial airbrush (we use a different airbrush for horizontal coating (Figure 4.5) and vertical coating (Figure 4.6)). This system has the advantage of being able to work in ambient conditions and in an automated way (making it more reproducible) and by this way up scale from the laboratory to a series production. On the other hand, it has the same disadvantage, since being a process under ambient conditions and with elements that are not specific for the manufacture of OSCs (both the milling machine and airbrushes) is very complex to optimize due to the multitude of parameters that you can find (speed, pressure, distance to the substrate, cone opening, temperature, deposition process ...).

Figure 4.3: Horizontal coating system (horizontal head).

Figure 4.4: Vertical coating system (vertical head).

Figure 4.5: Iwata HP-C for horizontal head.

Figure 4.6: Iwata HP-SB Plus for vertical head.

As for the head, support (Figure 4.7) was built to house the substrates (up to 9) and thus be able to place them for the different ways of depositing by spray, as well as the power to heat the substrates to favor the drying of the inks (for the vertical deposition support a heating plate (IKA C-MAG HS 7) is used and for horizontal a Peltier cell connected to a voltage source). The temperature is measured with a thermocouple.

Figure 4.7: Support to house the substrates.

As can be seen, the support plate has up to 9 holes for substrates and has a template that covers it from above in order to protect part of the ITO layer. When we deposit the ZnO layer, the ITO must go up with the part that protects upwards as well. When it is the active layer, we must turn only the protective layer, covering in this case for the most part the glass area. The next thing was to be able to start the machine and be able to function. For this it is necessary to write the programs, this uses an international system known as G ISO code (an international standard code to all CNC machines). This code has a series of common commands at the beginning of the program (similar to a computer program) that what they do is define different parameters such as in the plane that we are going to work (G17, G18), which tool to use, speed, types of coordinates , etc.). For our work, the code is much more simplified since parameters such as the type of tool or the speed of rotation of it are not necessary, an example of simple code is the following:

```
G64 G18 G90
T0 M6
M3
M8
G1 X0 Y0 Z0
G1 X25
```

Where we can find that i.e. G18 defines the work plane XZ, G90 the work in incremental coordinates. Each line is an order, in this case we can

omit the number of the line which is designed by N1, N2, N3... The usual format in which we can find these programs is a simple text format ".txt". In Appendix A we can find a list of the most common codes. The different programs made and used will be seen in detail in the next chapter.

4.2 Fabrication of the Organic Solar Cells

As we have seen in previous chapters, an organic solar cell is composed of layers of organic and inorganic materials in our case it is formed by: A glass substrate (Figure 4.8) of 20x20x1.1 mm with a transparent compound that acts as an electrode called ITO (Delta technologies, 4-8 Ω/sq).

Figure 4.8: Glass substrate with ITO

A layer of ZnO (Zinc oxide) is deposited on the transparent electrode, which helps to promote the transport of electrons and to eliminate part of the roughness that the ITO can have. The recipe is:

- Zinc acetate (dihydrated) (CAS 5970-45-6/sigma 399786)
- Methoxy-ethanol (CAS 109-86-4/sigma 284467)
- Ethanolamine (CAS 141-43-5/sigma 411000)

Figure 4.9: ZnO solution.

Next, a layer known as a photoactive layer, composed of a conjugated polymer P3HT (Sigma-Aldrich, 99.995% purity) and a fullerene derivative, the PCBM (Solenne, 99% purity), in a solution of dichlorobenzene. Proportion 1.1:1 (P3HT:PCBM).

Figure 4.10: Active layer solution.

Finally, we have a metallic electrode, in our case silver.

The way in which it is going to work is the following: The technique of conventional spin coating (SCS-G3P8 Spincoater) will be replaced layer by layer in the manufacturing process by other printing techniques like spray and screen-printing.

In the first place, the active layer has been chosen for its ease and flexibility when working it. For this layer we will use spray coating technique and the spin coating as a reference. The results of the substitution and the optimization of the parameters will be show in the next chapter. The next layer we will work it is ZnO. We will also use the spray coating technique. This layer could be a challenge because it has a lower viscosity and the parameters of drying must be well adjusted. Finally, with the silver electrode we will try to use screen-printing because the silver in our spray coating station with the airbrush it will be hard with the commercial inks. Normally the ITO comes integrated with the glass substrate in a standard way so it is not necessary to carry out deposition tests; in the same way, a long-term objective is the possibility of being able to print our own electrodes, either ITO or other materials (see Chapter 3.3). The silver electrode has been chosen as the last element because of its difficulty in working at room temperature, currently it is carried out by thermal evaporation in vacuum (Figure 4.12).

Figure 4.11: Manufacturing lab.

Figure 4.12: Spin coater (left) and vacuum chamber (right)

The manufacturing process would be as follows. First of all we clean the ITO substrates, approximately in half, placing heat to cover the part of the ITO that we want to conserve. Then put in an acid bath at about 70°C for 30 minutes where vapors will clean the area. The substrates are removed, rinsed in water and placed in an acetone bath for 5 minutes, then another bath in isopropanol in ultrasound for 3 minutes. They are rinsed again and introduced in water in ultrasound for 3 more minutes.

The solutions of ZnO and active layer are prepared with their respective recipes (as we shown before) and left the active layer in a heat at about 60 degrees and zinc oxide solution in a magnetic stirring. They could be deposited by spin and spray coating technique. For the spin coating we use $250\text{ }\mu\text{l}$ and 800 rpm for ZnO for 50 seconds and between 60 and $80\text{ }\mu\text{l}$, 1800 rpm for 5 minutes for the active layer. The edges should be cleaned with a stick carefully. In the ZnO, the side of ITO should be cleaned more than glass side and in the active layer both sides are cleaned equally. A post annealing is performed on both the ZnO layer (180°C for 5 minutes each substrate) and 120°C for 30 minutes at all for the active layer. The parameters in spray coating will be shown in each experiment.

For silver finally 3 silver wires are placed on the spring support of the bell. The first pump is plugged in to make a pre-vacuum, approximately up to 10^{-3} , then the other pump is plugged in and allowed to reach up to 10^{-5} once here, the current starts to flow. After evaporating we must gradually lower the current and once reached 0 to open we must do the reverse order to turn on the pumps.

At the same time, during this work we have been talking about environmental-friendly solar cells, in the case of perovskites, one of the most important lines of research is to reduce the content of lead, spiro-OMeTAD and halogenated solvents. . The required balance of increasing efficiency, improving useful life and reducing environmental impact is the line of work followed by researchers today[1].

One of the lines of research to carry out this work is the engineering of interfaces, especially focused on HTL and ETL. The most used materials in HTL have been spiro-OMeTAD[2–6], PCBM[7, 8], conjugated polymers such as P3HT[9], PTAA[10, 11] or PEDOT: PSS[12] and more recently transition metal oxides such as NiO, showing very good results in terms of extended lifetime[13, 14]. In addition to materials engineering, HTL-free architectures have received special attention mainly because on the one hand it would avoid the use of spiro-OMe-TAD (toxic due to the use of chemicals in its processing[15]) and, on the other hand, it would avoid contamination. active layer chemistry. For this, a kind of carbon electrode would be the most satisfactory approach to an HTL-free architecture (although it may be argued that it is an HTL layer when complemented by Ag or Au final metallization). The ease of manufacture and processing of carbon inks, as well as their infiltration in the active layer, make them the cheapest and most reliable option as a manufacturing method[16, 17].

When ETL is considered, the most frequently used material is TiO₂ (both in compact and mesoporous layers), followed by ZnO, in layers, nanoparticles or nanorod structures[9, 18, 19], aluminium oxide[20–23], molybdenum oxide[24–26] and zirconium oxide [18]. In the case of the perovskite cells in this study, the carbon-based ones, ETL not only improves electron transport but also prevents short circuits between carbon and mesoporous TiO₂ usually in contact with ITO or fluorine doped tin oxide (FTO). Regarding the active layer, the benchmark methyl-ammonium lead iodide (MAPI) It has been modified, primarily to eliminate lead toxicity. For this, it has usually been replaced by tin[27, 28]. Although initially this indicated a drop in efficiency, recent results show efficiencies greater than 20%[29, 30].

4.3 Characterization of the Organic Solar Cells

Within the characterization there is a wide range of measurement techniques applied in the field of OSCs, we will list the most used in our work and what can be obtained from them.

4.3.1 UV-Visible Spectroscopy

A Cary 50 UV-Vis spectrophotometer (see Figure 4.13) was used for optical characterization of films and devices. Visible ultraviolet spectroscopy (UV-Vis) refers to absorbance spectroscopy in part of the ultraviolet and the adjacent ones, that is, in the visible and adjacent spectrum. With this technique, we can measure the transition from resting to excited state (complementary to the fluorometry that measures it from the excited to the resting state). The principle is simple; molecules that contain electrons (linked and unbound) can absorb energy in the form of ultraviolet or visible light to excite those electrons at higher energy levels. For example, in the field that interests us, electrons that are more easily excited (less band gap between HOMO and LUMO more light in a greater range of wavelength can absorb). This can tell us if the material is better or worse absorbing light and then, good for use in solar cells.

Figure 4.13: Cary 50 UV-Vis spectrophotometer.

4.3.2 Atomic Force Microscopy

A DAFM on a Nanotec Electronica AFM system (see Figure 4.14) with a PLL board (bandwidth ~ 2 kHz), which maintained the cantilever at resonance was used to acquire the data. Images and spectroscopy were acquired using the amplitude as signal for the feedback channel (AM-DAFM) at small oscillation. Silicon tips (70kHz) with a nominal force constant of 3N/m were used. The nominal radius value for tip apex of these probes is specified as 15nm by the manufacturer. Atomic force microscopy (AFM) is a technique to obtain images and other information from a wide variety of samples, at extremely high (nanometer) resolution. Its development was the next step

of the family of scanning probe microscopes started with the original invention of the STM in 1981 by Gerd Binnig and Heinrich Rohrer while working at IBM. The atomic force microscope (AFM) intended to extend the possibilities of STM to insulating samples. Their original AFM consisted of a diamond shard attached to a strip of gold foil. The diamond tip contacted the surface directly, with the interatomic van der Waals forces providing the interaction mechanism. The operation of the AFM technique in a simple way is that a probe is kept in close contact with the surface of the sample by means of a feedback mechanism as it explores the surface.

Figure 4.14: DAFM on a Nanotec Electronica AFM system.

4.3.3 X-ray diffraction

A Bruker D8 Advance X-Ray diffractometer (see Figure 4.15) was used to characterize the deposited films. X-Ray diffraction (XRD) is an experimental technique used to analyze and determine the atomic and molecular structure and crystallinity of materials. These materials can come in various forms from powders and solids to thin films and nanomaterials. X-rays are diffracted in many directions by electrons because their wavelength is of the same order of magnitude as the atomic radius. By measuring the angles and intensities of these diffracted beams, the density of the electron within the crystal can be obtained. Thanks to this, the chemical structure and position of the atoms can be obtained.

Figure 4.15: Bruker D8 Advance X-Ray diffractometer.

4.3.4 Scanning electron microscopy

A Hitachi S-3500N Scanning electron microscope (see Figure 4.16) was used to characterize the surface of the films. Scanning electron microscope (SEM) scans an electron beam over a surface to create an image. The electrons that collide with the sample interact with its atoms, producing various signals that contain information about the topography and elements of the sample. The electron beam is scanned in a scan pattern, and the position of the beam is combined with the intensity of the detected signal to produce an image. Normally in conventional SEM the samples are observed in high vacuum.

Figure 4.16: Hitachi S-3500N Scanning electron microscope.

4.3.5 I-V characterization

For the characterization and measurement of the parameters of the devices, a voltage sweep with controlled voltage source (Keithley Mod. 230) and current measurement with an electrometer (Keithley Mod. 6514), own software implemented in LabView (on PC, communication GPIB IEEE488). Solar simulator ABET AM1.5 Class AAA (Figure 4.17). Stable temperature at 25°C (characterization laboratory). The sweeps are applied in what we call "forward" (applied voltage increasing from -1V to 1V) although it is completely adjustable, being able to do the reverse and with different jump size.

Ambient conditions measurement station mounted by an Arduino system and different sensors (humidity, oxygen, NO_x, H₂S, CO₂, CO, dust, particles and air quality). The measurements are stored in a text file on the computer for later processing. In order to carry out long-term stability studies, substrates were built with the help of a 3D printer, which, connected to the simulator, allow the measurement of up to 16 cells at a time (4 cells per substrate). In addition, thanks to the remote control, the system can be restarted if there is any type of fall (electronic issue), being a fairly reliable study under continuous lighting.

For the treatment of data, several programs have been written with the Matlab tool. This was done with the task of being able to handle a significant amount of data since each measure is a text file with columns and as many lines as points and resolution has your curve. An example is the following:

Figure 4.17: Solar simulator for IV characterization.

If we have a measurement system that is measuring every 30 minutes let's say only 4 cells and only 30 points, we have 4 files per half hour with 120 lines, in a study of 100 hours we are talking about 12000 data that would be almost an impossible task for studies of stability.

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Chapter 5

Fabrication and characterization of organic solar cells. Spray coating technique applied to the active layer

Throughout the previous chapters it has been shown what is an organic solar cell, what materials are used for its manufacture and how it is manufactured, presenting the many techniques that are available today [1–7]. This thesis, as already mentioned, aims to implement a mass manufacturing process, especially in ambient conditions, so that automation guarantees a high reproducibility in the fabricated devices, thus avoiding possible failures or excessive dispersion of performance due to small scale manual methods.

Implementing a full processing route with these characteristics involves the optimization of many factors that influence each step of the process. In order to simplify this complex task, a first step will be carried out by working with a lower number of variables that will be optimized in the implementation of the technique. Once this initial processing has been carried out with these reduced set of variables, then, new ones can then be introduced if it is considered necessary to improve the system, repeating this the process until it is fully optimized. This sequential strategy allows us to bring the system to an optimal point which not only seeks to improve the solar cell parameters, but also the manufacturing process itself, shortening times, saving energy, and lowering costs.

The procedures and parameters that have been set are:

- Recipes for each layer of the solar cell. Active layer (AL) and Zinc oxide (ZnO) layer. In this way, it is avoided to modify other properties such as the adherence of one layer to another. Indirectly, by keeping constant the quantities to be used of each material and the ambient conditions, other properties like the viscosity are also kept constant.
- Speed of deposition. Keeping this speed fixed for all layers allows us to simplify the implementation and optimization process, varying in this case only the deposition time or the necessary number of passes.

In this chapter and the following ones, the accomplished experiments, where this manufacturing process was implemented and optimized layer by layer, is shown. The first selected layer was the active layer, due to its flexibility when working with it, the task is carried out by modifying different available variables using the software programs created to control the automated spray coater. The different programs written and used in this chapter are described as follows and their codes are found in Appendix A:

Program 1: The movement covers the entire width of the substrate, moving from one side to the other, while it descends (in steps of 2 mm) to the end of the substrate. Each time this routine is carried out twice (one going down and one going up). It has been called 1T (one period). This is scheduled and executed as many times as it is required to move each substrate automatically at will. The movement is shown in the Figure 5.1:

Figure 5.1: Movement scheme of Program 1.

Program 2: The airbrush is placed in the center of the substrate, on one of the sides, indistinct left or right and simply make a horizontal move-

ment (parallel to the ground). In this way, with the appropriate distance and the nozzle opening of the same airbrush, the entire surface of the substrate can be swept. Each back and forth movement are called a scan. The movement is shown in Figure 5.2:

Figure 5.2: Movement scheme of Program 2.

Program 3: In this program, instead of going substrate by substrate with the program code, it was decided, to further optimize the time consumption, to coat between 2 and 3 substrates in one pass. This allows to have a simpler and shorter code, as can be seen in Figure 5.3.

Figure 5.3: Movement scheme of Program 3.

5.1 Parameter's optimization over glass and ITO-ZnO

In order to estimate the thickness of the deposited active layer and to know the amount of light absorbed as a function of that thickness, some previous measurements have been carried out using ultraviolet visible spectroscopy (UV-Vis) and atomic force microscopy (AFM) on layers deposited on glass substrates. The procedure was as follows: For the first of the coating programs (Program 1, see Figure 5.1), initial thickness measurements with the AFM were carried out with these first samples, which have been called based on the substrate they have and the number of periods in order to facilitate their identification.

- They have been made for each sample, its visible ultraviolet spectrum.
- A graph has been drawn with the absorbance obtained at 550 nm and its corresponding thickness obtained from the AFM.
- A linear fit has been made and extrapolated from 50 to 1000 nm.
- The error obtained from the standard error of the measurements has been estimated at 70 nm.

With these data and taking into account the calculated error, the thicknesses have been estimated for both the samples manufactured by this program and the others, including the thickness in the reference technique, although according to Padilla et al. [8] calculating the thickness through the visible ultraviolet between different techniques provides only a rough estimate of the thickness of the layer that is being deposited and characterized. Furthermore, the optical gap of each of the active layers has been obtained as indicated below. In total, two experiments of Programs 1 and 2 have been carried out.

5.1.1 Horizontal coating

Program 1

- **Glass/Active layer by different periods**

As mentioned above, for the first program, the samples with different coating periods applied to the active layer (AL) have been measured. They have been called Glass-AL1T, Glass-AL2T, Glass-AL3T, Glass-AL4T, Glass-AL5T, Glass-AL6T and Glass-AL8T, being 1T, 2T,

5.1. PARAMETER'S OPTIMIZATION OVER GLASS AND ITO-ZNO 77

3T...the different coating periods respectively. The airbrush conditions are:

- Nitrogen gas pressure: 0.5 bar.
- Distance to the substrate: 11 cm.
- Nozzle opening: 3/4 turn.

Figure 5.4: UV-Vis spectra of active layer over glass for different spray coating periods (Program 1).

The UV-Vis spectra obtained are plot in Figure 5.4. This Figure shows interesting values, such as the absorbance at 550 nm, which is important because it is used as a reference for thickness estimation. The optical gap of each film, which should be independent of the thickness since it is intrinsic to the used materials. Two regions are distributed in the whole specter, an amorphous region of P3HT chains and another of a semi-crystalline domain. This results from the dispersion of the nanoparticles in an organic solvent [9]. Likewise, the presence of three differentiated peaks around 510, 550 and 600 nm is found, which coincides with transition zones, as mentioned in scientific literature, corresponding to 0-2, 0-1 and 0-0 respectively, with 0 being the ground state and 2, 1 and 0 those of the excited state levels [9].

The values obtained for thickness, as well as the gap and peaks are in Table 5.1:

Name	Thickness (nm)	GAP (eV)	Peak 1 (nm)	Peak 2 (nm)	Peak 3 (nm)	Abs 1	Abs 2	Abs 3
Glass_AL1T	173	1.92	519	554	604	0.81	0.77	0.60
Glass_AL2T	323	1.92	515	556	605	1.27	1.24	0.99
Glass_AL3T	331	1.92	517	550	602	1.42	1.35	1.01
Glass_AL4T	377	1.92	517	556	603	1.65	1.50	1.09
Glass_AL5T	176	1.93	499	554	606	0.96	0.77	0.51
Glass_AL6T	578	1.91	517	557	600	2.33	2.27	1.78
Glass_AL8T	323	1.92	509	554	604	1.50	1.31	0.91

Table 5.1: Thickness, optical gap and peaks of glass-AL devices for different periods (Program 1).

It must be emphasized that the gap remains constant in all the samples. Even though a certain linearity of the increment in absorbance with respect to the thickness is seen, an anomalous values were found in the Glass-AL5T and Glass-AL8T samples, which possibly remained heterogeneous and perhaps the chosen measurement point was where the layer was thinner, thus delivering a different value. The results obtained reveal that even with samples with a very different thickness, the peaks appear at very similar points. Later it will be seen that if a thermal annealing is applied, these peaks change as a consequence of the processing temperature, a fact that may be explained by PCBM aggregation [9, 10]. This experiment was the starting point to confirm that absorbance increases with thickness and can be used as a reference for the following experiments, which are aimed to check if this is indeed the case, or if, on the contrary, as it is supposed, there is an optimal thickness, as usually happens in the reference spin casting technique.

