



A study of the degradation of organic solar cells

MEMORIA

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*To my parents, bothers and my
love for their help and support*

Summary

The field of small molecule solar cells has incredibly developed during the last decade. In fact, their efficiency increased from 3% in 2005 to 13% in 2016. However, they still face a major problem of stability: these cells degrade very quickly in contact with air or under illumination.

This study focuses on the uses of measurement techniques to follow the degradation of the cells. We studied the use of both electrical and imaging technics to get a better understanding of the degradation mechanisms aiming to identify the weakest layer and to improve its stability.

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Content

Content	6
Introduction	8
Chapter 1 – Global Context	10
I. The power of the sun	10
II. Photovoltaic:	11
III. Organic solar cells:	12
III.1. Physics of organic photovoltaics (OPV)	12
III.2. The development of OPV:	13
III.3. PIN concept in OPVs:	14
III.4. Tandem cells:	15
Chapter 2 – Degradation of organic solar cells	17
I. Degradation mechanisms	17
II. Degradation of the active layer	18
III. Degradation of the electrodes	19
Chapter 3 – Methods for device characterisation	21
I. J-V characteristic	21
II. Microscopy and optical scanning	22
III. Electroluminescence imaging	22
IV. Lock in thermography imaging	24
V. Loss analysis of organic solar cells using different imaging technics:	26
Chapter 4 – Photo degradation of organic tandem solar cells	34
I. Device characteristics and aging conditions	34
II. Electrical characterisation	35
III. Electroluminescence imaging of photo degradation:	39
IV. Thermography imaging:	41
V. Conclusion	42
Chapter 5 – Heat and oxygen-related degradation of tandem cells	43
I. Device characteristics and aging conditions	43
II. Electrical characterisation	43
V.1. The experimental results	43
V.2. I-V characteristic simulation	45
V.3. Extraction, or injection barrier?	46
VI. Electroluminescence imaging of dry heat degradation:	48

VI.1. Spectrally-resolved EL.....	51
Chapter 6 – Conclusion	53
Bibliography	54

Introduction

As a result of industrial development and population growth, the global demand for energy has exponentially increased these past few years. Since the beginning of the 21st century, demand for energy, especially from liquid fuels, as well as limits on the rate of fuel production, have created a bottleneck leading to the 2000s energy crisis. We are reaching the limit of the available fossil energy resources. Thus, we urgently need to think of an alternative to the fossil energy in order to tackle this particular issue.

Among the new energy sector, solar energy is becoming more and more appealing mainly because of its abundance. Indeed, every 8 hours, we receive from the sun more than our annual energy consumption. There are two ways of directly transforming this energy: either we use the thermal power of the sun, or we use the photovoltaic effect to produce electricity.

The Photovoltaic market is dominated by crystalline silicon (90% according to SolarBuzz)[1] due to their high efficiency and sustainability. The commercial solar cells nowadays have a lifetime of 25 years with efficiency around 20% [1]. However, due to the need for electrical grade silicon, as well as huge material loss during the cell fabrication process, the production of Si solar modules are both demanding in terms of cost and energy. To save costs and materials, researchers have been developing new cell concepts based on thin films deposition on glass or PET substrates. Thus, in this particular technology, we need to differentiate between organic and inorganic solar cells. The inorganic thin film technology is mainly focusing on Copper Indium Gallium Selenide (CIGS) solar cells due to their high efficiency, 21.7% for single cells and (15-17%) for modules [2-3]. However the cost for the fabrication of such cells is important due to the rare elements used in the process.

On the other hand, organic solar cells are made of cheap semiconductor materials based on conjugated polymers or low molecular-weight solution processed semiconductor molecules (so called small molecule). The organic photovoltaic (OPV) field has been continuously improving during the last decades to reach the efficiency of

13.2% [4]. This record proves that OPV devices are competitive to the standard thin film technologies. However, OPV devices show an important issue regarding their long-term stability, especially for those deposited on PET substrates. Thus, to aim for an industrialisation of this technology, there is a need for improvement in order to guarantee the cells' stability.

My placement at *Heliatek* gave me the opportunity to study the degradation mechanisms of organic solar cells. My first assignment was to study the use of the available characterisation technics to follow the degradation of organic solar cells. I had to look at both electrical and optical characterisation technics, and choose the most relevant for the study. Then, I studied the degradation of tandem organic solar cells under different aging conditions, in order to characterise the main degradation mechanisms and the effect of external agents on the deterioration of the solar cells. I studied the cells under light and dry heat conditions, and found fundamental differences between the degradation of the cells under these aforementioned conditions.

Chapter 1 – Global Context

The following chapter begins with showing the potential of solar energy, before explaining the photovoltaic effect. The last part focuses mainly on organic solar cells. The aim of this last part is to give an overview of the physics of OPV's.

I. The power of the sun

We receive from the sun more than 3 times the annual world energy consumption on a daily basis, as cited in the 2014 International Energy Agency report [5]. The large magnitude of solar energy available makes it a highly appealing source of energy, Figure 1.1 illustrates the potential of solar energy compared with other conventional energy sources.