Program 2

- **Glass-ITO-ZnO-Active layer by different scans**

In this program the active layer is deposited by different number of coating scans in contrast with Program 1. Four glass-ITO-ZnO deposited by spin coating substrates are used to deposit the active layer by using different number of scans. The samples are called ITO-ZnO-AL4scans, ITO-ZnO-AL8scans, ITO-ZnO-AL12scans and ITO-ZnO-AL16scans being 4, 8, 12 and 16 scans of active layer respectively. The conditions are:

- Nitrogen gas pressure: 0.5 bar.

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- Distance to the substrate: 9 cm.
- Nozzle opening: 1 turn.
- Substrate temperature: 55°C.

The UV-Vis spectra and the parameters are shown in Figure 5.5 and Table 5.2:

Figure 5.5: UV-Vis spectra of active layer over glass-ITO-ZnO for different spray scans (Program 2).

The obtained thicknesses, optical gap, peak and absorbance values are:

Name	Thickness (nm)	GAP (eV)	Peak 1 (nm)	Peak 2 (nm)	Peak 3 (nm)	Abs 1	Abs 2	Abs 3
ITO-ZnO-AL4scans	138	1.94	481	604	650	0.85	0.41	0.24
ITO-ZnO-AL8scans	314	1.94	487	604	650	1.8	0.69	0.32
ITO-ZnO-AL12scans	445	1.94	484	604	650	2.62	0.87	0.40
ITO-ZnO-AL16scans	916	1.93	482	604	650	6.73	0.88	0.42

Table 5.2: Thickness, optical gap and peaks of glass/ITO/ZnO/AL samples for different scans (Program 2).

In Figure 5.5, two great differences can be observed with respect to Figure 5.4 (coating using Program 1 and only depositing the active layer on the glass). The first difference is the amount of absorbance,

mainly related to the thickness obtained by using this coating program, and the second difference is the displacement of the three main peaks, as well as their intensity, less pronounced in the case of peak 2 and peak 3. This smoothing has its main justification due to the number of layers under the active layer, which makes it difficult to locate these peaks, which are located around 600 and 650 nm. This shift towards the infrared fringe is explained by the aggregation of the PCBM compound after annealing, as mentioned above. Note that the calibration of the thickness measurement is done only with the active layer on glass and that ZnO is optically transparent in the visible, which is the range used for said estimation (as will be shown in the UV spectrum in Chapter 6).

5.2 Parameter's optimization of full devices. Manufacturing and characterization

In this part, the experiments carried out have been classified according to the orientation (vertical or horizontal with respect to the substrate) of the spray for its manufacture. They can be found organized in horizontal coating and vertical coating. For each of them, a different airbrush has been used as mentioned above, as well as a different CNC program. Each device has 4 solar cells, named from A to D (see Figure 5.6).

Figure 5.6: Final device with four solar cells. From A to D.

5.2.1 Horizontal coating

Program 1

- **Active layer by different periods. From 2T to 8T**

For this experiment, different periods of the active layer were used to coat the substrates in comparison to the control substrate. The spray coating conditions that were used are:

- Nitrogen gas pressure: 0.5 bar.
- Distance to the substrate: 11 cm.
- Nozzle opening: 3/4 turn.

In this experiment 10 substrates were used, totalling 40 devices. The first two samples are the control devices, fabricated by spin casting technique. In the other 8 samples, the active layer was deposited by spray coating using Program 1 with different periods. One using 1T, five using 2T, one 4T and the last one 8T. The deposition of the zinc oxide layer was carried out by using the original recipe, spin casting, and in the same way the deposition of the silver electrode was carried out by thermal vacuum evaporation. After manufacturing, the samples are characterized. The results are shown in Table 5.3:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (A)	0.06	0.53	-4.69	0.71	28
Control (B)	0.06	0.60	-5.44	1.09	33
Control (C)	0.06	0.40	-4.38	0.54	31
Control (D)	0.06	0.47	-4.59	0.66	31
SprayAL2T (A)	0.09	0.53	-4.25	0.93	41
SprayAL2T(D)	0.09	0.47	-4.30	0.82	41
SprayAL8T (D)	0.12	0.13	-2.30	0.08	27

Table 5.3: Initial electrical parameters of the manufactured organic solar cells. Spin coated (Control) and AL-spray devices (SprayAL) by different periods (Program 1).

Low short circuit current density and fill factor values are still observed, but with good open circuit voltage values. This may be due to large bulk and surface recombination which reduces photo current generation. Since the cells have a relatively good V_{OC} despite the roughness

of the ZnO layer, it can be considered that they are not short-circuited although their shunt resistance (not very large) contributes significantly to reduce the filling factor. Some heterogeneity of the active layer is still present showing that the coating process is still not fully optimized. Series resistance is also large, indicating that electrical contact to electrodes is not guarantying a highly efficient charge collection. The cells are stored in the dark and are measured again after 3 days. The results are shown in Table 5.4.

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (A)	0.06	0.60	-4.87	0.79	27
Control (B)	0.06	0.60	-5.01	0.99	33
Control (C)	0.06	0.60	-5.15	0.99	32
Control (D)	0.06	0.53	-5.46	1.10	38
SprayAL1T (A)	0.12	0.13	-3.85	0.17	33
SprayAL1T (B)	0.12	0.20	-6.04	0.29	24
SprayAL1T (D)	0.12	0.20	-6.14	0.29	23
SprayAL2T (A)	0.09	0.13	-4.53	0.98	37
SprayAL2T (B)	0.09	0.6	-4.37	0.99	39
SprayAL2T (F)	0.06	0.53	-5.51	1.27	43
SprayAL2T (G)	0.06	0.53	-5.02	1.19	45
SprayAL2T (H)	0.06	0.53	-3.98	0.92	43
SprayAL4T (D)	0.09	0.33	-3.32	0.34	31
SprayAL8T (D)	0.12	0.27	-2.72	0.20	27

Table 5.4: Electrical parameters of the organic solar cells (Control and SprayAL) after three days stored in darkness by Program 1.

A change in electrical parameters can be observed. Some have indeed improved, for example AL2T (A) sample with 0.98% power conversion efficiency. In addition, devices that had not worked initially, now are operating devices like Spray AL2T (F), reaching 1.27% in PCE. A total of 30 cells out of 40 have worked. Of the 16 total cells where the active layer has been deposited by spray for 2T periods, at least 5 have obtained values around 1% or more and 10 around 0.5%.

The initial and after storage J-V characteristic curves for the best solar cells are shown in Figures 5.7 and 5.8 respectively.

Figure 5.7: Initial J-V curves comparing the best SprayAL2T (A) cell and the Control (B) device using the Program 1 in horizontal coating.

Figure 5.8: J-V curves after being stored in darkness three days comparing the best SprayAL by different periods (Program 1) devices and the best Control device.

(a) Control (D)

(b) SprayAL2T (F)

Figure 5.9: Initial (a) and after three days (b) J-V curves for the best Control and SprayAL2T devices by Program 1.

In Figure 5.7, the best initial Control and SprayAL2T devices are shown, being in this case very similar device in electrical parameters. On the other hand, Figure 5.8, the devices after storage in the dark, the cells manufactured using the spray technique have a slightly better filling factor when compared with the control device. This improvement is mainly due to the recovery after storage that has been observed in the current density (J_{SC}), while keeping the open circuit voltage (V_{OC}) constant. In Figure 5.9, the evolution of J-V curves of Control (D) and SprayAL2T (F) devices are shown. The 5.9 (a) curves (Control device) shown a small increment of the electrical parameters in contrast with 5.9 (b) (Spray device). The initial Spray device curve is probably

caused by a bad contact in the characterization system. This increment may be due to the internal structural evolution that occurs in the cell once it is stored in the dark. A priori, this process is independent of the type of deposition used for manufacturing and it is intrinsic to the materials used, but it has been observed that there has been a greater improvement in parameters of devices manufactured using the spray coating technique.

- **Active layer by different periods with high pressure**

For this manufacture procedure four samples have been fabricated. The samples have different periods in the deposition of the active layer, 1T, 2T, 4T and 8T respectively. The same experimental conditions of the previous experiment have been reproduced with the only difference in gas pressure. The experimental conditions are the following:

- Nitrogen gas pressure: 1.5 bar.
- Distance to the substrate: 11 cm.
- Nozzle opening: 3/4 turn.

Due to the high pressure of the gas in the coating procedure, the obtained layer was not uniform, and the obtained samples showed only resistive behavior, with hardly any photo current generation. After several tests it was decided not to work with high pressure in the spray coating process.

Program 2

An additional problem is observed in the experiment is that a lot of material is wasted when depositing the active layer. Furthermore, a lack of uniformity is also observed. This led to a modification of the software programs to control the automated process of coating the active layer. The new program tried to optimize both the time and the deposited material, trying to coat the layer in a more uniform way and to save material (and therefore reduce costs) by making the process more efficient. This program is called Program 2 (Figure 5.2).

- **Active layer by different scans**

In this experiment fabrication and characterization were realized on several cells manufactured simultaneously on different substrates in this scan strategy. These first results correspond to the manufacture of five

devices with four cells each one, heating is also applied to the substrate in order to improve drying and adhesion of the active layer[11]. Each substrate coated by the spray technique requires a different number of scans. The control sample is fabricated by spin casting. The samples are: one by 4 scans, 8 scans (finally due to gas problems, there were about 10), 12 scans and 16 scans, in order respectively.

And the deposition conditions are:

- Nitrogen gas pressure: 0.5 bar.
- Distance to the substrate: 9 cm.
- Nozzle opening: 1 turn.
- Substrate temperature: 55°C.

The results are shown below:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (A)	0.09	0.2	-1.08	0.05	24
Control (B)	0.09	0.27	-1.57	0.13	30
Control (C)	0.09	0.13	-8.29	0.24	21
Control (D)	0.09	0.13	-3.92	0.13	25

Table 5.5: Initial electrical parameters for the best cells (Control devices).

Only the control devices have worked and even with very low values. Therefore, it is possible that there was a badly executed process in the preparation of the samples and again, and perhaps problems with the gas supply, which made compulsory the application of a few extra passes to one of the devices. Additionally, an unexpected colour gradient of the active layer, different of standard procedure was also indicative of a batch problem. Although the J-V curves did not deliver useful electrical parameters, the samples have been characterized by visible ultraviolet spectroscopy. with the aim of finding the cause of the defective fabrication: either the number of scans or the problems that arose related to gas supply during manufacturing. Once the origin of the problem is identified, it will enable the possibility to estimate which number of scans is the optimal one for this spray coating program. The spectra and the results are shown in Figure 5.10 and Table 5.6 below:

Figure 5.10: UV-Vis spectra for Control and AL spray coating devices with different number of scans by Program 2.

Name	Thickness (nm)	GAP (eV)	Peak 1 (nm)	Peak 2 (nm)	Peak 3 (nm)	Abs 1	Abs 2	Abs 3
Control	143	1.93	508	555	605	0.78	0.64	0.41
AL4scans	42	1.93	509	555	605	0.33	0.29	0.23
AL8scans	192	1.93	506	555	605	0.99	0.81	0.53
AL12scans	282	1.92	500	555	605	1.42	1.13	0.72
AL16scans	230	1.93	503	555	605	1.19	0.95	0.63

Table 5.6: Thickness, optical gap and peaks of devices for control and spray coating devices by different scans (Program 2).

The value obtained for the reference thickness (device manufactured by spin casting) is 143 nm with an absorbance of 0.66. It confirms that the absorbance increases with the thickness of the layer and that the optical gap remains constant as in the previous experiments. In these full devices, the AL thickness measurement are realized between silver contacts and again, highlight the ZnO optical transparency. Regarding the peaks of the measured spectra, according to Figure 5.5 (same airbrush conditions and scans), the maximum peak is less pronounced in the 16 scans device, which may confirm, as mentioned above, that there was a problem during the manufacture process. Once again, great uniformity

is observed in the sample layers when using this program in comparison to Program 1, which, added to the material savings that occurs, it confirms the motivation to continue working on this program. With this in mind, and the absorbance values obtained for the spray devices compared to those of the control substrate, (around 150 nm thick), it confirms that there is not an intrinsic problem with the program itself, but the process is not yet fully optimized, including the possible failure arising with the gas supply during the manufacture of these samples.

- **Active layer by different scans. Influence of thermal annealing**

For this manufacture process, and taking into account the latest obtained results, it was decided to optimize the active layer deposition by using this program on a glass substrate, with a spray nozzle pressure of 0.7 bar, while maintaining the other parameters equal, In this way a more uniform layer was achieved. The parameters for this experiment were:

- Nitrogen gas pressure: 0.7 bar.
- Distance to the substrate: 9 cm.
- Nozzle opening: 1 turn.
- Substrate temperature: 55°C.

A total of 5 samples were manufactured: one control sample by spin casting and four samples by spray coating with 4, 8, 12 and 16 scans respectively, as in the previous experiment. Unlike the previous experiment, in the characterization by UV-vis spectroscopy they have been measured before and after the thermal annealing treatment at 120°C to find differences in the absorbance of the layer due to the temperature. The electrical parameters obtained after the manufacture of the devices are shown in Table 5.7:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
AL4scans_120 (A)	0.06	0.27	-3.22	0.23	27
AL12scans_120 (A)	0.06	0.13	-2.77	0.12	32
AL12scans_120 (B)	0.06	0.47	-3.12	0.35	24
AL12scans_120 (C)	0.06	0.47	-3.16	0.35	24
AL12scans_120 (D)	0.06	0.47	-3.28	0.39	26

Table 5.7: Initial electrical parameters for the best cells fabricated with different number of scans by Program 2.

In this case, the percentage of devices that have worked is even lower than in the previous case, but with a difference, the 12 scans spray coated test cells have worked better, thus pointing out a promising optimization option. After characterization, they are stored in the dark for five days until their next measurement, the results of which are shown below:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (B)	0.06	0.47	-7.48	1.55	45
AL4scans_120 (A)	0.06	0.47	-3.97	0.56	30
AL12scans_120 (A)	0.06	0.53	-3.78	0.56	28
AL12scans_120 (B)	0.06	0.53	-4.89	0.75	29
AL12scans_120 (C)	0.06	0.53	-4.78	0.76	30
AL12scans_120 (D)	0.06	0.53	-4.33	0.69	30

Table 5.8: Electrical parameters for the best cells Control and spray cells by different scans using Program 2 five days stored in darkness.

It is observed that one of the control cells, after a few days in the dark, works with an efficiency of 1.55% and like the other four spray cells, they have managed to raise their current and power conversion efficiency values, which coincides with what was observed in previous experiments. In most cases, the efficiency is doubled after the first two or three days in the dark; but in other cases, it can be five times higher. The respective J-V curves of the first and five days after in darkness of these cells can be observed in Figure 5.11 and 5.12:

Figure 5.11: Initial J-V curves for the best AL spray devices by different scans using Program 2.

Figure 5.12: J-V curves for the best cells comparing Control and AL spray devices by different number of scans using Program 2 after being stored five days in darkness.

The recovery of some of the cells can be verified, as well as the improve-

ment of which the active layer has been deposited by means of the spray technique, where filling factors of around 30% are already seen, closer to those obtained by the control technique. Again, it is observed that the recovery of the devices occurs mainly in the current, confirming the hypothesis of a small internal structural reorganization or chemical modification due to the lack of encapsulation while the cells are stored in in darkness. Finally, UV-Vis spectroscopy experiments have been carried out, as mentioned before, measuring pre-annealing and post-annealing samples. To correctly identify the samples, they have been named according to their technique (the reference fabricated by spin casting is “Control”), the number of scans and the temperature being 120°C post-annealing and 55 pre-annealing, i.e., AL12scans_120. The spectra and values taken are shown in Figure 5.13 and Table 5.9:

Figure 5.13: UV-Vis spectra for the control and AL spray devices by different scans using Program 2 measured before and after annealing.

Name	Thickness (nm)	GAP (eV)	Peak 1 (nm)	Peak 2 (nm)	Peak 3 (nm)	Abs 1	Abs 2	Abs 3
Control_55	80	1.92	478	607	675	0.65	0.25	0.09
Control_120	129	1.93	504	607	675	0.75	0.36	0.12
AL4scans_55	170	1.94	485	607	675	1.09	0.41	0.15
AL4scans_120	232	1.94	501	607	675	1.22	0.55	0.16
AL8scans_55	222	1.94	494	607	675	1.28	0.50	0.20
AL8scans_120	298	1.94	499	607	675	1.48	0.70	0.21
AL12scans_55	383	1.94	496	607	675	2.14	0.76	0.24
AL12scans_120	450	1.94	503	607	675	2.32	0.95	0.25
AL16scans_55	410	1.94	479	607	675	2.64	0.72	0.21
AL16scans_120	603	1.94	499	607	675	3.50	1.16	0.24

Table 5.9: Thickness, optical gap, and peaks of the devices by different scans before and after annealing using Program 2.

Two main facts can be observed, the first one is that the thickness varies depending on the temperature before and after post-annealing, which allows us to obtain a thicker layer at a higher temperature, regardless of the technique used to deposit the layer, being the post-annealing the ideal, since the reference is observed to be between the optimal values of 100-150 nm as it can be seen in Table 5.9. The second fact is that even though the device was also saturated with ultraviolet with 16 passes, these high values were not obtained. Again, values very similar to the previous experiment have been obtained, although with the first peak slightly less displaced in most of them, which may indicate that the spray coating and the measurement were done correctly. If these values are compared to the electrical parameters measured for these devices, it is observed that the device with the highest number of passes is the one with the best initial value, being the reference cell the one that does not work. After storing these devices in the dark, they were measured again, obtaining the following results: the reference cell works with values of more than 1.5% and the cell of 16 passes per spray improves to almost 0.8%. This fact points out that the initial idea that we should obtain similar optimal thicknesses for all coating procedures is not valid and that in techniques such as spray coating, a greater thickness with greater absorbance could provide better electrical and stability parameters.

- **Active layer deposition by different scans. From 6 to 12**

UV-Vis characterization of the samples, with different thicknesses and different thermal annealing process commented above have confirmed the need of further optimization of the process by modifying the air-brush deposition parameters such as the number of passes of the active layer. In this experiment the same parameters of the airbrush are main-

tained but in this case the number of scans in the spray deposition are modified. The parameters are:

- Nitrogen gas pressure: 0.7 bar.
- Distance to the substrate: 9 cm.
- Nozzle opening: 1 turn.
- Substrate temperature: 55°C.

Five substrates have been coated, one for control (spin casting) and four by using the spray technique in the deposition of the active layer. The number of scans in this case is 6, 8, 10 and 12 respectively. After this, they are taken to the solar simulator and characterized. A summary of results is presented in Table 5.10:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (C)	0.09	0.33	-5.51	0.46	25
AL12scans (A)	0.12	0.4	-2.33	0.25	27
AL12scans (B)	0.12	0.4	-1.59	0.15	23
AL12scans (C)	0.12	0.5	-1.78	0.24	28

Table 5.10: Initial electrical parameters for the best Control and AL spray cells by Program 2.

It is again observed that only four cells have worked and that 3 of them are sprays with 12 scans, indicating that this number of passes is the optimal configuration for this program. After characterization and as in previous experiments, they are stored in darkness for five days and re-measured. The results are shown below:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (C)	0.09	0.53	-5.04	2.01	50
AL12scans (A)	0.12	0.53	-3.07	0.50	30
AL12scans (B)	0.12	0.47	-2.30	0.37	34
AL12scans (C)	0.12	0.40	-1.96	0.22	28

Table 5.11: Electrical parameters for the best Control and AL spray cells by Program 2 after five days in darkness.

The control cell has increased its power conversion efficiency, which almost quadrupled and doubled its fill factor. The improvement is mainly

due to the open circuit voltage since the photo current has slightly decreased. This is due to the structural reorganization or chemical modification due to the lack of encapsulation, as it mentioned before, which has also been observed in some stability studies with intermittent lighting where, in periods of darkness, a certain recovery of efficiency was observed due to oxygen re-adsorption[12]. On the contrary, in the cells deposited by spray, if there is an increase in the current. This may indicate the different processes that occur in both manufacturing techniques and that should be studied. This can be seen more clearly in the Figures 5.14 and 5.15:

Figure 5.14: Initial J-V curves for the Control (C) and AL12scans Spray cells by Program 2.

After five days stored in darkness:

Figure 5.15: J-V curves for the best Control and AL spray cells by Program 2 after being stored in darkness five days.

An increment in the current density of the cells manufactured by spray coating is observed, especially in the AL12scans (C) cell, as well as the improvement in the voltage of all cells including the control one, something that has been observed previously. Although they are not very high values, the control cell and the best spray cell under the solar simulator were selected for a long stability test that is presented in Chapter 7. The comparison between initial and after 5 days in darkness are shown in Figure 5.16.

(a) Control (C)

(b) AL12scans (A)

Figure 5.16: The evolution of J-V curves for the Control (C) device (a) and best AL12scans spray device (b) by Program 2. Initial and after 5 days stored in darkness.

In both cases, an improvement in the parameters is observed, even quadrupling its efficiency in the case of the control device (a) and doubling it in the one manufactured by spray (b), something that has already been observed previously.

- **Active layer by different scans. 12 scans**

In the experiment, 6 samples (a total of 24 cells) have been manufactured. The focus of this experiment is to fine-tune the spray method for 12 scans, which according to the results presented above seems to be optimal. Four substrates are prepared to deposit the active 12 scans

spray layer, and two by spin casting to be used as control devices. The conditions for the spray coating technique are the same as in the previous experiments, as indicated below:

- Nitrogen gas pressure: 0.7 bar.
- Distance to the substrate: 9 cm.
- Nozzle opening: 1 turn.
- Substrate temperature: 55°C.

The results for the of the J-V characterization of the fabricated cells are in Table 5.12:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (F)	0.09	0.20	-2.91	0.21	36
Control (G)	0.09	0.27	-3.28	0.29	33
Control (H)	0.09	0.20	-3.28	0.27	42
AL12scans (H)	0.06	0.40	-1.92	0.20	26
AL12scans (I)	0.09	0.40	-1.17	0.19	41

Table 5.12: Initial electrical parameters for the best Control and AL12scans spray cells by Program 2.

Efficiencies and current densities are still low, although in this case there was a problem with the solvent wetting of the substrates that prevented a correct adhesion of the active layer. Despite this, only one complete control device did not work while the other three were functional devices. Similarly, the samples were stored in the dark and characterized by J-V curves one day after. The results are summarized in Table 5.13:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (F)	0.09	0.53	-4.04	0.91	42
Control (G)	0.09	0.53	-4.48	1.06	44
Control (H)	0.09	0.53	-4.22	0.89	40
AL12scans (H)	0.06	0.53	-1.90	0.56	37
AL12scans (M)	0.09	0.47	-1.69	0.31	39
AL12scans (N)	0.09	0.47	-1.74	0.31	38
AL12scans (O)	0.09	0.47	-1.88	0.34	38

Table 5.13: Electrical parameters for the best Control and AL12scans cells by Program 2 after being stored in darkness one day.

As in previous experiments, some of the cells recover (they start working as functional devices), as well as those that were already working improve their performance. As an exception, cell AL12scans (C) stops working, possibly due to its low initial open circuit voltage value or a poor stability. To see the evolution of these parameters, the following best J-V curves have been represented in Figures 5.17 and 5.18:

Figure 5.17: Initial J-V curves for the best Control and AL12scans cells by Program 2.

After one day stored in darkness:

Figure 5.18: J-V curves for the best Control and AL12scans spray cells by Program 2 after being stored in darkness one day.

The spray coated cell, after storage in the dark, improves its V_{OC} , and although it keeps the photo current practically the same, it improves both its efficiency and its fill factor. This behavior has previously been observed in both control and spray coated cells. Despite observing certain operating patterns, the manufacture process must continue to be optimized since low currents and low power conversion efficiencies are still obtained.

- **Active layer by different scans. Influence of substrate temperature. 12 scans**

For the following experiment, eight devices have been manufactured (two for control and six for spray on the active layer), in this case, four substrates had temperature on the substrate during deposition (55°C) and the other four not (room temperature) in order to check whether or not heat influences the manufacturing[13].

Regarding the spray conditions for manufacturing, the following parameters have been applied for the eight devices fabrication:

- Nitrogen gas pressure: 0.7 bar.
- Distance to the substrate: 9 cm.

- Nozzle opening: 1 turn.
- 12 scans of the active layer.

After manufacturing, all the cells have been electrically characterized and the results are as follows:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
AL12scans_Heated (F)	0.12	0.33	-4.15	0.40	31
AL12scans_Heated (G)	0.12	0.13	-4.18	0.20	28
AL12scans_Heated (H)	0.12	0.13	-1.12	0.04	26

Table 5.14: Initial electrical parameters for the best AL12scans with temperature on the substrate solar cells by Program 2.

As can be seen in the Table 5.14, only three have worked and these ones are only the spray coating with previous thermal annealing process, although with very low current and voltage values. Also, a low number of samples were operational. As in previous experiments, the samples were stored in the dark and measured one day later, leaving as follows:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
AL12scans_Heated (F)	0.12	0.50	-4.66	1.30	50
AL12scans_Heated (G)	0.12	0.10	-5.14	0.20	31
AL12scans_Heated (H)	0.12	0.50	-0.78	0.10	36

Table 5.15: Electrical parameters for the best AL12scans with temperature on the substrate solar cells by Program 2.

Again, the electrical parameters of the cells improve after storage, especially the open circuit voltage, thus improving power conversion efficiency and filling factor, although low current values are still obtained. This may be due to the electron transport layer, which as will be presented in the next chapter is critical. It must be emphasized that the temperature treatment of the substrate is an important factor, since none of those manufactured without the thermal annealing has worked. To analyze the results in detail, the J-V curves of the first day and the following days are presented below:

Figure 5.19: Initial J-V curves of the sprayed active layer devices with heat in the substrate by Program 2.

Figure 5.20: J-V curves of the sprayed active layer devices with heat in the substrate by Program 2 stored in darkness one day.

It is observed that the current values barely undergo a small improvement in cells F and G; this behaviour has already been seen previously.

On the contrary, it is decreasing in a small measure for cell H, which may indicate stronger losses by surface or bulk recombination in some of the layers. On the other hand, there is an inverse behaviour in voltage, where cell H undergoes a strong increment, maintaining a final power conversion efficiency like the initial one, but improving its filling factor. For device F, having undergone an improvement in its parameters, values of power conversion efficiency of 1.30% and a filling factor of 50% are reached.

• **Active layer by different scans. From 12 to 20**

In this experiment, four substrates were used, depositing the active layer by spray coating. In this case, the number of scan passes is greater than in previous experiments but keeping the one that is known to give the best results (12 passes). The samples were prepared with; 12 passes, 14 passes, 16 passes and 20 passes respectively. The conditions used are:

- Nitrogen gas pressure: 0.7 bar.
- Distance to the substrate: 9 cm.
- Nozzle opening: 1 turn.
- Substrate temperature: 55°C.

After manufacturing, the samples were characterized by J-V curves, but the devices were not operational. They failed to provide photocurrent. Then, the devices were stored in darkness and measured one day later. The results are shown in Table 5.16:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
AL12scans (B)	0.09	0.40	-1.87	0.20	27
AL12scans (C)	0.09	0.33	-2.83	0.31	33
AL12scans (D)	0.09	0.40	-1.10	0.14	31

Table 5.16: Electrical parameters of the best AL spray solar cells by Program 2 after being stored in darkness.

Some of the cells recovered, but with parameters low electrical parameters, but again, the cells manufactured with 12 scans are the only ones that worked. The increase thickness expected for a higher number of

scans have not provided additional light absorption, and on the contrary, have made the cells fail initially. J-V curves of the new recovered cells are shown in Figure 5.21:

Figure 5.21: J-V curves for the best Al spray devices by Program 2 recovered after being stored in darkness one day.

Despite the low values obtained, a similar trend is observed in all samples, indicating a high reproducibility of the system. If, in addition, it is emphasized that again, the cells manufactured by using 12 scan passes give the best results.

5.2.2 Vertical coating

In the next group of experiments and to improve the quality of the deposited films, the Iwata HP-SB Plus airbrush was used to work in vertical position for the spray coating. In this case, program 3 have been used. Due to the change of orientation, all the parameters for the coating process have been readjusted.

Program 3

- **Active layer by time. Influence of the substrate distance. From 10 to 18 cm**

For this experiment, a total of 9 substrates (36 cells in total) have been manufactured. Three control devices were manufactured by spin-coating and six devices were manufactured by spray coating the active layer. As the airbrush and the technique are completely new, a starting point based on the previous horizontal experiment was applied adapted to the requirements and limitations of the vertical (Z axis) of the milling machine and the new airbrush. The selected parameters are:

- Nitrogen gas pressure: 0.5 bar.
- Substrate temperature: 55°C.
- Deposition time: 30 seconds.

The experiments start with a pressure slightly lower than the previous ones obtained as optimal, because the HP-SB Plus airbrush does not allow to regulate the opening of the nozzle, which is completely open delivering a maximum fixed spray output. In the new experiments, the spray coating deposition is now carried out by executing Program 3 (see Figure 5.3) for a certain time as can be found in similar systems[14]. The deposition time is 30 seconds and the influence of the distance between nozzle and substrate is analyzed. The different distances used in the coating processes are 10, 15 and 18 cm[15]. After manufacturing, they have been characterized. Of the manufactured cells, only two control cells have worked, so parameters must still be optimized further. In addition, in the coating with the substrate at 18 cm, the airbrush begins to drip, which is a problem since it makes the spraying process inhomogeneous, generating a gradient in thickness in the substrates, one of which is completely lost for an operating device. Considering the inconveniences found in the first vertical spraying experiment, new parameters were tried to optimize and achieve the optimal set up.

- **Active layer by time. Influence of the pressure**

As in previous experiments and after tests with different distances, the pressure of the nozzle system was increased to get thicker layers. The new conditions are:

- Nitrogen gas pressure: 1 bar.

- Distance from the substrate: 10 cm.
- Substrate temperature: 55°C.
- Deposition time: 30 seconds.

A total of three substrates with 4 cells each have been used to manufacture new devices. One control (spin casting) and two by spray coating. Certain intermittenencies were observed during the coating process, which are believed to be due to the airbrush model used in the experiment. Despite this fact, some of samples were functional devices; their J-V characterization results are shown below:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
AL1bar (B)	0.06	0.40	-1.86	0.21	29
AL1bar (C)	0.06	0.47	-1.73	0.25	32

Table 5.17: Initial electrical parameters for the vertical spray active layer 1 bar deposition by Program 3.

Even though there were problems during the coating process as mentioned before, one of the spray coated devices worked; but not the reference one. After characterization, they are stored in darkness and re-measured one day later:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (A)	0.09	0.53	-4.15	0.95	43
AL1bar (A)	0.06	0.13	-4.51	0.11	19
AL1bar (B)	0.06	0.47	-2.25	0.40	38
AL1bar (C)	0.06	0.47	-1.81	0.30	36
AL1bar (G)	0.09	0.80	-1.60	0.30	24

Table 5.18: Electrical parameters for the Control and vertical spray active layer solar cells by Program 3 after being stored in darkness one day.

As in previous cases, many cells start working, and others improve its performance. In the case of the reference device, it is observed that it reaches almost 1% in just one day when stored in darkness, despite the previous lack of functionality. This remains the norm in all the experiments that have been carried out so far, regardless of the method

used. For spray-coated devices, similar efficiencies and currents are seen in all of them, despite the problems found during the spray coating procedure, which indicates that there is at least some reproducibility when using this technique once the manufacture parameter have been optimized. To see this evolution of the electrical characterization, the J-V curves are shown in Figure 5.22:

Figure 5.22: Initial J-V curves for the vertical spray active layer 1 bar deposition by Program 3.

After one day:

Figure 5.23: J-V curves for the Control and vertical spray AL solar cells by Program 3 after being stored in darkness one day.

An increment in power conversion efficiency is observed for the case of

the devices that were already working at the beginning of the experiment, AL1bar (B) and AL1bar (C); this is mainly due to the increment in the open circuit voltage and not in its photocurrent, which remains constant. This would explain the possible structural reorganization effect that may be occurring in the solar cell during its storage in darkness, mainly due to the zinc oxide layer as has been included in the device. Again, some cells like AL1bar (B) duplicate its efficiency after only one day stored in darkness.

- **Active layer by time. Influence of the pressure, time, and distance**

After a series of experiments in which high distances to the substrate and different pressure have been tested, a combination of selected manufacture parameters was tested. The aim is to achieve a combination that makes reproducible the best results obtained for the reference devices fabricated by spin casting. Four substrates with 4 cells each have been manufactured. Two control samples by spin casting and two by spray using Program 3. The spray coating conditions are as follows:

- Nitrogen gas pressure: 0.8 bar.
- Distance to the substrate: 10 cm.
- Temperature of the substrate 55°C.
- Deposition time: 150 seconds.

The decision to increase the time is due to the estimation made about the time it takes to deposit 80 μl (the volume used in the control cells for the active layer) under the given conditions of pressure and distance, on a glass substrate. The parameters obtained from the cells in the characterization after manufacture are:

Name	Area (cm^2)	V_{OC} (V)	J_{SC} (mA/cm^2)	PCE (%)	FF (%)
Control (A)	0.12	0.20	-2.97	0.13	22
Control (F)	0.12	0.30	-1.71	0.12	27
ALsprayPTD (B)	0.09	0.53	-5.63	1.06	35
ALsprayPTD (C)	0.09	0.53	-6.19	1.16	35

Table 5.19: Initial electrical parameters for the Control and ALspray solar cells by Program 3 with 0.8 bar, 55°C, and 10 cm from the substrate in the conditions spray.

The devices with the best parameters are those manufactured by using the spray coating technique. These values are also almost identical, which reinforces the reproducibility of the system, both when it works and when it does not. In this case, values greater than 1% in power conversion efficiency are obtained; acceptable current densities and good open circuit voltage values have been achieved. Although the filling factors can be improved, the initial hypothesis that the distance used for this type of vertical deposition and this airbrush model was not adequate is verified. In addition, the application of the new program and the new parameters, including time of coating achieves a notable improvement of results. The J-V curves obtained are the following:

Figure 5.24: Initial J-V curves for the Control and AL spray solar cells by Program 3 using 0.8 bar, 60°C on the substrate and 10 cm from the spray system.

The difference is clear between the control devices and those manufactured using the spray technique. These results again reinforce the difficulty of fine tuning this system in which a multitude of parameters influence and where a small variation in one of them causes the device to function or not. Highlight the importance of testing a large set of parameters and its combinations, varying their magnitude, and trying to optimize the system is a challenge. Finally, reproducibility of the

experiments and an understanding of the correlation between experimental conditions and performance of manufactured solar cells have been achieved.

5.3 Conclusions

In this chapter, the spray coating technique has been applied to the manufacture of organic solar cells. Especially, its use has been applied to the deposition of the active layer by using different automated programs to control a three-axis milling machine with the spray coater nozzle attached to its head. Despite the difficulty of working in air and the required optimization of a large number of parameters that influence the coating process by means of this technique, it has been shown that it is not only viable, but also devices with equal or greater efficiency than those prepared by the laboratory scale spin casting process have been obtained, even without a full optimization of the process[16].

These best spray AL organic solar cells and their combination of parameters are:

Name	Program	Initial PCE (%)	After storage PCE (%)	Coating	Table
SprayAL2T	1	0.93	1.27	Horizontal	3 and 4
AL12scans	2	0.40	1.30	Horizontal	14 and 15
ALsprayPTD	3	1.16	-	Vertical	19

Table 5.20: Best combination of parameters for AL spray coating organic solar cells (more parameters see tables respectively).

The best initial parameters can be found in Program 1 and 3 (Table 5.20), obtaining values around 1%. Unfortunately, despite these values and these results obtained, only program 1 is the one that manages to maintain and improve said efficiency. On the other hand, Program 2 has been shown to obtain the greatest % improvement after dark storage, achieving three times its efficiency. It has been possible to observe a similar behaviour of the performance parameters when compared to the reference devices, such as the improvement of the devices after storage in the dark after manufacturing, which occurred even in devices that initially did not work and recovered its functionality after storage. This has been observed mainly in the improvement in the electrical parameters, especially in the open circuit voltage, which indicates that there is a structural reorganization within the device during the storage time. This effect has been observed independently of the type of manufacturing technique used to fabricate the solar cells. This

recovery peak is usually found in the first 5 days of storage. Regarding the obtained photo current, it is still very low in all cases, leading to a low power conversion efficiency of the spray coated solar cells. Further optimization to obtain an optimal active layer thickness and morphology that allows the maximum photo generation of current is required. Similarly, for the final electrode evaporation, which lead to high series resistance and poor charge carrier collection. These effects can be reduced by optimizing the electron transport layer, to obtain more competitive devices. The next chapter addresses the study of the optimization of the deposition parameters by the spray technique of the ZnO electron transport layer in addition to the active layer.

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Chapter 6

Fabrication and characterization of organic solar cells. Spray coating technique applied to the electron transport layer and active layer

In Chapter 5, the optimization of the active layer deposition process by spray coating technique has been shown, as well as the characterization of these devices using various techniques to optimize both the electrical operating parameters of the cell and the manufacturing process. For manufacturing, a series of programs called Program 1, 2 and 3 (Chapter 5) were written.

The next chapter showed the process of optimization of the zinc oxide layer deposition by means of the spray technique and the following characterization techniques: UV-Visible, atomic force microscopy (AFM) and scanning electron microscopy (SEM), to know the thickness, the morphology, and the elemental composition of the samples, as well as what is found in the literature and the experience obtained with the active layer, a starting point can be obtained. Building on results of the previous chapter, the fabrication procedure (or recipe) and parameters such as speed, nozzle pressure or solution temperature have also been set for active and transport layers. The final set experiments shown in this chapter demonstrate that only a few fundamental parameters need to be adjusted, while others like the opening of the nozzle remains fixed to simplify the number of influencing variables. With the results that are obtained from each experiment, an attempt is made to determine if it is possible to deposit a uniform ZnO layer using this technique and what parameters are optimal.

Although the layer considered below is the active layer, fundamental component of the solar cell, it was decided to work with it at a later stage due to the difficulty to deposit a uniform layer and due to the high reactivity since the work is carried out in ambient atmosphere (air). Actually, there is some groups in the literature like[1], included in the substrate along with the semi-transparent back electrode and in other cases that it can be purchased (Infinity OPV) (if it is in the form of nanoparticles like the one studied in this work) or it is deposited in another type of dispersion with aluminium (AZO) or different deposition technique[2–4]. This chapter will show the results obtained from the application of the spray coating technique to the ZnO layers and the active layer of the OSCs. First, the results of the characterization of the materials by means of UV-Vis, SEM and AFM measurements on ITO and glass will be shown. Next, the electrical characterization of the complete devices using different programs and a conclusion with the best results and its parameters obtained.

6.1 Parameter's optimization over glass and ITO

UV-Visible spectroscopy

As in the previous chapter, the absorbance has been measured with the visible ultraviolet spectrometer. The ZnO layer is deposited by spray coating with Program 1 by different periods (1T, 2T and 4T).

Figure 6.1: Absorbance versus wavelength of the ZnO layer on glass by the spray coating technique with Program 1.

As can be seen in Figure 6.1, the absorbance is very low (it does not exceed 0.3) so it is considered optically transparent and that is why in the calculation of the thicknesses of the active layer of the previous chapter, it has not been considered when we are considering a complete device.

Morphology and elemental analysis by SEM

By using a Scanning Electron Microscope (SEM), the morphology of the ZnO layer can be observed on the micro-scale. Before showing the results of the experiments, it is interesting to see what can be found in the substrates when depositing the ZnO layer on different substrates: glass and ITO. These substrates have been analyzed using the SEM and Energy Dispersive X-ray spectroscopy (EDX) techniques and provide useful information about the surface morphology and composition, the identification of certain elements present in the layers can help to clarify why sometimes the manufactured devices have not worked optimally and what is happening internally in this critical layer. The samples have been named as sample 1 (ITO + ZnO) and sample 2 (Glass + ZnO). The measurements have been made in different areas and with different magnifications to be able to appreciate the obvious differences. Three measurements are shown, at different magnifications (300x, 1000x and 3000x), to observe the morphology of the film, as seen in Figure 6.2. In it, again, on the left side (a), (b) and (c) are the images of the ITO + ZnO layer (sample 1) of different size ($573 \times 398 \mu\text{m}^2$, $172 \times 119 \mu\text{m}^2$, $57 \times 40 \mu\text{m}^2$ respectively) at first sight the ZnO surface is very rough and non-uniform, seems that the spray deposition has created a kind of crater areas where the airbrush has directly affected. Around these areas, a vein-like structure ($1.26 \mu\text{m}$ width) shows the aggregation of the ZnO nanoparticles[5, 6]. On the other hand, on the right-hand side (d), (e) and (f) the same ZnO layer but in this case deposited on glass (sample 2) shows a completely different morphology, where the film is very uniform and there is not almost contrast at all SEM scales.

Figure 6.2: SEM images of the ITO + ZnO layer (sample 1 at different magnifications (300x, 1000x and 3000x) with elongated structure (a), (b) and (c). SEM images of the glass + ZnO layer (sample 2) at different magnifications (300x, 1000x and 3000x) with a homogeneous morphology (d), (e) and (f).

If Figure 6.2 (a) is taken as a reference and we reduce its magnification to 200x ($862 \times 637 \mu\text{m}^2$), two areas have been chosen (yellow area and green area) where to perform EDX measurements to see the elements present (Fig-

ure 6.3 (a)). Both areas are well differentiated since in the yellow area there is hardly any structure in the form of veins, leaving the centre of the crater in view. On the other hand, in the green zone, attention has been focused on this venous structure, aggregation of the ZnO layer.

Figure 6.3: SEM image (a) at 200x magnification of the ITO + ZnO layer (sample 1) where the yellow (crater) and green (elongated structure) areas the EDX measurements have been made. EDX spectra of the yellow (b) and green (c) areas with the different elements found.

Element	Atomic Number	Zone	Atomic C. (%)	Zone	Atomic C. (%)
In	49	Yellow	5.5	Green	19.5
Zn	30	Yellow	15.7	Green	23.5
Si	14	Yellow	4.8	Green	0.8
O	8	Yellow	58.9	Green	54.5
C	6	Yellow	15.1	Green	1.8

Table 6.1: Elements found in the yellow and green areas together with their atomic concentration in the EDX spectra of the ITO + ZnO layer (sample 1).

Table 6.1 shows the results obtained from the EDX spectrum of Figure 6.3 (b) and (c). It is expected that the elements found are the same, although in different atomic concentrations. The oxygen and zinc peaks are similar to those found in the literature[7]. The following characteristics are observed for the main components:

1. Oxygen: First predominant element with 58.9% in yellow zone and 54.5% in green zone.
2. Zinc: Second predominant element with 15.7% in yellow zone and 23.5% in green zone. Even though the size of the green zone is greater, it should be noted that the amount of O is less in said zone, unlike Zn.
3. Indium: In the crater (yellow zone) four times less indium is observed (5.5% yellow zone vs 19.5% green zone), where one would expect to find more because the thickness of the film there is less and there should be more signal from the substrate.

On the other hand, the appearance of carbon can only be due to contamination or to remnants of it in the ZnO dispersion, here however the concentration of carbon is higher in the crater (15.1% yellow zone vs 1.8% green zone).

Finally, a little silicon appears that must come from the glass on which the ITO film has been deposited.

Figure 6.4: SEM image (a) at 500x magnification of the glass layer + ZnO (sample 2) with homogeneous morphology and EDX spectrum (b) of the elements found.

Element	Atomic Number	Atomic C. (%)
Zn	30	12.6
Si	14	0.2
O	8	47.1
N	7	7.1
C	6	32.9

Table 6.2: Elements present together with their atomic concentration in the EDX spectrum of the glass layer + ZnO (sample 2).

In Figure 6.4 (a) the glass layer + ZnO (sample 2) is shown at 500x magnification ($327 \times 244 \mu\text{m}^2$). In contrast to the previous case (Figure 6.3 (a)), the layer is flat, with no structure at this scale, although the elemental composition is similar according to Figure 6.4 (b):

1. Oxygen: Again, oxygen is the predominant element in the sample along with Zinc, with a concentration of 47.1%, very similar to the previous case.
2. The second element is Zinc, with a concentration of 12.6%. In this case, the sample size is smaller but gives a higher concentration of Zn than in more flat case with ITO (crater zone).

Once again, they are contained in carbon and silicon as in the previous case, highlighting the low silicon content (0.2%) indicating a greater homogeneity of the ZnO layer leaving. As expected, however, in this case there

is not indium, obviously, since there is no ITO in this sample, but appears nitrogen that probably comes from the gas of the airbrush.

Figure 6.5: SEM images of the interface of sample 1 ITO + ZnO and of sample 2 glass + ZnO. (a): Heterogeneous morphology at the ITO + ZnO interface; (b): Contrast showing the zones with In (top) and Zn (bottom); (c): Contrast showing the zones of In (top) and Na (bottom); (d): Homogeneous morphology of the glass + ZnO interface; (e): Contrast of the layers of Si (top) and Zn (bottom); (f): Contrast of the Ca (top) and Na (bottom) layers.

In Figure 6.5 (a) and (d), two morphology images of ITO + ZnO (sample 1) and glass + ZnO interface (sample 2) are shown being the layer of ZnO of sample 2, Figure 6.5 (d) more homogeneous, with ZnO at the bottom and the ITO at the top. In Figure 6.5 (b), thanks to the contrast of the compositional mapping of elements where the zinc is clearly located in the lower part of the image (red), it is interesting to note that, in the small craters formed in the ZnO layer, there are traces of indium (yellow) still visible. In Figure 6.5 (c), the contrast made in yellow (indium) and light blue. It is interesting that the sodium corresponds entirely with the ZnO layer, in an indication that traces of Na are present in the ZnO layer. It is a clear indication of sodium ions migration, a phenomenon which has been reported to lead to cell failure by potential induced degradation (PID) [8, 9]. In Figure 6.5 (e), the contrast is made for silicon (green) and Zn (red), close to the interface some voids are visible, green dots, indicating the presence of Si belonging to the glass substrate. Finally, in Figure 6.5 (f), again the presence of Na (light blue) is detected in the ZnO layer, while Ca (dark blue) is detected as a component of the glass substrate

X-ray Diffraction (XRD) analysis

To study the crystalline structure of the ZnO layer and how the annealing influences it, XRD spectra were performed in the ITO + ZnO sample before and after annealing at 170°C for 10 minutes. The spectra obtained are shown in Figure 6.6.

Figure 6.6: XRD spectra of the ITO + ZnO layer deposited by spray coating technique with program 1 before and after heating, the ITO and ZnO crystallographic planes are indicated in the Figure.

Three different peaks corresponding to ZnO (31.2° , 34.5° and 35.7°) are observed, which are identified with the (100), (002) and (101) crystallographic planes in Figure 6.6, where all the peaks show good similarity to the wurtzite hexagonal structure[10, 11]. A significant change is that while peaks 100 and 101 appear in both cases, with and without heating, the peak of less intensity, (002), practically disappears after heating the sample. Five peaks corresponding to ITO are found in 21.5° , 31.2° , 35.7° , 51.5° and 60.5° which are identified with the (211), (222), (400), (440) and (622) planes, all of them corresponding to cubic structure of the ITO[12]. As in ZnO the intensity peaks of the ITO are lower after heating the sample. In planes (100) and (101) there are double contribution of the ZnO and ITO in the intensity of the peaks but in both cases the relative intensity between them remains constant. To study how the temperature affects the crystallization of the ZnO layer, the full width at half maximum height (FWHM) of the (100) ZnO plane is analyzed by fitting the peak with a Gaussian curve. The results are shown in Figure 6.7 and Table 6.3.

Figure 6.7: Gaussian fits for the 100-plane peak at 30.5 degrees comparing the width before (a) and after (b) heating to observe significant crystallization changes

Sample	Area (a.u.)	Centre position (degrees)	FWHF (degrees)
ITO + ZnO	365.4	30.3	0.4
ITO + ZnO heated	233.8	30.3	0.4

Table 6.3: Values of the Gaussian fits for the samples before and after heating.

Figures 6.7 (a) and (b) show the fits for the peak of the (100) plane of the ZnO layer on ITO before and after heating, the result of the fitting indicates that the FWHM remains constants after the annealing, indicating that there is no change in the crystallinity of the layer with the thermal treatment.

AFM analysis

Since the height and roughness of the layers surface cannot be measured in SEM in a direct way, a series AFM images have been taken to quantify the height of the features found in the ITO + ZnO samples, as well as the roughness of the surfaces. Again, the nomenclature used would be sample 1 for ITO + ZnO and sample 2 for glass + ZnO.

Figure 6.8: AFM image (size $40 \times 40 \mu\text{m}^2$) of the ZnO layer on ITO deposited by spray coating by Program 1. Blue line marking the height profile measure.

In Figure 6.8, an AFM image of sample 1 is presented, where the characteristic vein-shaped structure already shown in the SEM measurements (Figure 6.2 (c)) of this combination reappears again in the AFM topographic image. The colour code in the image indicates the height as it is shown in the right part of the figure, where the white colour corresponds to a height of $4.21 \mu\text{m}$. In this case, the root-mean-square (RMS) roughness of this surface for this zone of $40 \times 40 \mu\text{m}^2$ is about $3.6 \mu\text{m}$. Considering that the layers of the manufactured devices are of the order of nanometers, it is unusual to find this size of structures[13]. To study in detail the height of these veins like structures a line profile has been acquired and it is shown in Figure 6.9. The length of the line is $20 \mu\text{m}$ and its strong Z-value variations show features between 1.4 and $1.0 \mu\text{m}$ height, something that had already been observed

in the previous SEM images but without quantified height (Figures 2a, with the structures in the form of veins). We emphasize the difficulty to get these AFM images due to the height contrast of these features as compared with the size of the image and the lower roughness of the surrounding areas. Since the structures obtained are of a very large size, it was not possible to obtain a clear and complete image.

Figure 6.9: Height profile obtained for sample 1 of the AFM image of the blue line of 20 μm .

Figure 6.10: AFM image (size 40x40 μm^2) of the ZnO layer on glass deposited by spray coating by Program 1.

The AFM results for sample 2 are shown in Figure 6.10. The ZnO layer is deposited on glass and in this case, if compared to Figure 6.8, these vein-

shaped structures are not found, as observed before in the SEM images (Figure 6.2 (d)), where a greater uniformity of the layer was observed. Note that the height scale of the image is now 500 nm. The RMS roughness found is 36 nm for the $40 \times 40 \mu\text{m}^2$ image, much smaller than that obtained in sample 1 and closer to the optimal values obtained according to Oh et al. and Yuan et al.[14, 15].

Figure 6.11: AFM image (size $20 \times 20 \mu\text{m}^2$) of sample 1 of the ZnO layer on ITO deposited by the spray technique using Program 1.

To look at in more detail in these veins like structure, another area of sample 1 was measured, in this case in a $20 \times 20 \mu\text{m}^2$ image is shown in Figure 6.11. Again, the same structures as Figure 8 are observed, but new structures inside these features are revealed, the structures of this image are much less high than the ones found in Figure 6.8, since the scale bar maximum is now 500 nm in this case the average roughness obtained is 71 nm, a value more acceptable, indicating the huge inhomogeneity in the morphology of these samples. If it is now measured in the same way and in the same image size, in a $20 \times 20 \mu\text{m}^2$ image and for sample 2 (Figure 6.12) an average roughness of 37 nm is obtained. The morphology observed is the same as in Figure 6.10, but now small grain can be resolved. This different roughness in different areas, although they are the same samples, coincide with the results obtained in the SEM images of Figure 6.2 where different structures are observed on the surface.

Figure 6.12: AFM image (size $20 \times 20 \mu\text{m}^2$) of sample 2 of the ZnO layer on glass deposited by the spray technique using Program 1.

To verify that the roughness is not induced by the roughness of the ITO substrate, images of bare ITO have been taken. Figures 6.13 and 6.14 show the structure of ITO at different sizes (20×20 and $5 \times 5 \mu\text{m}^2$) and where an average roughness of 6 and 4 nm, respectively, has been found, with the typical morphology of the ITO. This verifies that the ITO is not actually inducing a greater roughness and that this may be related to a different wetting behavior of the ZnO nanoparticles of adhering to the ITO or to the glass.

Figure 6.13: AFM image of $20 \times 20 \mu\text{m}^2$ ITO layer.

Figure 6.14: AFM image of $5 \times 5 \mu\text{m}^2$ ITO layer.

6.2 Parameter's optimization of full devices. Manufacturing and characterization.

Thanks to the experience acquired during the previous chapters and the results obtained from the characterization of the materials in this layer, parameters like those applied in the active layer can be taken as a starting point.

Due to the specific system assembled in this work, it is not easy to reproduce certain conditions such as those shown in Zhao et al.[16], where the solution is vaporized in a kind of cloud (mist) in an ultrasonic spray or in Amala Rani et al.[17], where a pyrolytic spray is used. Although it is true that in most specific equipment is used for spray manufacturing, there are some laboratories that have built their own system like the one shown in this work and from which some parameters can be obtained[18].

The ZnO layer as it mentioned in Chapter 3, has the function of transporting the electrons produced after the dissociation of the exciton into holes and electrons. in the solar cell (ETL layer). The active layer used is the same as in previous chapters, made up of a conjugated polymer (P3HT) and a derivative of fullerene (PCBM) in dichlorobenzene, forming what is known as bulk heterojunction.

The ZnO nanoparticles (Zn acetate dehydrated, CAS 5970-45-6/sigma 399786) are dissolved in Methoxy-ethanol (CAS 109-86-4/sigma 284467) and Ethanolamine (CAS 141-43-5/sigma 411000). For the active layer, the P3HT:PCBM mix in 1,1:1 ratio is dissolved in dichlorobenzene. The results of the

manufacture of solar cells depositing the ZnO layer and the active layer by spray by different programs are shown:

6.2.1 Horizontal coating

Program 1

- **ZnO layer by different periods. From 1T to 3T**

For this first experiment, eight samples with four cells each have been manufactured to apply, verify, and optimize the deposition of the ZnO layer by the spray technique with different coating periods, keeping the active layer constant, with 2T being the chosen value. Since it was the one that obtained the best results as shown in the previous chapter. These eight samples, in the case of the ZnO layer, have been arranged respectively in order, one with 1T, three with 2T and four with 3T. The airbrush manufacturing conditions that have been used as a starting point are the same for both layers and coincide with those used in the previous chapter for Program 1, they are the following:

- Nitrogen gas pressure: 0.5 bar.
- Distance to the substrate: 11 cm.
- Nozzle opening: 3/4 turn.

Some results for the newly manufactured cells are shown in Table 6.4:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
ZA1T (C)	0.09	0.20	-2.25	0.16	34
ZA1T (D)	0.09	0.27	-2.27	0.20	32
ZA3T (B)	0.06	0.53	-0.21	0.04	40

Table 6.4: Electrical parameters for ZA1T/ZA3T spray organic solar cells by Program 1.

In the experiment only 1T device can be used for PV performance analysis. Despite obtaining low values of current density and PCE less than 0.5% and considering the previous chapters, as well as the characterization of the layer in the first part of this chapter, it is a good starting point. Low voltage values may indicate that there is no improvement after storing in the dark. It should be noted that,

although only three cells were shown, there was a total of 10 cells out of a 24, although with values like that observed in the cell with 3T. In the same way and as in previous chapters, they have been stored in the dark and have been measured again the next day and two months later to check if some of the manufactured cells improve, in this case the improvement has been measured two months later, resulting:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
ZA1T (D)	0.09	0.20	-0.85	0.05	32

Table 6.5: Electrical parameters for ZA1T spray organic solar cell after 2 months in darkness by Program 1.

After two months stored in the dark, only one of them works and with low PCE values, very close to a resistive behavior so it can be said that in addition to not being the appropriate parameters for the best efficiency, it is neither stable. The measurements carried out a day later delivered resistive behavior in all cases. In the same way, the J-V curves corresponding to devices C and D only recently manufactured have been drawn:

Figure 6.15: J-V for the ZA1T spray organic solar cells C and D by Program 1.

In the curves shown in Figure 6.15 the low current and voltage values obtained, as well as the great slope they have, closer to a resistance than

a solar cell. Therefore, different deposition conditions must continue to be tested to try to optimize the deposition of this layer.

- **ZnO layer by different periods. 4T periods**

In this experiment, the active layer is again kept constant, and the experiments were designed to test sample fabrication with a different number of periods for the ZnO layer deposition, using in this case 4T with a total of four devices with four cells each. To reduce possible variables and focus only on the ZnO layer, the airbrush parameters have also remained constant, with the following operating conditions:

- Nitrogen gas pressure: 0.5 bar.
- Distance to the substrate: 11 cm.
- Nozzle opening: 3/4 turn.

The obtained results are presented in Table 6.6:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
ZA4T (E)	0.09	0.33	-3.11	0.34	32
ZA4T (F)	0.09	0.27	-2.68	0.27	29
ZA4T (G)	0.09	0.33	-2.45	0.35	33
ZA4T (H)	0.09	0.40	-2.50	0.24	24

Table 6.6: Electrical parameters for some ZA4T spray organic solar cells by Program 1.

A total of six cells out of sixteen have been functional, with the four shown above being the best. In this case, the efficiencies and currents obtained are slightly higher, but maintaining similar voltage and fill factor values. After initial measurements, they are stored in the dark for five days and characterized:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
ZA4T (O)	0.09	0.40	-0.44	0.05	30
ZA4T (P)	0.09	0.46	-0.84	0.11	27

Table 6.7: Electrical parameters for some ZA4T spray organic solar cells stored in darkness five days by Program 1.

Only a total of three cells have delivered some photoactive behavior when measured after five days. The best ones are the two shown in Table 7, which are different from those initially shown in Table 6; this fact may indicate how in the previous experiment, in addition to low currents, its low open circuit voltage can lead to low stability because there is any hardly any photo-generation due to the strong recombination. The J-V curves initially obtained, as well as those stored for five days in the dark, are shown below respectively:

Figure 6.16: J-V curves for the ZA4T spray organic solar cells after fabrication by Program 1.

Figure 6.17: J-V curves for the ZA4T spray organic solar cells O and P after five days stored in darkness by Program 1.

These curves show very clearly in a graphical way the great slope they have, being very close to what could be a resistance (with low values of parallel resistance and high values for series resistance), thus having a low filling factor. This fact, added to the initial values obtained, indicates that it is still far from being able to manufacture this layer by this technique and that different conditions must continue to be tested.

Program 2

As in previous chapters and after a series of experiments, it has been decided to accomplish manufacturing with Program 2, where the deposition is carried out through several specific scan routines to try to optimize the material used. The choice of the new starting parameters is guided mainly by the experience obtained for the previous case of active layer deposition; the parameters selected now as a starting point are the ones that have provided the best results. In the case of the ZnO layer, although experience with the previous program plays an important role, it is still a different method. In most of the literature that can be found, very specific spray deposition systems are used[3–6] or ZnO gel dispersions easier to work with, conditions very different from those found here. In the same way, similar systems are also found with the same type of nanoparticle dispersion[5], which, together with what was obtained in the previous chapter, considering the different viscosity and nature of this layer have served as support to obtain that starting point, which will be shown below.

- **Active layer 12 scans. ZnO layer by different scans. 20 scans**

For this experiment, a total of four substrates with four cells each have been manufactured, the first control and the next three completely by spray, with 20 scans the ZnO layer and 12 scans the active layer. The airbrush deposition parameters for the ZnO layer are:

- Nitrogen gas pressure: 0.5 bar.
- Distance to the substrate: 9 cm.
- Nozzle opening: 1 turn.
- Substrate temperature: 80°C.

And for the active layer:

- Nitrogen gas pressure: 0.7 bar.
- Distance to the substrate: 9 cm.

- Nozzle opening: 1 turn.
- Substrate temperature: 60°C.

After the manufacture of these devices, their electrical parameters have been characterized, resulting in the values shown in Table 6.8:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
ZA20scans (C)	0.03	0.07	-0.66	0.01	29
ZA20scans (D)	0.03	0.13	-0.58	0.02	31
ZA20scans (F)	0.06	0.13	-0.55	0.01	29
ZA20scans (G)	0.06	0.13	-0.37	0.01	30
ZA20scans (K)	0.06	0.13	-0.57	0.02	31
ZA20scans (L)	0.06	0.13	-0.50	0.02	27

Table 6.8: Initial electrical parameters of the organic solar cells with 20 scans ZnO layer by Program 2.

Once again, it is possible to appreciate the low values of the electrical parameters that, despite being with another program, are of the same order of magnitude, which may indicate something deeper, intrinsic in the assembled machinery and not with the spray process. itself, as the literature has shown. The J-V curves obtained, corresponding to the manufactured cells shown in Figure 6.18 are:

Figure 6.18: Initial J-V curves of the organic solar cells with 20 scans of ZnO layer by Program 2.

A low filling factor and open circuit voltage can be observed. These values according to Kang et al.[19] indicate that the quality of the deposited layer is poor, with hardly uniformity and / or excessively thick or thin, which implies that there may be shunts and low electron transport.

6.2.2 Vertical coating

Program 3

For this group of experiments, an airbrush for vertical deposition model HP-SB Plus. This new model, unlike the previous HP-SB Plus, allows to regulate the opening of the nozzle as happened in the model for horizontal deposition, this will allow better control of the injection flow and the size of the drops. In addition, thanks to the use of Program 3, the deposition time is drastically reduced.

- **Influence of deposition time. ZnO layer 60 seconds per substrate**

The first of this group of experiments is aimed at evaluating a starting point and the operation of this new airbrush. A total of three devices have been manufactured, one of control reference, entirely by spin coating and two by depositing the ZnO layer and activating it by spraying. Each device as always has four cells and the deposition conditions per layer are as follows:

ZnO layer:

- Nitrogen gas pressure: 0.5 bar.
- Distance from the substrate: 10 cm.
- Nozzle opening: $\frac{1}{2}$ turn.
- Temperature of the substrate: 60°C.
- Deposition time: 120 seconds (60 per substrate).

Active layer:

- Nitrogen gas pressure: 0.6 bar.
- Distance from the substrate: 10 cm.
- Nozzle opening: $\frac{1}{2}$ turn.
- Temperature of the substrate: 60°C.

- Deposition time: 100 seconds (50 per substrate).

The conditions between the two layers are very similar, in addition, the total deposition time was written as a function of the number of substrates that are deposited at the same time, in this case three. In the ZnO layer, with these parameters, it is deposited around 250 μl for each substrate, trying to equal the amount deposited by the spin technique. The same happens with the active layer, depositing around 80 μl .

The results obtained after characterization are:

Name	Area (cm^2)	V_{OC} (V)	J_{SC} (mA/cm^2)	PCE (%)	FF (%)
Control (C)	0.09	0.47	-2.77	0.42	33

Table 6.9: Initial electrical parameters of the Control (C) organic solar cell by spin coating technique.

None of those manufactured by the spray technique have worked, but they are stored in the dark for two days to see if there is any improvement by recombination and they are measured again.

Name	Area (cm^2)	V_{OC} (V)	J_{SC} (mA/cm^2)	PCE (%)	FF (%)
Control (C)	0.09	0.53	-3.71	1.06	54

Table 6.10: Electrical parameters of the Control (C) organic solar cell by spin coating technique after two days in dark storage.

After two days in the dark, again none of the cells manufactured by spray can photo generate any current, and those which have, deliver low electrical parameters, very similar to those obtained with Program 1 and 2. The control cell for its part, manages to double its efficiency.

- **Influence of distance from the substrate. ZnO layer deposited with airbrush at different distances (from 8 to 10 cm)**

Building on previous experiment and its results, different tests were carried out on glass, again adjusting the different parameters of the airbrush to further adjust the deposition time. After this, the results obtained are that to deposit both 80 and 250 μl of active layer and ZnO respectively a program of 10 and 75 seconds is needed per substrate respectively. With this and by setting the airbrush settings, it is decided

to study the influence of the distance from the airbrush to the substrate to deposit the ZnO layer. Therefore, the parameters that have been set for both layers for this experiment are:

ZnO layer:

- Nitrogen gas pressure: 0.6 bar.
- Nozzle opening: $\frac{1}{2}$ turn.
- Temperature substrate: 80°C.
- Deposition per substrate: 75 seconds.

Active layer:

- Nitrogen gas pressure: 0.8 bar.
- Distance from the substrate: 9 cm.
- Nozzle opening: $\frac{1}{2}$ turn.
- Temperature substrate: 60°C.
- Deposition per substrate: 10 seconds.

With these parameters, the deposition distance of the ZnO layer is set to 8, 9 and 10 cm. The total number of substrates manufactured is twelve with four cells each, three control and nine per spray, two at 8 cm, four at 9 cm and three at 10 cm. Some results after characterization:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (B)	0.09	0.53	-1.83	0.52	53
ZA8 (C)	0.06	0.47	-2.91	0.44	32
ZA8 (D)	0.06	0.53	-2.86	0.47	31
ZA9 (E)	0.03	0.47	-1.64	0.19	25
ZA9 (F)	0.03	0.53	-6.77	1.17	32
ZA9 (G)	0.03	0.40	-1.25	0.14	28
ZA9 (H)	0.03	0.40	-1.86	0.16	22
ZA9 (J)	0.06	0.33	-3.18	0.35	33
ZA9 (O)	0.06	0.47	-3.43	0.40	25
ZA9 (P)	0.06	0.47	-3.30	0.50	33
ZA10 (C)	0.09	0.47	-0.13	0.02	29

Table 6.11: Initial electrical parameters of the Control (B) and ZnO layer/Active layer organic solar cells by spray coating (Program 3) for different substrate distances for the ZnO layer.

In Table 6.11, most of the cells fabricated per spray that have worked are those made at 9 cm distance, only two worked at 8 cm and some at 10 cm being C the best one with very low efficiency. Good current and voltage values were obtained when compared to previous experiments and it is observed that the ZA9 (F) cell obtains values above 1% of efficiency, although with poor values of fill factor. These cells are stored in the dark four days and are measured again resulting in:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (B)	0.09	0.47	-1.90	0.43	49
ZA9 (G)	0.03	0.53	-3.05	0.34	21
ZA10 (C)	0.09	0.53	-1.43	0.24	31

Table 6.12: Electrical parameters of the Control (B) and ZnO layer (different substrate distances)/Active layer by spray coating organic solar cells (Program 3) after four days stored in darkness.

After four days in storage, in Table 6.12 that only three cells remain functional, improving in this case even the control cell. Despite the good results obtained initially, these results seem to indicate and be consistent with those previously obtained in other experiments, confirming that this deposition is not totally uniform, giving cells that are not very stable. The J-V curves obtained initially and after four days are shown below:

Figure 6.19: Initial J-V curves of the initial organic solar cells fabricated by spin (Control (B)) and spray coating (ZAX (X)). Sprayed ZnO with different substrate distances from 8 to 10 by Program 3.

It is clearly reflected that despite the good efficiency obtained by the ZA9 (F) cell, its filling factor is poor, which may indicate its low stability with high values of series resistance (and low of shunt resistance, an indicator of high recombination). A high reproducibility of the procedure and results are shown, and although the parameters are far from optimal, they are functional devices, and all the manufactured cells behave very similarly.

Figure 6.20: J-V curves for Control (B), ZA9 (G) and ZA10 (C) by Program 3 with different substrate distances for the ZnO layer after four days stored in darkness.

(a) Control (B) cell

(b) ZA9 (G) cell

(c) ZA10 (C) cell

Figure 6.21: Initial and after four days stored in darkness J-V curves for Control (B) cell, ZA9 (G) and ZA10 (C) solar cells fabricated by Program 3 with different substrate distance for ZnO layer.

It is appreciated that the control cell is the one that keeps the best shape (Figure 6.20 and Figure 6.21) with a slight improvement after storage. It should be noted that, comparing the control cell and the one manufactured by spray, and unlike the deposition only of the active layer, in this case, the cells manufactured by spray have a poor V_{OC} value, in addition to the low current. Depending on the shape of the curve, this leads to high series resistances which may be related to low stability.

- **Influence of wettability. Treatment of the ITO substrate with dodecyl phosphonic acid**

For this last experiment, the use of phosphonic acid has been proposed to improve the wetting properties of the ITO surface for subsequent ZnO deposition. With this purpose, it is intended to check whether the low stability and the low electrical parameters are more related to the deposition of the layer or to its adherence to the ITO layer. Some studies demonstrate the use of phosphonic acid create modifications on the ZnO nanoparticles surface creating stronger covalent bonding's[20]. The process is straightforward, introducing one more step in manufacturing. 5 ml of 10 mM dodecyl phosphonic acid in ethanol are prepared. Once the ZnO layer is going to be deposited, one or two drops of the solution are deposited by drop casting on the substrate and allowed to air dry. After this, it is placed in an isopropanol bath and dried with the airbrush with inert gas (Nitrogen). From here the process is the same. It should be noted that this process has been used on all manufactured samples, spin, and spray coating.

After analyzing the results obtained in previous experiments, the distance to the sample was set at 9 cm, since this is the one that delivered the best devices. The same happens with the program now used and the rest of the deposition parameters, which are:

ZnO layer:

- Nitrogen gas pressure: 0.6 bar.
- Distance from the substrate: 9 cm.
- Nozzle opening: $\frac{1}{2}$ turn.
- Substrate temperature: 80°C.
- Deposition time per substrate: 75 seconds

Active layer:

- Nitrogen gas pressure: 0.8 bar.
- Distance from the substrate: 9 cm.
- Nozzle opening: $\frac{1}{2}$ turn.
- Substrate temperature: 60°C.
- Deposition time per substrate: 10 seconds

The total number of samples manufactured is 10, two by control and eight by spray coating. The best parameters obtained after manufacturing are:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (C)	0.09	0.20	-2.66	0.17	32

Table 6.13: Initial electrical parameters of the Control (C) by spin coating using dodecylphosphonic acid for ZnO layer.

In this case, only the control cells are initially functional, being the C the one that obtains the highest values. It should be noted that there were problems during the deposition of the airbrush, which initially did not allow the gas to escape uniformly and had to be repaired; this caused the substrates to be exposed to the open air for a longer time than usual. After fabrication and initial characterization, the cells were stored in the dark for two days and characterized again. The results are shown in Table 6.14, where it can be observed that the control cells do improve and that in this case one of the cells manufactured by spray works, although with low values in the electrical parameters, especially short circuit voltage.

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control (B)	0.09	0.47	-2.57	0.53	44
Control (C)	0.09	0.53	-3.71	1.06	54
ZAwet (F)	0.09	0.13	-2.83	0.11	29

Table 6.14: Electrical parameters of the control and spray coating organic solar cells by Program 3 with dodecylphosphonic acid for ZnO after two days stored in darkness.

The J-V curves obtained are:

Figure 6.22: J-V curves for the best organic solar cells by spin and spray coating (Program 3) with dodecylphosphonic acid treatment after two days stored in darkness.

It is observed that despite the low value of current, voltage and filling factor obtained (Table 6.13 and Figure 6.22), after two days in dark storage, the Control (C) improves remarkably and spray cells such as ZAwet (F) work, although with low values.

6.3 Conclusions

Throughout this chapter, the different experiments carried out to characterize the ZnO layer through various techniques and the optimization of this layer through the spray coating technique have been shown. For this and as in Chapter 5, the different programs written for the three-axis milling machine have been used. This layer was an additional challenge if we compare it with the active layer, since it has been shown that not only the specific parameters used of manufacturing the layer, but the technique used to deposit it has a significant influence on its properties. Despite everything, devices have been manufactured using this technique, optimizing time and energy. The best solar cells manufactured by the spray technique applied to the active layer and the zinc oxide layer are:

Name	Program	Initial PCE (%)	After storage PCE (%)	Coating	Table
ZA4T (G)	1	0.35	-	Horizontal	6
ZA9 (F)	3	1.17	-	Vertical	11
ZAwet (F)	3	-	1.06	Vertical	14

Table 6.15: Best combination of parameters for ZnO/AL spray coating organic solar cells (more parameters see tables respectively).

In Table 6.15, the best solar cells found are shown. Unlike chapter 5 and the active layer, in this case the solar cells show poor stability in air if the ZnO layer is deposited by this spray technique. Furthermore, in program 1 the low efficiency obtained initially makes it impractical for use. In Program 3, there are two opposite points, in one case it works initially but not after storing it and in another after not having worked initially, two days after storing it in the dark it works with values around 1%. In addition, it has been found that many of the manufactured cells have not worked, this is mainly due to the heterogeneity of the ZnO surface when it is manufactured by spray as shown in the characterization of the materials. This behavior indicates that functional devices can be manufactured by spray coating in air. The power conversion efficiency reached values higher than 1%, good for a starting point. Nevertheless, optimization of parameters for this layer deposition must continue to improve the electrical parameter of solar cells fabricated by means of the air spray technique, which is a viable with great potential for reducing the time and cost of manufacture. The results obtained from the other automation programs, with their low current and voltage values (the recovery in darkness of these devices being much lower than when the layer is deposited by the spin coating technique) have been useful to narrow the very large ranges of possible manufacturing parameters. As future work, experimentation should continue, testing with other types of substrates[21] other than ITO in view of the results obtained if we compare it with glass, where the surface of the ZnO layer obtained is much flatter and more homogeneous.

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Chapter 7

Stability of devices. Perovskite and organic solar cells

Within photovoltaics, it has already been shown that not only the power conversion efficiency and (and additionally, open circuit voltage and short circuit) that a solar cell or panel has is important, but also how stable it is. That is why, in addition to an initial and subsequent characterization after being stored, it is necessary in many cases (if not in all of them, at least a significative sampling) a prolonged study of the evolution of these electrical parameters over time. These studies are known as stability and/or degradation studies. Non-encapsulated OSCs have some stability limitations when compared with crystalline silicon or inorganic thin-film technologies, which highlights the importance of studying the encapsulant materials and methods [1]. Organic materials degrade quickly due to external environmental agents, mainly oxygen and moisture, as well as UV radiation [2–4]. The degradation causes an alteration of the electrical properties of the cells such as power conversion efficiency (PCE), open circuit voltage (V_{OC}), short circuit current (I_{SC}) and fill factor (FF). In recent years, the study of stability and degradation in OSCs has been crucial and focused mainly on increasing their lifetime. A set of protocols called ISOS were proposed to create standard methodologies, delivering results that could be comparable between different laboratories around the world. These protocols, although not mandatory, are recommended and cover a wide range of different variables and environmental conditions to be measured such as oxygen, humidity, ultraviolet radiation, and temperature [5].

In this chapter, the results obtained in different stability studies for different solar cells will be shown, in particular:

- Stability study for spray organic solar cells with PCBM as fullerene

acceptor.

- Stability study for organic solar cells with O-IDTBR as non-fullerene acceptor.
- Stability study for carbon-based mesoporous perovskite solar cells with different molecular additives.

7.1 Introduction

Within the OSCs, a variety of materials available for the fabrication of the active layer in the bulk heterojunction have been mentioned being the P3HT:PCBM the benchmark for many years. Actually, new electron acceptors such as non-fullerene derivatives (NFAs) like O-IDTBR, thanks to the combination of stability, good light absorption, easy synthesis, low cost and compatibility for use with environmentally friendly solvents [6]. One of the families of these NFAs is indacenodithiophene (IDT) and indacenodithienothiophene based acceptors, especially those that allow to improve aggregation. OSCs made with these NFAs combined with P3HT have achieved efficiencies of up to 6.7% on ITO-coated glass substrates [1, 2, 7, 8]. In addition, this material, as well as the non-chlorinated solvents used in its manufacture, allows R2R series manufacturing so that it can be scaled up to industry [7]. Besides, the burn-in degradation effect (when the solar cell rapidly reduces its PCE by degradation of several electrical parameters, mainly photocurrent, in the first hours of work) is strongly reduced when NFAs are used in the solar cells, with just around 5% relative PCE loss during the first 2000 hours, compared to almost 34% in only a few hundred hours in fullerene-acceptor solar cells [2].

Throughout all the work presented so far in this PhD thesis, OSCs whose active layer is composed of a bulk heterojunction that is made of a polymeric material and PCBM, a derivative of fullerene. In the case presented here, besides this conventional approach, this derivative of fullerene has been replaced by a non-fullerene material, in order to increase its efficiency and to improve the stability of the solar cell. In addition to this fully organic approach, at the end of Chapter 4 it was mentioned that there is a type of solar cell that has been the centre of special attention since ten years ago, due to its rapid development with fast power conversion efficiency improvements. Perovskite solar cells, and more recently silicon/perovskite tandem cells have reported up to 29.6% efficiency [9, 10]. In the case of only using perovskite as active layer material, thanks to methyl ammonium lead iodide in combination with another wide band gap material, efficiencies of up to

20% are reported. However, most of these solar cells have low short-term stability. Most long-term stable perovskite solar cells are in a PCE range of between 10% and 15%. Therefore, perovskite solar cells have not only focused in recent years to improve efficiency but also to extend their lifetime. Unlike organic solar cells, these perovskite cells present an added difficulty in the conventional stability studies shown (ISOS [5]) and applied to perovskite cells [11], due to the hysteresis observed in them when I-V characterization is carried out with voltage sweeps reducing or increasing its value. This hysteresis generates discrepancies among researchers when it comes to analyzing long-term stability studies, therefore, a series of new recommended use procedures have been established [12]. Numerous recent studies have focused on the addition of molecular additives in the active layer for extended lifetime. The use of these additives has increased the useful life of the initial window from 500 hours to 1000 hours, in the beginning, then to 8600 hours, and more recently to 10000 hours [13].

In this work, four different molecular additives have been used: the well-known 5-aminovaleric acid iodide (5-AVAI) and three alternatives: 4-aminobenzoic acid (PABA), terephthalic acid (TPA) and 3-phosphonopropionic acid (3-HPP). The expected effect in all of them is the increase in the useful life and the reduction of the hysteresis [14]. The 5-AVAI is an additive widely employed in triple mesoscopic solar cells [15, 16]. Increasing efficiencies and stability because of the interaction of its amino and carboxylic groups with halide perovskites has been reported [17–19]. TPA, a frequently used chemical in the petrochemical industry, has previously been incorporated in the perovskite precursor solution, resulting in better moisture resistance and better device thermal and ambient stability [20, 21]. PABA is an amino acid that can block UV radiation and is commonly used in cosmetic products as a sunscreen and it has been reported that can enhance V_{OC} , FF and PCE in PSCs; this additive contributes to improving the morphology in the perovskite film and decreasing the carrier trap states, leading to an improvement of the performance of the devices [22, 23]. Finally, H3PP is a beta amino acid with an amino group and a phosphonic group. This small molecule was used in this work as an organic modifier due to the strong anchoring capability of the phosphonic group.

7.2 Experimental and results

In this section, the three different sets of experimental results including the stability study will be presented. First, the stability study with the spray coating technique with a fullerene acceptor, secondly the study with the O-

IDTBR non-fullerene acceptor and finally the perovskite carbon-based case.

7.2.1 Stability study of the spray organic solar cells with PCBM as fullerene acceptor

Thanks to the results in previous chapters it has been possible to analyze how organic solar cells behave, when using PCBM as an electron acceptor. In some cases, specifically where the active layer is deposited by the spray technique and the control cells by spin coating, a recovery behavior was observed in its electrical parameters. These behavior, as will be seen later, is closely related to the open circuit voltage.

On the other hand, in cases where in addition to the active layer, the ZnO layer was deposited by the spray technique, it is observed that this initial open circuit voltage, in most cases, was low, which coincides with the null improvement of the cells.

In both cases it has been decided to study the stability of the devices without encapsulation with better initial electrical parameters. The selected cells are placed under the solar simulator, measuring their electrical parameters every half hour until there is no measurable current density. After this, the parameters are represented as a function of time. With this study it is possible to obtain a perspective of the operation under continuous lighting stress.

Active layer by horizontal spray coating technique

In this first experiment, only the active layer is deposited by the spray technique. For this, Program 2 (see Chapter 5, Figure 5.2) with different number of scans. A total of five samples have been manufactured, one of control (by spin coating) and four by depositing the active layer. The number of the scans are 6, 8, 10 and 12 respectively. The airbrush deposition conditions are:

- Nitrogen gas pressure: 0.7 bar.
- Distance to the substrate: 9 cm.
- Nozzle opening: 1 turn.
- Substrate temperature: 55°C.

The initial values of the best cells are:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
Control	0.06	0.53	-7.22	1.73	45
AL12scans (A)	0.06	0.53	-4.90	0.79	30
AL12scans (B)	0.06	0.53	-4.43	0.70	30
AL12scans (C)	0.12	0.40	-1.90	0.20	26

Table 7.1: Initial electrical parameters of the control cell and the horizontal AL spray coating devices by Program 2.

An ISOS-L-1 protocol has been used. All the parameters have been characterized, although the two most representative of their behaviour, the J_{SC} and the PCE, will be shown, both normalized to their corresponding maximum value.

Figure 7.1: Evolution of normalized J_{SC} vs time in hours for control and AL12scans cells (Program 2) with their exponential fitted curves.

Figure 7.2: Evolution of normalized PCE over time in hours for control and AL12scans cells (Program 2).

In Figure 7.1, the progression of the short circuit current density follows an exponential law in both techniques (spin and spray), conserving more quantity in the spin coating technique, although both reaching have the same useful life, about 200 hours. It should be noted that two differentiated slopes are observed in both techniques, more marked in those manufactured using the spray technique, mainly due to the lower uniformity of the deposition because it is not completely optimized. This initial marked slope is known as burn-in, an effect well known in the literature, where the devices are capable of losing a large part of their efficiency in the first hours of operation [24].

Regarding the PCE (Figure 7.2) there are clear differences, it is seen that the homogeneity of the measurements in the spin technique is worse, this is possible because the efficiency depends on more factors in addition to the current, such as the open circuit voltage, the which fluctuates due to some recombination effect.

To know in depth, the processes that take part in the degradation, a series of fittings have been made in J_{SC} evolution versus time curves, as shown in Figure 7.1. It is worth emphasizing that linear functions have been also tested but the best fits have been obtained for exponential functions [25]:

A biexponential decay behavior is observed in the normalized J_{SC} of the Control and AL12scanspray (C) cells. From the fit of the experimental curves there is an indication of the coexistence of two processes with different degradation constants (k_1 and k_2):

$$J_{SC} = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \quad (7.1)$$

A single exponential is observed in the others solar cells:

$$J_{SC} = A_1 e^{-k_1 t} \quad (7.2)$$

It should be emphasized that both cases of exponential fit, either indicating double or single processes, provide, respectively for both fabrication systems a good fit for J_{SC} . Both processes are closely related to two fundamental variables, temperature, and humidity, k_1 and k_2 respectively [26–28]. This indicates, if we appreciate in detail the graph that in bi-exponential processes, humidity plays a determining role and gains a greater weight together with temperature, which allows the second phase of degradation, the stable phase, to obtain a greater slope and a higher rate of degradation. On the contrary, in single processes, it is the temperature that acquires all the weight in the degradation, which mainly influences the initial burn-in, allowing a more stable and longer second phase. The values of the degradation constants obtained by the fitted curves are the following:

Name	k_1 (h^{-1})	k_2 (h^{-1})	R^2
Control	0.08	-0.03	0.99
AL12scans (A)	0.07	-	0.99
AL12scans (B)	0.07	-	0.98
AL12scans (C)	0.09	0.01	0.99

Table 7.2: Values of the degradation constants and R^2 values of the fitted curves.

It can be verified that the values of k_2 are lower than those of k_1 , this is so because they are more closely related to humidity than to temperature, as has been seen in the literature (since these are obtained thanks to the Arrhenius equation). This also confirms the most stable phase with the lowest slope.

From the data shown in Figure 7.2 the parameter T_{80} can be calculated (it is an important parameter that measures the time it takes to solar cell to maintain up to 80% of its initial performance). This parameter enables a fair comparison of different cells at one single point in the degradation process. The values of T_{50} (half of its useful life) and T_{20} (practically the end of its life) are also calculated and shown in the Table 7.3. In order to analyze in more in depth the low current obtained by the devices, the series and parallel resistances of the devices where experimentally obtained from fits at certain important points, at the beginning, in T_{80} , T_{50} and T_{20} also shown in Table 7.3.

Name	T ₈₀ (h)	T ₅₀ (h)	T ₂₀ (h)	Initial R _S (Ω/cm^2)	R _S T ₈₀ (Ω/cm^2)	R _S T ₅₀ (Ω/cm^2)	R _S T ₂₀ (Ω/cm^2)	Initial R _{SH} (Ω/cm^2)	R _{SH} T ₈₀ (Ω/cm^2)	R _{SH} T ₅₀ (Ω/cm^2)	R _{SH} T ₂₀ (Ω/cm^2)
Control	1.5	19.5	67	160.7	178.9	216.8	254.5	1.4x10 ⁴	9.7x10 ³	7.4x10 ³	1.6x10 ³
AL12scans (A)	3	7.6	19	696.7	780.7	644.3	530.3	5.3x10 ³	1.2x10 ⁴	1.2x10 ⁴	1.2x10 ⁴
AL12scans (B)	3.1	8	19	795.4	878.1	860.9	1.4x10 ³	4.5x10 ³	1.1x10 ⁴	1.2x10 ⁴	1.4x10 ⁴
AL12scans (C)	4	16.5	73.5	546.8	1.3x10 ³	1.3x10 ³	1.4x10 ³	2.1x10 ³	2.7x10 ³	4.0x10 ³	4.7x10 ³

Table 7.3: Summary of the T₈₀, T₅₀, T₂₀, series resistances and shunt resistances for different lifetimes of the control and AL12scans cells (Program 2).

When considering T_{80} , the cells manufactured using the spray technique deliver longer times, that is, they retain 80% of their initial performance for a longer time. Therefore, it suggests that the so-called burn-in effect is more attenuated than in the control cells manufactured by the spin technique. This contrasts with the parameters T_{50} and T_{20} , if we compare the control cell with those A and B of those manufactured by spray, which indicates a strong stabilization in this second phase of degradation. On the other hand, the spray cell C, the exception of which is the T_{50} value, is the one that manages to obtain a slower and more stable degradation despite being the one with the lowest initial electrical parameters. The high values obtained in the series resistors coincide with the low current values obtained and the filling factors. This may be mainly due to the lack of encapsulation and rapid degradation of the contacts [29]. It should be noted that, in addition, in all cases it is seen how the series resistance follows a linear increase as the cell degrades, as well as the parallel resistance is barely modified, decreasing slightly in some cases. There is only one exception, with the spray cell A, where it is observed that after the initial burn-in, it can recover part of that resistance and entering a more stable phase of degradation.

Active layer and ZnO layer by horizontal spray coating technique

In Chapter 6 the manufacture of organic solar cells has been approached by depositing both layers, active and ZnO, by means of the spray coating technique. After the results of Chapter 5, the focus of attention was focused on the optimization of said ZnO layer in which good initial efficiency results were obtained, reaching 1%. Regarding stability, some problems were found in some cells, which had the problem that they barely lasted a few days even when stored in the dark or did not even function initially. In this experiment, it was decided to evaluate the stability under continuous lighting conditions of the ISOS-L-1 protocol of four samples with four cells each. In each of these samples the ZnO layer and the active layer were deposited by Program 1 (see Chapter 5, Figure 5.1) with 4T periods and 2T periods respectively.

The airbrush conditions are:

- Nitrogen gas pressure: 0.5 bar.
- Distance to the substrate: 11 cm.
- Nozzle opening: 3/4 turn.

The initial electrical parameters after manufacture are shown in Table 7.4:

Name	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	PCE (%)	FF (%)
ZA4T (E)	0.09	0.33	-3.11	0.34	32
ZA4T (F)	0.09	0.27	-2.68	0.27	29
ZA4T (G)	0.09	0.33	-2.45	0.35	33
ZA4T (H)	0.09	0.40	-2.50	0.24	24

Table 7.4: Initial electrical parameters for the ZA4T spray organic solar cells by Program 1.

Only one of the samples has given results above 0.1% of PCE to be able to carry out a degradation study. As in the active layer experiment, after these results are placed under the solar simulator and measured every half hour. Normalized J_{SC} and PCE are shown in Figure 7.3 and 7.4:

Figure 7.3: Evolution of normalized J_{SC} over time in hours for ZA4T cells (Program 1) with their exponential fitted curves.

Figure 7.4: Evolution of normalized PCE over time in hours for ZA4T cells by Program 1.

Although the initial values obtained in the cells were low, they had a useful lifetime of about 55 hours in total for the ZA4T (F) cell and about 20 hours for the H cell. This low stability has been observed as mentioned earlier at the beginning of the experiment, where most of the cells either did not work initially or after a few days in storage they stopped working, and these results reinforce the theory that the ZnO layer should be optimized for this system. The evolution of J_{SC} and PCE in Figures 7.3 and 7.4 is quite similar, somewhat different from what happened in the active layer, being homogeneous and continuous in both Figures.

In the same way, the adjustments of the J_{SC} curves (Figure 7.3) have been carried out to analyze in depth which parameters directly affect this rapid degradation. For this case, we found a bi-exponential behavior in the three cells. The calculated parameters being those shown in Table 7.5:

Name	k_1 (h^{-1})	k_2 (h^{-1})	R^2
ZA4T (F)	0.66	0.11	0.99
ZA4T (G)	0.49	0.10	0.99
ZA4T (H)	1.05	0.19	0.99

Table 7.5: Degradation parameters of the fitted curves for the ZA4T spray cells by Program 1.

In Table 7.5, in all cases, all the main effect of the degradation (where we find the initial steepest slope, called the burn-in effect) depends on the constant k_1 , with a value even of 1 in the H cell, the one with the least stability. On the other hand, constant k_2 has a significant influence on all of them, being again the highest corresponding to the H cell. This constant k_2 , It is related to the humidity of the environment and it has a greater influence in the cases where the ZnO layer is deposited by spray due to its heterogeneity that together with the desorption of oxygen from the layer during UV excitation [24].

From Figure 7.4, the values of T_{80} , T_{50} y T_{20} :

Name	T_{80} (h)	T_{50} (h)	T_{20} (h)
ZA4T (F)	1.2	2.6	6.6
ZA4T (G)	0.9	2.6	5.6
ZA4T (H)	1.2	2.6	5.6

Table 7.6: Summary of the T_{80} , T_{50} and T_{20} for the ZA4T spray cells by Program 1.

The values obtained are of the order of just one hour for the T_{80} , which is not comparable to other experiments carried out in storage in air under ambient conditions where they report a T_{80} of between 30 and 40 days . If, on the other hand, they are compared with results obtained in the deposition only by spray of the active layer, although the T_{80} values are close to those shown here (similar burn-in effect), the complete stability of the cells is far from the obtained in said cells.

7.2.2 Stability study of organic solar cells with O-IDTBR as non-fullerene acceptor

In this case, a detailed stability study of flexible fully roll-to-roll (R2R) processed ITO-free organic solar cells using three fast aging tests comparing plastic and glass encapsulation. The devices were tested under different conditions: a weathering chamber with real conditions close to ISOS-LT-1, ISOS-T-3 using a thermal chamber and ISOS-L-1 conditions (a continuous lighting system under solar simulator). This work was carried out in collaboration with the research group of Prof. Jens Wenzel Andreasen at Technical University of Denmark (DTU). The results were compared with previously reported stability studies for similar cells [26, 30–32].

Experimental and results

OSCs were fabricated on flexible substrates in open-air using R2R compatible processes. The Polyethylene terephthalate (PET) substrate has printed finger-like silver electrodes and PEDOT: PSS as a front electrode followed by a thin ZnO layer as the electron transport layer (ETL) [33]. The bulk heterojunction photoactive layer is formed by the blend of P3HT acting as donor and the non-fullerene O-IDTBR material as acceptor. The molecular structure of the donor and acceptor materials is illustrated in Figure 7.5(a) and (b). Using previously optimized parameters [34], the ink with the photoactive materials was prepared, with a concentration of 40 mg/ml in a 1:1 ratio in dichlorobenzene (DCB) with 5% (v/v) of 4-bromoanisole (BrA) as additive. The active layer ink was slot-die coated at 60°C, with a speed of 0.6 m/min and a flow rate of 0.08 mL/min, resulting in a film with a dry thickness of 480 nm. A layer of PEDOT: PSS (Heareus Clevis FET) was then slot-die coated on top of the active layer as hole transport layer (HTL). Heat curing silver paste (DuPont 5025) was used to flexographically print the finger-like back electrode. The schematic structure of the inverted architecture OSCs in this work is shown in Figure 7.5(c).

Figure 7.5: The molecular structure of the components of the active layer: (a) P3HT acting as donor (b) in combination with the non-fullerene acceptor O-IDTBR. (c) The schematic structure of the flexible ITO-free solar cells.

The substrate is cut into pieces with a 1 cm² active area. Finally, and unlike the cells manufactured by spray, these are encapsulated in the form of a sandwich, using two materials, plastic, and glass. A layer of UV-cured epoxy glue is applied on both sides.

For the optical characterization, QEX10 system (PV Measurements Inc.) were used for external quantum efficiency (EQE) and optical transmittance (Figure 7.6). A solar simulator (Figure 7.7) with Keithley 2400 source-meter unit connected under controlled temperature and AM1.5G, 1000 W/m² illumination, calibrated with a monocrystalline silicon reference cell certified by Fraunhofer for the electrical characterization. The EQE and transmittance were measured every 24h/48h from 300 nm to 900nm (5 nm step size) calibrated by a silicon photodiode. The continuous monitoring in EQE and transmittance were only performed for the ISOS-LT-1 and ISOS-T-3.

Figure 7.6: QEX10 system for EQE and optical transmittance measurements.

Figure 7.7: Solar simulator with temperature substrate control to electrical characterization and ISOS-L-1 stability study.

Three different degradation studies have been carried out with three different systems. The ISOS-L-1 is a continuous illumination test at constant

temperature, 35°C in this case, using the same solar simulator of the electrical characterization. For ISOS-LT-1 a Q-Sun (Figure 7.8) system was used. Q-Sun is designed to create real weather and climatic conditions like solar irradiation, ambient temperature, humidity, and even rain. In this case, the illumination is carried out with Xenon lamps that mimic the solar spectrum including the UV part to further increase degradation effects. To simulate a real day and to have a fast degradation process, a cycle of 12 hours, repeating it twice during a whole day was created. The conditions try to reproduce a sunrise and sunset with low irradiance and medium humidity (Step 1 and 3), a noon with high irradiance (Step 2) and a night with high humidity and zero irradiance (Step 4). The details of the cycle are described in Table 7.7 and Figure 7.10.

Figure 7.8: Q-Sun weathering chamber used for the ISOS-LT-1 accelerated degradation study.

ISOS-LT-1	Duration (h)	Conditions	Temperature (°C)	Humidity (%)	Irradiance (kW/m ²)
Step 1	2	Light + humidity	40	60	0.55
Step 2	4	Light	60	45	1
Step 3	2	Light	40	60	0.55
Step 4	4	Dark + humidity	38	80	0

Table 7.7: Cycle of a real day simulation using the Q-Sun chamber, complying with ISOS-LT-1 protocol.

The ISOS-T-3 was carried out by Thermotron system (Figure 7.9). This chamber is designed to carry out accelerated degradation processes by applying very harsh weather conditions. The cycle is divided in 10 steps total duration of 6 h and in full darkness, and it is reproduced four times in 24 h. The cycle alternates between -40°C to 85°C including intermediate temperatures using different ramp rates from $0.7^{\circ}\text{C}/\text{min}$ to $3^{\circ}\text{C}/\text{min}$ as indicated in Table 7.8 and Figure 7.10.

Figure 7.9: Thermotron chamber used for the ISOS-T-3 thermal stress simulation.

ISOS-LT-1	Duration (min)	Ramp rate ($^{\circ}\text{C}/\text{min}$)	Temperature ($^{\circ}\text{C}$)	Humidity (%)
Step 1	40	1.4	-40	Non controlled
Step 2	15	0	-40	Non controlled
Step 3	65	0.7	10	55
Step 4	25	3.1	85	55
Step 5	15	0	85	55
Step 6	25	3.1	10	Non controlled
Step 7	65	0.7	-40	Non controlled
Step 8	15	0	-40	Non controlled
Step 9	65	1	25	Non controlled
Step 10	30	0	25	Non controlled

Table 7.8: Cycle of thermal stress simulation using the Thermotron system, complying with ISOS-T-3 protocol.

Figure 7.10: ISOS-LT-1 weathering chamber cycle (a) and ISOS-T3 thermal chamber cycle (b). Temperature and relative humidity.

The main initial parameters are presented in Table 7.9. The V_{OC} , J_{SC} , PCE and FF depending on the kind of encapsulation and the time T_{80} , is also included in the last column of Table 7.9.

ISOS	Encapsulation	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)	T_{80} (h)
ISOS-LT-1	Glass	0.7	7.6	61	3.3	14.5
	Plastic	0.7	6.0	59	2.5	12.0
ISOS-T-3	Glass	0.7	5.7	46	1.9	86.5
	Plastic	0.7	6.0	58	2.5	78.0
ISOS-L-1	Glass	0.7	8.3	56	3.4	34.7
	Plastic	0.7	6.6	59	2.8	12.0

Table 7.9: Initial electrical parameters of the solar cells and T_{80} for the three ISOS-LT-1, T-3, and L-1 for devices with 1 cm² active area.

In Table 7.9, it is observed that in two of the three systems (ISOS-LT-1 and ISOS-T-3), in both encapsulations, the T_{80} values show a similar behav-

ior with a minimum difference of hours between both values. On the contrary, in the ISOS-L-1 the difference is significant, being the value in glass almost three times that in plastic, this indicates that the short-term behavior is slightly better in the encapsulation in glass, as well as the rest of electrical parameters. On the other hand, in Figure 7.11(a), for the ISOS-LT-1 the behavior is similar in both encapsulations, the same thing that happened with their T_{80} values. For the ISOS-T-3, in Figure 7.11(b), although initially the T_{80} was slightly superior in glass than in plastic, the long-term behavior for plastic (<700h) is better than for glass (<400h). It might be because the coefficient of thermal expansion of the plastic encapsulants is closer to that of the OSCs, with a stronger influence during mid-life of the cells. Finally, in the ISOS-L-1 (Figure 7.11(c)) the behavior follows the same trend as the initial T_{80} shown, being better in glass than in plastic.

Figure 7.11: Initial and aged J-V curves in (a) Q-Sun chamber (ISOS-LT-1), (b) Thermal chamber (ISOS-T-3) and (c) under solar simulator under controlled temperature (ISOS-L-1).

In general, the open circuit voltage (V_{OC}), do not follow a clear tendency in the different degradation experiments, Figures 7.12(a), 7.13(a) and 7.14(a), since V_{OC} is not a reliable parameter to study the degradation processes. The decrease of the PCE and J_{SC} (Figures 7.12, 7.13 and 7.14) is strong for all OSC, the latter indicates a loss of photo generated carriers. The fill factor (FF) has also decreased (Figures 12b, 13b and 14b), in coincidence with a simultaneous increment in the series resistance (Table 7.10). This is due to contact degradation and reduction of shunt resistance (indicative of increased bulk recombination) produced by the degradation of the active layer by exposure to oxygen due to a poorer encapsulation [29]. The loss of photo current between measurements is more pronounced in the ISOS-LT-1 test (weathering chamber) than in the ISOS-T-3 test (thermal chamber); probably due to the harsher lighting and humidity stress cycles received.

ISOS	Encapsulation	Initial R_S (Ω/cm^2)	R_S T_{80} (Ω/cm^2)	R_S T_{50} (Ω/cm^2)	R_S T_{20} (Ω/cm^2)	Initial R_{SH} (Ω/cm^2)	R_{SH} T_{80} (Ω/cm^2)	R_{SH} T_{50} (Ω/cm^2)	R_{SH} T_{20} (Ω/cm^2)
ISOS-LT-1	Glass	9.83	29.60	50.36	70.81	4100	3575	2296	1852
	Plastic	24.06	35.08	45.24	102.71	3290	3763	3278	2229
ISOS-T-3	Glass	58.46	81.31	135.55	76.39	4330	2865	1930	1079
	Plastic	23.59	32.90	40.19	N/A	2370	4265	4053	N/A
ISOS-L-1	Glass	18.55	32.34	82.24	58.77	3550	3299	2605	2275
	Plastic	19.60	37.17	58.77	112.99	2948	3019	2275	1238

Table 7.10: Evolution of the series and shunt resistances at different devices lifetime.

Figure 7.12: Evolution of the electrical parameters vs time (glass and plastic encapsulation) for the ISOS-LT-1 test (Q-Sun). For J_{SC} and PCE, exponential fitting is shown.

Figure 7.12 shows the evolution of the key photovoltaic parameters obtained for the ISOS-LT-1 test (weathering chamber). They provide detailed information about the degradation process of the OSCs and the influence of the different encapsulation materials. PCE is dependent on the evolution of other parameters such as V_{OC} , J_{SC} and FF. The values shown in the graphs have been normalized to the maximum initial value. The V_{OC} and the FF behavior have a clear link to the series and shunt resistances evolution induced by the degradation experiment as it mentioned before. The initial drop in PCE suffers the so-called "burn in" effect, which makes it rapidly and drastically decrease, only to stabilize later. This is more pronounced in the glass encapsulation device, meaning that this might be caused by ingress of oxygen and moisture through the edges of samples where the two glass encapsulants are glued by epoxy. In fact, the rigidity of the glass, combined with the

manual processing using clamps may explain a different sealing along the four edges due to unbalanced pressure, which results in a poorer sealing in one of the edges. The plastic encapsulation is carried out using a laminating machine, thus providing a more uniform sealing along all the edges of the sample. In all the cells, the degradation curves of the PCE and J_{SC} are fitted using exponential functions (single or biexponential), as shown in previous experiments in this chapter, however only the fittings of J_{SC} are analyzed in detail, since this parameter gives better information of the degradation mechanism than PCE.

The exponential models obtained are those shown in Eq. 7.1 and 7.2 in previous experiments. For the ISOS-LT-1 (Figure 7.12), a single exponential behavior is observed for both encapsulations. This points to temperature as the main degradation mechanism [26–28].

Figure 7.13: Evolution of the electrical parameters vs time (glass and plastic encapsulation) for ISOS-T-3 (Thermotron). For J_{SC} and PCE, exponential fittings are shown.

In Figure 7.13, the ISOS-T-3 test results shown a biexponential fit for plastic and a single exponential for glass (Figure 7.13(c)) is used for this system, showing in this case two different mechanisms. As mentioned earlier in this work, these two mechanisms are closely linked to temperature and humidity. In contrast, the plastic device shows a better stability than glass device reaching up 700 hours. This behavior seems to indicate that the plastic encapsulation protects the device from getting less oxygen and moisture from the environment, better thermal cycling (from -40°C to 85°C) and constant manipulation resilience. In this case, the first exponential degradation process is followed by a second, much slower process that can be attributed to the effect of UV light, in contrast to the first process, due to ambient conditions (ingress of moisture and oxygen into the cell).

Figure 7.14: Evolution of the electrical parameters vs time (glass and plastic encapsulation) for the continuous illumination ISOS L-1 test. For J_{sc} and PCE exponential fittings are shown.

In the last case, the evolution of photovoltaic parameters for ISOS-L-1 degradation test (continuous illumination) are shown in Figure 7.14. Figure 7.14(c) and 7.14(d) shows a similarity in the evolution of the J_{SC} and the PCE. The J_{SC} shows two distinct zones, with a very steep slope at the beginning (high initial degradation due to burn-in) and a stabilized second phase with a lower slope for both plastic and glass. While the PCE decreases constantly until 60% of its initial value for the plastic case.

It should be emphasized that both cases of exponential fit indicating double or single processes, provide respectively, a good fit for J_{SC} and PCE for glass or plastic encapsulation in the ISOS-L-1 tests. In every degradation test that was carried out, glass encapsulation achieved longer lifetimes for the OSCs except for the thermal chamber (ISOS-T-3) where plastic is a better choice to extend the OSCs working life due to the extreme temperatures of the test. The degradation constants k_1 and k_2 obtained from the J_{SC} fits for all tests are shown in Table 7.11.

ISOS	k_1 (h ⁻¹)	k_2 (h ⁻¹)	R^2
ISOS-LT-1 Glass	0.006	-	0.98
ISOS-LT-1 Plastic	0.005	-	0.96
ISOS-T-3 Glass	0.002	-	0.92
ISOS-T-3 Plastic	0.03	0.001	0.91
ISOS-L-1 Glass	0.003	-	0.99
ISOS-L-1 Plastic	0.01	-	0.99

Table 7.11: Degradation constants obtained from the exponential fit for glass and plastic in different degradation system.

As mentioned above, these degradation constants are closely related to fundamental factors in stability processes such as temperature (k_1) and humidity (k_2). The degradation rates included in Table 7.11 are similar to those reported by Gevorgyan et al. when the cells are encapsulated, and the slower degradation process is attributed to the effect of UV light [26]. According to Table 5.11, despite the fact that ISOS-LT-1 has a stage of high humidity in darkness, it does not seem decisive for the rapid degradation of the samples, since it is more strongly dependent on the temperature reached due to the different irradiances tested are predominant. On the other hand, in the ISOS-T-3, where the thermal stress is very strong, k_1 is lower, also showing a very small k_2 in the plastic encapsulation system, which indicates that it is probably that some moisture due to condensation between the stages of extreme cold and heat has remained inside the structures due to a break in the encapsulation. Finally, when continuous lighting ISOS-L-1 test is carried

out, with the system exposed to the environment (where temperature is controlled, but humidity is not), a single exponential behavior is recovered. On the other hand, the plastic encapsulation sample presents better sealing but shows the highest k_1 .

Figure 7.15: Evolution of the EQE vs time for ISOS-LT-1 for both encapsulations (glass and plastic respectively).

Figure 7.16: Evolution of the EQE vs time for ISOS-T-3 for both encapsulations (glass and plastic respectively).

To analyze in detail the different behavior of the encapsulations, further wavelength-dependent measurements have been carried out to explore photoelectronic properties of the OSCs and compare the effect of extrinsic degradation agents [35], such as photo oxidation and possible oxygen and moisture

ingress when using two different encapsulants. Figures 7.15 and 7.16 show the evolution of the external quantum efficiency (EQE) at different stages of the degradation ISOS-LT-1 and ISOS-T-3 tests. Considering that the thickness of the absorber layer is the same in all cases, during the tests P3HT degrades faster than O-IDTBR. As seen in Figure 7.15(a), for glass encapsulation and ISOS LT-1 test, the EQE photo current of the spectral region where P3HT is expected to contribute (450-650 nm) decrease faster than the EQE photo current at the O-IDTBR main contribution region (650-800 nm) [7]. It indicates that in glass encapsulation P3HT degrades faster than O-IDTBR during the ISOS-LT-1 test. In plastic encapsulation (Figure 7.15(b)), the photo current decreases more uniformly over the spectral range and time. In Figure 7.15 and 7.16 the local maximum around 420 nm corresponds mainly to the photo current contribution of the secondary absorption peak of O-IDTBR located at 400 nm that in blend with P3HT shifts to 420 nm [34]. In Figure 7.16 the EQE photo current at the O-IDTBR contribution regions decrease at a slower pace than the photocurrent at the P3HT region of contribution. It might be indicative of micro structural modifications and possible phase separation for which further studies are necessary (see Figure 7.17). As shown before during the ISOS-T-3 experiments, the plastic encapsulation protects better the solar cells from the environment, allowing the continuation of the experiment for more than 700 h (Figure 7.11(b) with a stable photocurrent ($\sim 5 \text{ mA/cm}^2$) and V_{OC} ($\sim 0.55 \text{ V}$). Figure 7.15 and 7.16 also verify that materials such as O-IDTBR can reduce the burn-in effect produced at the beginning of cell operation, when compared to cells with materials such as PCBM in the active layer. Additionally, the PEDOT: PSS is also degraded by moisture since it is a highly hygroscopic material and ingress of moisture in the cell might have happened, most probably through the edges of the sample, thus contributing to the degradation of charge extraction layer.

Figure 7.17: Normalized to maximum EQE values for ISOS-LT-1 glass device (a), plastic device (b), ISOS-T-3 glass device (c) and plastic device (d).

Losses in photo current are also possibly due to degradation of the electrodes or the encapsulant, which will affect all internal photo generated current independently of absorption wavelength. The series resistance of the devices increases during the degradation experiments in almost all combinations of encapsulation and degradation test protocols. The increment in R_s is an indication of internal deterioration of the layers and interfaces, complemented by a probable surface recombination in the electrode/transport layer interfaces, which in this case contributes to the lowering of the shunt resistance. This last point is confirmed by the increase in the reverse saturation current of the solar cell as seen in the dark current before and after degradation of the solar cell shown in Figure 7.18.

Figure 7.18: Initial and final dark J-V curves for ISOS-LT-1 test with glass encapsulation.

(a)

(b)

Figure 7.19: Evolution of the transmittance vs time for ISOS-LT-1 for both encapsulations (glass and plastic respectively).

Figure 7.20: Evolution of the transmittance vs time for ISOS-T-3 for both encapsulations (glass and plastic respectively).

Figures 7.19 and 7.20 show the transmittance evolution over time for both encapsulation materials. For ISOS-LT-1 degradation test (Figure 7.19), external factors influence the degradation of the encapsulation. Different irradiation times produce photon losses in the transmittance of the Glass/Epoxy/Glass encapsulation type, especially in the visible region, where some fluctuations can be seen. For the plastic encapsulation (Figure 19b), after a minor change in transmittance in the first hours of illumination, the signal remains constant up to more than 700 h. On the other hand, in the ISOS-T-3 shown in Figure 7.20, the differences between one encapsulation and another are less noticeable, specifically keeping the plastic practically intact. Nevertheless, both experiments indicate that the plastic encapsulation provides better protection against environmental degradation agents. This fact may be mainly due to the encapsulation method, in which for the case of plastic, both sides

are laminated, passing the OSCs between two pressing rolls while for glass the sealing is done with tweezers holding the two glass slides resulting in a probably less homogeneous sealing.

7.2.3 Stability study for carbon-based mesoporous perovskite solar cells with molecular additives

In this study, we present results which build upon a large amount of previous published work on molecular additives. We have used a carbon-based HTL-free architecture with the addition of a ZrO_2 scaffold layer. The fabricated cells provide a range of good efficiencies ($>10\%$ in the best case) with large lifetimes for one of the additives that has been studied in more detail (5-amino valeric acid iodide, 5-AVAI). Then, other additives have been tested with the same architectures and optimized thickness of the layers and additive concentration, although with lower resulting PCE and lifetimes. This work was carried out in collaboration with the research group of Prof. Mónica Lira-Cantú at Catalan Centre for Nanoscience and Nanotechnology (ICN2).

Experimental and results

Hybrid perovskite solar cells were fabricated following a standard procedure [36, 37]. The active layer was the benchmark methyl-ammonium lead iodide (MAPI) perovskite structure. A n-type TiO_2 electron transporting layer was deposited on the transparent conducting substrate, leading to a n-i-p structure, and therefore the architecture of the cell was normal (also called regular or standard) [38]. Metal oxide electron transporting layers were screen-printed on top of a fluorine doped tin oxide (FTO), CVD coated glass substrate, with sheet resistance $R_s \sim 8 \Omega/\text{sq}$ and total transmission around 80% in the 400-800 nm band (SOLEMS TEC 7/2.2). A first compact c- TiO_2 layer was deposited by spray pyrolysis from a 10% molar Titanium di-isopropoxide bis-acetylacetonate (Sigma Aldrich) solution in isopropyl alcohol dried and thermally annealed at 450°C for 10 min in air. The following layers were deposited by screen printing. The pastes used for screen printing were TiO_2 paste DSL 30NR-D (Dyesol), ZrO_2 paste Zr-Nanoxide ZT/SP (Solaronix, particle size 20-40 nm, at 18% wt. in suspension with terpineol and other organic binders). These structures were covered by a screen-printed carbon-based layer (using carbon paste C2150317D3, Gwent Group), delivering a structure called the "shell". Different threads were used in a commercial SA111576 Uniprint PM screen printer, with aperture of $40 \mu\text{m}$ for the metal oxide pastes and $90 \mu\text{m}$ for the carbon paste. The screen-printed layers were considered mesoporous after a thermal annealing process of 30

min at 450°C. This shell was then infiltrated by spin-coating (the so-called 'single step' method), with the perovskite solution prepared by using the usual precursors lead iodide PbI_2 (purity 99%, TCI), MAI $\text{CH}_3\text{NH}_3\text{I}$ (purity 98%, Dyesol) dissolved in γ -butyrolactone (GBL, purity 99%, Sigma Aldrich) and a final back hole collecting electrode was again screen-printed using conductive silver paste C2081126P2 (Gwent Group). A schematic structure of the band gaps, conduction and valence band (for the semiconducting materials) and work function for the carbon and metal electrodes are presented in Figure 7.21. Ideally, the MAPI + additive active layer infiltrates the carbon and the mesoporous layers of ZrO_2 and TiO_2 . The ZrO_2 layer prevents the electrical short-circuit between the TiO_2 electron transporting layer and the carbon scaffold, which is acting as hole collecting layer (and connected to the Ag electrode). This reference structure was modified with the inclusion of different additives into the active layer: 5-AVAI, TPA, PABA and H3PP (molecular structures shown in Figure 7.21(b)). In all cases, additives were mixed at 3% molar concentration with the MAPI perovskite precursors before infiltration. The same solvent GBL was used in all cases, except for TPA, where dimethyl formalimide anhydrous (DMF, purity 99% Sigma Aldrich) was used. All molecular additives were included in the bulk of the active layer during the solution stage of MAPI preparation. Four kinds of samples were tested, as described in Table 7.12, the first group of three samples (A, B, C) all contained 5-AVAI but differed in the concentration of 5-AVAI added to the solution precursor of the MAPI active layer. The optimum weight concentration that delivered the best PCE results for the 5-AVAI additive (3% molar) was used as the optimal concentration for the other additives.

Cells	Additive	Scan	J_{SC} mA/cm ²	V_{oc} V	FF %	PCE %	HF ₁ mW/cm ²	HF ₂ mW/cm ²
A	5-AVAI (1%)	F	20.6 ± 1.5	0.73 ± 0.06	38 ± 6	5.7 ± 0.2	3.42	1.73
		B	24 ± 2	0.76 ± 0.06	59 ± 7	10.6 ± 1.4		
B	5-AVAI (5%)	F	12.9 ± 1.3	0.67 ± 0.07	27 ± 4	2.3 ± 0.8	6.68	4.33
		B	25 ± 3	0.70 ± 0.07	54 ± 6	9.3 ± 0.9		
C	5-AVAI (3%)	F	12.3 ± 1.7	0.60 ± 0.06	24 ± 5	1.7 ± 0.7	7.69	4.50
		B	26 ± 3	0.76 ± 0.06	57 ± 7	10.9 ± 1.7		
D	PABA	F	4.5 ± 0.4	0.70 ± 0.06	46 ± 7	1.43 ± 0.12	3.79	2.63
		B	9.7 ± 0.5	0.77 ± 0.07	69 ± 10	2.5 ± 0.7		
E	TPA	F	11 ± 2	0.70 ± 0.06	42 ± 5	3.3 ± 0.9	¹ -2.97	¹ -1.89
		B	8 ± 2	0.70 ± 0.07	46 ± 6	2.7 ± 0.9		
F	H3PP	F	2.8 ± 0.4	0.63 ± 0.06	51 ± 9	0.90 ± 0.10	1.16	0.81
		B	3.6 ± 0.4	0.70 ± 0.07	55 ± 9	1.4 ± 0.2		

Table 7.12: Electrical parameters of the perovskite solar cells calculated as an average of 24 cells of each group. Scan column indicates forward (F) or backwards (B) sweep of voltage during the J-V measurement. HF₁ and HF₂ are the hysteresis factors, as defined in Equation 7.3 and 7.4

¹ This cell presented reversed hysteresis when compared to the other cells.

Figure 7.21: (A) Schematic structure of band gaps and work function of the different layers of the solar cells; (B) Molecular structure of the four additives used in the methyl-amino lead-iodide (MAPI) layer: 5-amino-valeric acid iodide (5-AVAI), terephthalic acid (TPA), para-4-aminobenzoic acid (PABA) and 3-phosphono-propionic acid (H3PP); (C) SEM image of the shell used to infiltrate the MAPI, showing the layers of compact and mesoporous TiO₂, mesoporous ZrO₂ and carbon; (D) XRD of anatase TiO₂ at different temperatures.

The structure of the samples was characterized by a transversal scanning electron microscopy image where the thickness of the different layers was measured (Figure 7.21(C)). The thickness of the layers constituting the infiltrated shell are: 600 nm mp-TiO₂; 2 μm mp-ZrO₂ and 10 μm carbon. An X-ray diffractogram of the TiO₂ layer was measured at different temperatures, showing that crystallinity is achieved after 450°C thermal annealing; the diffractogram was fitted to reference code 00-004-0477 demonstrating a tetragonal anatase phase (I41/amd space group) as shown in Figure 7.21(D). Current-voltage (I-V) characteristics of the unencapsulated samples were measured by applying a voltage bias between the electrodes and sweeping the voltage between -1V to +1V (forward) and from +1V to -1V (backward) in order to measure the hysteresis appearing in most samples. The sweeping procedure was carried out always at the same voltage scan rate of 0.06 V/s. Voltage was applied with a programmable voltage source Keithley Mod. 230 and current was measured with an electrometer Keithley Mod. 6514. Since I-V curves were measured both forward and reverse at an initial stage, the hysteresis is obtained and quantified as the difference between the areas of

integrated current from $V = 0$ to $V = V_{OC}$ for both traces. This method provides a 'hysteresis factor' (HF_1) defined as:

$$HF_1 = \int_0^{V_{OC}} (I_{backward}(V) - I_{forward}(V))dV \quad (7.3)$$

Which provides a value slightly different when compared with the difference of delivered power at MPP (maximum power point) between forward and backward bias, which can be defined as a second, single point, 'hysteresis factor' (HF_2) defined as:

$$HF_2 = P_{mpp,backward} - P_{mpp,forward} \quad (7.4)$$

both HF_1 and HF_2 are included in Table 7.12 with other standard parameters.

For the long-term degradation experiments, I-V measurements were carried out for 1000 h (one every hour and only in backward bias between +1 V and -1 V), while the samples were kept polarized at maximum power point until a new I-V curve was measured (this is in line with ISOS-L1 and ISOS-V3 protocols [5]). This protocol was applied by using LabView-based software developed in our laboratory. The I-V characteristics were measured under ambient atmosphere (air), with stable laboratory temperature (25°C) and relative humidity (40% $\pm$ 2%). The illumination was provided by an ABET AM1.5 Class AAA solar simulator, kept at constant irradiance of 1 kW/m² for 1000 h (a mask was used guaranteeing that active area of the cell was 7.1 mm²). This time under 1 Sun irradiance is equivalent to several months under ambient conditions depending on the particular geographical location for an outdoor experiment, in particular for Southeast Spain with insolation values of more than 1900 kWh/m² per year in some locations, the degradation experiment can be considered to an equivalent outdoor illumination of more than six months. The experiment is not equivalent to a full outdoor experiment, since irradiance variations and temperature cycling (during day and night) as well as possible rain, wind, dust, and other effects were not taken into consideration. Electrical parameters (short circuit current (I_{SC}), open circuit voltage (V_{OC}) and power conversion efficiency (PCE)) of each of the one thousand I-V curves measured for each sample during each degradation experiment were obtained; additionally, maximum power point current and voltage (IMPP and VMPP) and power delivered at MPP (PMPP) were also recorded for backward bias, which allowed us to calculate the filling factor (FF) for the backward branch of the J-V curve.

The results are organized in two parts: the first one corresponds to initial sample characterization and hysteresis analysis for the six kinds of samples,

of which 24 samples were prepared, thus providing some statistics. Best cell values are provided in the tables. The long-term degradation study is presented in the second part and was carried out in each case with the best cell of each kind that was identified by the initial experiment.

Figure 22 shows the best cell results for the initial characterization by current density-voltage (J-V) and power density-voltage (P-V) curves of the MAPI samples with 5-AVAI additive at different weight concentration: 1% (A), 5% (B) and 3% (C). The grouping rationale has been applied after the long-term experiment since three samples delivered a much shorter lifetime than the others. The hysteresis shown by all samples is large, with the exception of one cell (A), although as can be seen in the second part, this did not translated into the longest lifetime, which was obtained by cell C, which has a significant hysteresis.

Figure 7.22: Current density-voltage (J-V) (a) and power density-voltage (P-V) (b) curves of the best MAPI perovskite solar cell with 5-AVAI additives, with different weight concentrations: 1% (A), 5% (B) and 3% (C), all of them showing hysteresis between the forward (slashed line) and backward (continuous lines) sweep.

In figure 7.22, the J-V and P-V curves for the PABA (D), TPA (E) and H3PP (F) additives are shown. In this case, the initial power efficiency was lower and hysteresis larger than in the previous 5-AVAI group. Furthermore, cell E (TPA) operated in a different way since the larger power was delivered in forward sweep (as illustrated by the minus sign in the calculated hysteresis factors shown in Table 7.12).

Figure 7.23: Current density-voltage (J - V) (a) and power density-voltage (P - V) (b) curves of the best MAPI perovskite solar cell with 5-AVAI additives, with different weight concentrations: 1% (A), 5% (B) and 3% (C), all of them showing hysteresis between the forward (slashed line) and backward (continuous lines) sweep.

The average electrical parameters of the six groups of samples (24 samples per group) are included in Table 7.12, which is presented to emphasize the rationale guiding the sample preparation strategy: once the 'shell' was optimized (thickness of respective layers as described above); then, the concentration of 5-AVAI, the first additive used, was explored, starting with a low concentration (1%, cell A), then 5% (cell B), then higher concentrations which all delivered failed cells, and back to 3% (cell C) which delivered the best PCE and longer lifetimes. Based on this, the same concentration was applied to the other additives to compare all of them at the same weight concentration (3%, cells D, E and F).

All samples suffered a degradation during the long-term experiment, three of the samples showing a rapid degradation after 100h (D, E, F) while the other three (A, B, C) showing much longer lifetimes. Loss in photo current and power conversion efficiency in this case was only appreciated when the experiment was carried out up to 1000h. In A, B, C, D and F samples, the J - V curves were recorded by sweeping the voltage backwards (or reverse), that is from 1V to -1V with a scan rate of 0.06 V/s. For sample E, the voltage was applied forwards (from -1V to 1V) at the same scan rate. One full J - V curve was recorded every hour during the 1000h experiment; between two sweeps, the samples were kept un-der illumination at maximum power point (operating conditions). Figure 7.24 shows the evolution of short circuit

current (J_{SC}) and power conversion efficiency (PCE). The logarithmic scale in the current axis emphasizes the evolution and also demonstrates that a non-exponential trend is followed.

Figure 7.24: Short circuit current (J_{SC} , (a) and (b)) and power conversion efficiency (PCE, (c) and (d)) of the six samples. Logarithmic axis for short circuit current emphasizes the rapid drop for the set of D, E, F samples (up to 250 h) while the A, B, C had much longer lifetimes, extended more than 1000 h. For better visualization, left figures show the first 250 h of the experiments while right figures show the complete experiments.

To quantify the lifetime of the cells and to compare the different additives with other published data, standard parameters were used. From the PCE time evolutions shown in Figure 7.24, T_{80} , T_{50} and T_{20} could be extracted (shown in Table 7.13). These parameters are defined as the time when PCE has been reduced to 80%, 50% and 20% of its initial value and provide a single point parameter to compare lifetimes of the devices. The detailed trend of the full curve has not been fitted since no clear exponential trend was observed. Although a kink in samples with non optimal 5-AVAI weight concentrations was observed, this is still not fully understood but points out that obtaining the optimal concentration (in this case, around 3%) is important not only because it extends the lifetime but also because it qualitatively changes the pattern of degradation.

Cell	Additive	T_{80} (h)	T_{50} (h)	T_{20} (h)
A	5-AVAI (1%)	142	328	448
B	5-AVAI (5%)	125	375	544
C	5-AVAI (3%)	550	801	955
D	PABA	0.6	16	48
E	TPA	0.6	1.8	12
F	H3PP	13	21	36

Table 7.13: Lifetime parameters extracted from degradation trends shown in Figure 7.24. T_X is the time at which power conversion efficiency is X% of the initial nominal PCE.

The best lifetime values were found for cell C (3% wt 5-AVAI additive) with $T_{80} = 550$ h. As can be observed in Figure 7.24 and Table 7.13, cells with 5-AVAI showed much better performance than with the other additives. The results for 1% and 5% 5-AVAI additive were similar in terms of T_{80} , with cell B (5% 5-AVAI additive) presenting slightly better behavior than the cell with lower 5-AVAI content. The qualitative change of degradation mechanism commented above remains unclear, since it happens both for higher and lower concentrations than the optimal one. A benchmark infiltrated carbon-based mesoporous perovskite solar cell is the one published by Mei et al. with the following parameters for the optimized MAPbI₃ active layer (without AVAI) a J_{SC} of 13.9 mA/cm², a V_{OC} of 855 mV, and a FF of 61%, yielding a PCE of 7.2%; the inclusion of AVAI raised the photo current up to 22.8 mA/cm², V_{OC} was 858 mV, and FF = 66%, with an improvement of PCE up to 12.84% [17]. The same group pointed out that MAPI cells without AVAI showed T_{80} around 400 hours, and in the most recent results with AVAI stability has grown up to an impressive 9000 hours at maximum power point and by cycling day/night operational according to recommendations of IEC61215:2016 [39].

The addition of AVAI in our samples has delivered good performance both in electrical parameters, with the best cell with higher photo current but lower open circuit voltage, $J_{SC} = 21.47$ mA/cm², $V_{OC} = 810$ mV, FF = 66.53% yielding a good PCE = 11.56% (best cell after light soaking). The trend of degradation showed various stages with different degradation speed. Although there was a non exponential trend of the J_{SC} data (Figure 7.24), which also impacted PCE time evolution, it can be interpreted as multiple stage degradation mechanisms. In the best cell (3% 5-AVAI additive), two regions were distinguished, the first one with a very smooth slope, and after

approximately 600 h, a second region with a more pronounced slope. The behavior of the J_{SC} for cells A and B were more complex with more steeped line shapes. The cells without 5-AVAI showed very pronounced slopes, which could be approximately divided into two regions: an initial very fast decay and a second one with a less pronounced decay. For cell E (TPA additive) the degradation was very fast with a T_{80} lower than 1h. There was no clear relation between the size of the hysteresis and the lifetime, since longer lifetimes coupled with larger hysteresis (and viceversa) and therefore a correlation between both effects was ruled out in this case. It has been suggested that the addition of 5-AVAI improves the penetration of the solution during the infiltration of the shell and increases the surface contact, resulting in a lower defect concentration [40]: this effect strongly points that the main effect of 5-AVAI inclusion is avoiding oxygen penetration towards the MAPI, thus extending its lifetime. The role of 5-AVAI is crucial in the formation of superoxide species, which decrease the lifetime of the PSC as result of a combination of different processes, including defect concentration, oxygen diffusion and grain morphology. Devices with 5-AVAI present smaller grains with more surface defects to react with oxygen, due to the higher surface/volume ratio. However, this effect is counterbalanced by an overall lower defect concentration due to the binding of 5-AVAI to iodide vacancies. These vacancies have been reported to be energetically favorable sites for the superoxides formation when the iodide vacancies are occupied by a trapped electron, as they act as trap states in the perovskite bandgap. Additionally, the other effect which lowers the overall superoxide yield is a more compact perovskite layer due to 5-AVAI inclusion, leading to poor oxygen diffusion into the film and thus extending its lifetime [41].

This balance of ultimately beneficial effects of the addition of 5-AVAI is extended to the reduction of oxygen ingress via ETL, either TiO_2 or ZrO_2 , like the effect found by Mei et al. [17]. Furthermore, the MAPI crystal structure is modified by 5-AVAI by forming hydrogen bonds between its carboxyl and the iodide ions of MAPI and ammonia groups. Additionally, the presence of the 2D perovskite $(HOOC(CH_2)_4NH_3)_2PbI_4$ acting as capping layer on top of a 3D tetragonal phase of MAPI has been shown to strongly enhance stability [18]. The addition of 5-AVAI to the perovskite precursor solution provides additional resistance to degradation. However, the origin of the stability improvement is not yet clear, and it is evident from our results that other molecular additives are not beneficial for the extension of the lifetime.

Additionally, the ZrO_2 layer with optimized thickness of 2 μm provides an isolation that prevents ion migration and a short circuit between the carbon and the TiO_2 layer; it is not probable that ZrO_2 is providing additional protection to atmospheric degradation agents such as moisture and oxygen

[37]. This effect was observed previously, and we consider that the extended lifetime observed in our samples was due to a combination of the effect of the molecular additive and the ZrO_2 layer, but with stronger effect from the additive (improvement in the 5-AVAI case, poor results with the other additives, in both cases containing the same ZrO_2 layer). The carbon top electrode also acts as a barrier against moisture due to the hydrophobic properties of carbon.

7.3 Conclusions

Three different stability studies for different solar cells have been shown in this chapter reporting different lifetimes. In the first case study, organic solar cells have been studied using PCBM as an electron acceptor together with the conjugated polymer P3HT in the active layer, first depositing only the active layer using the spray technique as the active layer and the ZnO layer. In both cases, a stability study was carried out following the guidelines of the ISOS-L-1 protocol. The lifetimes obtained for these unencapsulated cells have been 180 hours and 54 hours for both cases, respectively. In addition, the evaluation of the degradation tests indicates that the deposition of the ZnO layer by spray, compared to the deposition of the active layer, does not improve the stability, but rather accelerates the degradation process due to the increase in the constant k_2 (degradation constant related to humidity).

Bulk heterojunction organic solar cells based on P3HT:O-IDTBR have been fabricated to study the effect of different materials (glass, plastic) as encapsulants. The OSCs have been characterized by J-V, EQE and UV-Vis transmittance measurements during the degradation tests carried out according to recommended ISOS protocols. An exponential degradation rate has been found, with bimodal behaviour for glass in ISOS-L-1 and plastic in ISOS-T-3. The J-V parameters and EQE and UV-Vis spectra evolution point to a worsening of the carrier transport and to an increased interface recombination as the main causes for the degradation of the solar cell PCE. The longest achieved T_{80} lifetime is 86 hours for glass-encapsulated devices under an accelerated ISOS-T-3 protocol. The global evaluation of the degradation tests indicates that plastic is a better long term encapsulant, likely reducing ingress of oxygen and humidity into the cell when compared to glass encapsulants. This effect is probably due to the different processing that has been carried out in each case; there is evidence that encapsulation of the rigid glass is poorer than the flexible plastic (carried out respectively by hand and by automated machine lamination). The ingress of moisture might affect strongly the PEDOT: PSS/Ag and Ag: PEDOT: ZnO transporting layers

and electrodes as PEDOT: PSS is highly hygroscopic and when it is degraded the transport properties are worsened. It is reflected in an increment in the series resistance of the equivalent circuit of the solar cell. Finally, the optimization of the encapsulation process seems to be more important than the encapsulant material itself to provide longer lifetimes.

Extended lifetimes have been obtained when 5-aminovaleric acid iodide (5-AVAI) was used as an additive in the active layer of methyl-ammonium lead iodide solar cells. Other molecules were tested as additives, all of them providing poorer results than the 5-AVAI. The best samples with 5-AVAI had PCE higher than 10% and extended lifetime with $T_{80} = 550$ h. The long lifetime observed in a 1000 h illumination test was the combined effect of engineered interfaces: On the one hand, the molecular additive 5-AVAI was mixed in the active layer, occupying the space between the crystalline grains of the perovskite active layer, but also creating an interlayer at the interface between ETL and carbon layers, preventing ion migration and ingress of moisture and oxygen from the carbon electrode side. Other additives were not effective for this purpose. On the other hand, ZrO_2 , with optimized thickness of 2 μm , prevented ion migration into the TiO_2 layer, but its beneficial effect was lower than the use of the 5-AVAI molecular additive.

Regarding the stability obtained with these devices (similar lifetimes between control and spray cells), it is still too early to be able to determine whether they report longer times than those manufactured by the spin casting technique and it is necessary to continue studying them. Likewise, the use of NFAs in the active layer together with an improvement of the encapsulation techniques open the possibility of longer lifetimes for bulk heterojunction solar cells. Finally, even though it has been shown that the use of the addition of molecules in the active layer of perovskite cells to improve stability should be the line to be followed in future work together with reducing their toxicity.

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Chapter 8

Conclusions and future work

The main aim of this work has been to manufacture organic nanostructured solar cells using the spray coating technique. For this purpose, an experimental system consisting of a conventional automated three-axis milling machine and an airbrush attached to its head has been created. From this point, a series of software programs to control the coating process have been written and used to manufacture of solar cells and optimize the process, with a focus on improving the structural and electrical properties of layers and devices fabricated with the spray coating machine. Additionally, optimization of the use of materials was carried out, with highly reduced waste when compared to conventional spin coating technique. This chapter summarizes the main conclusions of the work carried out during the PhD thesis. Finally, some possible future lines of work are proposed.

Implementation of the manufacturing system

One of the first aims was to implement a conventional serial manufacturing system such as the spray coating technique to manufacture organic solar cells. The choice of such a system is due to its flexibility and ability to be implemented in a production line, being able to go from a laboratory-scale system to an industrial scale easily. In addition, a three-axis milling machine allows not only to work with rigid planes glass substrates, but also enables the possibility of using new current flexible plastic substrates or even working on curved rigid surfaces. It has been shown that this system is viable and allows to shorten manufacturing times, reduce material waste, increase reproducibility and yield of the production line, thus being able to manufacture twice as many cells in half the time, saving energy in the process.

Active layer deposition by spray coating in inverted architecture devices

It has been shown that the application of the spray technique for the active layer of OSCs is not only viable, but also provides similar efficiencies to the conventional laboratory-scale spin coating manufacturing process. Efficiencies greater than 1% have been achieved in any of the different horizontal and vertical spray systems, being able to manufacture twice as many devices in the same time. In addition, it has been shown that another advantage of this manufacture is the high reproducibility of the system, making it much more reliable.

Active layer and ZnO layer deposition by spray coating in inverted architecture devices

The ZnO layer is one of the most difficult challenges that this work faced since a change in its deposition method and the material where it is deposited, produces changes important in their behaviour. The results obtained when depositing this layer by means of the spray technique report low currents, as well as very low voltage values (unlike the deposition of only the active layer); this indicates a high internal recombination where photo generation hardly occurred. Despite all difficulties, power conversion efficiencies of around 1% have been achieved using this technique.

Stability of organic solar cells with fullerene and non-fullerene acceptors and of perovskite cells with molecular additives

Another aim of this work was to be able to study how different solar cells manufactured by different methods behave under simulated environmental conditions. For this, three different stability studies were carried out for different solar cells. In the first case, organic solar cells with a fullerene derivative as an electron acceptor (PCBM) was manufactured using the non-encapsulated spray technique, and subsequently subjected to continuous lighting degradation experiments (ISOS-L-1), reporting better T_{80} than cells manufactured using the spin technique, having an equal total life time in both cases.

For organic cells with non-fullerene O-IDTBR electron acceptors, three accelerated degradation experiments were performed according to the ISOS protocols, one simulating real environmental conditions (ISOS-LT-1), another under extreme temperature conditions (ISOS-T-3) and finally one un-

der continuous lighting (ISOS-L-1). In this case, the devices were encapsulated in glass and plastic, having a similar behaviour in all cases except ISOS-T-3, where a better behaviour of the plastic encapsulation was found, reporting an extended lifetime of 700 hours.

Finally, a stability study of carbon-based perovskite solar cells was carried out, to study the addition of molecules to improve their lifetime on solar cells with high power conversion efficiency ($>10\%$). The addition of the 5-AVAI molecule has been shown to improve the stability of solar cells, without losing efficiency in the first 1000 hours.

Global conclusion

This PhD work has confirmed the possibility of using the spray technique for the manufacture of nanostructured organic solar cells by various programs, reporting efficiencies of more than 1%. In addition, the high reproducibility and robustness of the created system allows to manufacture up to nine substrates at the same time, with four cells each in less than two hours, having a high potential for scalability, going from the laboratory to mass production. Additionally, degradation tests following ISOS protocols have been successfully applied to investigate strategies for lifetime extension, in particular, organic solar cells with non-fullerene acceptors and perovskite solar cells with molecular additives have shown extended T_{80} lifetimes to hundreds of hours under constant 1 Sun illumination.

Future work

Due to the results obtained, one of the lines of work to follow is the possible optimization of the ZnO layer, not only in terms of the deposition process but also in the search for its application on other substrates since it has been shown that its behaviour is different when applied on ITO or on glass. An improvement in this layer would represent a very important advance, since the photocurrent generated would be increased, the internal recombination produced during storage in the dark would decrease, increasing the initial efficiency of the cells and their long-term stability. Likewise, the next step to be taken would be the complete manufacture of spray devices, including the rear electrode, either by silver inks or by carbon inks, thus leaving a device completely manufactured by this technique, reducing costs in terms of time and energy.

Appendix A

G-Code Programs

Program 1

```
G64 G17 G91
T0 M6
M3
M8
L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L3 L1 L3
L1 L3 L1 L3 L1 L3 L1 L3 L1 L3 L1 L3 L1
G1 X140 Z0
L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L3 L1 L3
L1 L3 L1 L3 L1 L3 L1 L3 L1 L3 L1 L3 L1
G1 X-140 Z-80
L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L3 L1 L3
L1 L3 L1 L3 L1 L3 L1 L3 L1 L3 L1 L3 L1
G1 X140 Z0
L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L2 L1 L3 L1 L3
L1 L3 L1 L3 L1 L3 L1 L3 L1 L3 L1 L3 L1
M30
G98 L1 F 70
G1 X-60 Z0 G1 X60
G98 L2 F40
G1 Z0
G1 Z2
G98 L3 F40
G1 Z0
G1 Z-2
```

The Program 1 is a loop with three different movement defined by L1, L2

and L3. The code correspond to 1T period for 4 substrates. If more period are need, the loops (L1, L2 and L3) can be repeated.

Program 2

```

G64 G17 G91
T0 M6
M3
M8
L1
G1 X50
L2
G1 X-50 Z-45
L1
G1 X50
L2
M30
G98 L1 F 50
G1 X-40 Z0
G1 X40

```

Again, the Program 2 is a loop with two movements, L1 and L2. This code is for 2 scans and 4 substrates. More scans need more loops can be repeated.

Program 3

```

G64 G17 G91
T0 M6
M3
M8
G0 X0 Y0 Z0
G91
L1 L1 L1 L1 L1 L1 L1 L1
M30
G98 L1 F 50
G1 Y80 Z0
G1 Y-80

```

Program 3 for of 30 seconds for active layer for 3 substrates. Only one loop called L1.

```

G64 G17 G91
T0 M6
M3
M8
G0 X0 Y0 Z0
G91
L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1 L1
L1 L1 L1
M30
G98 L1 F 50
G1 Y80 Z0
G1 Y-80

```

Program 3 for of 102 seconds for ZnO layer for 3 substrates. Only one loop called L1.