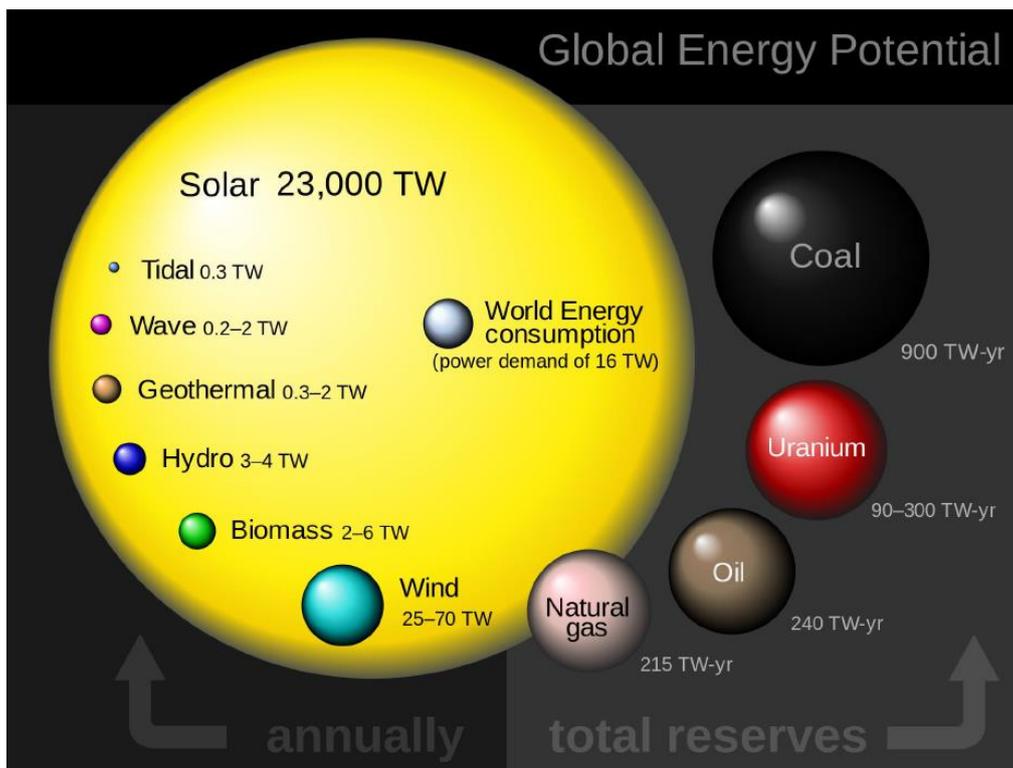


Figure 1.1 the Annual energy potential of different energy sources [6]

Moreover, this energy is spread and available across the globe; and humanity has been benefiting passively from this energy for ages. During the last decade, along with

progress in technology, we have been able to transform this energy into a more convenient one. While it has mainly been used for heating, sunlight may be transformed as well into electricity. It is undeniable that these facts make the solar energy the most promising renewable energy. However, this energy source presents many challenges for the solar industry. First of all, this energy is intermittent and far from reliable, although it is possible to modulate it to suit specific needs. This energy is not dense enough, which consequently means that large receptor areas are essential for its use. Finally, there is an issue regarding the cost of this energy, as it is still more expensive than the energy sources conventionally used nowadays in many regions of the world. Thus, to tackle these challenges, improvement needs to be made to the current technology with a focus on increasing the efficiency, reducing the cost, and ensuring its sustainability [7].

II. Photovoltaic:

Photovoltaic refers to the excitement of electrons into a higher state of energy by photons of light, allowing these electrons to act as charge carriers for an electric current. Some materials, when exposed to light, emit an electron. Alexandre-Edmond Becquerel has first observed this effect in 1839 [8]; and it was not until the middle of the 20th century that the first practical solar cell was demonstrated [9]. Solar cells are basically made of the photoactive material that creates the charges, as well as the contacts which harvest these charges and transport them to the circuit. The material demonstrating this effect is called ‘semi-conductor’. The latter is a non-conductor material with a small gap between the conduction band and the valence band. When these materials are excited with a photon with energy above the gap, an electron goes up from the valence band to the conduction band. The electron leaves behind a hole that has a positive charge, and both charges can travel through the material to the contacts. The energy gap between the conduction and the valence band is the maximum electric potential that we can get from this generator [10].

At first, solar cells were exclusively meant for space programs – which kept their prices high, as efficiency was the sole aim. Nowadays, we have reached 45% efficiency. With the energy crisis, people started looking for an alternative to the fossil energy. In order to get competitive in the market, researchers have started looking for ways to reduce the cost of solar energy. The solar panel market is dominated by

crystalline silicon (90% according to *SolarBuzz*) due to their high efficiency and sustainability. Current commercial solar cells have a lifetime of 25 years with efficiency around 20%. Other materials are catching as well the attention of researchers, such as organic solar cells that present a low cost alternative to the silicon solar cells.

III. Organic solar cells:

Organic solar cells are a type of solar cell which uses organic electronics, a branch of electronics that deals with conductive organic polymers or small organic molecules [11] for light absorption, and charge transport to produce electricity from sunlight resulting from the photovoltaic effect.

III.1. Physics of organic photovoltaics (OPV)

Organic polymers, and small molecules used in OPV, are mainly conjugated systems. A conjugated system is formed where carbon atoms covalently bond with alternating single and double bonds. An example of organic photovoltaic material is shown in Figure 1.2. The overlapping of the orbitals of these different atoms forms delocalized molecular orbitals. The most important molecular orbitals for solar cells are the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). Indeed, for the photovoltaic effect, the electrons in the HOMO level are excited to the LUMO where they are extracted.

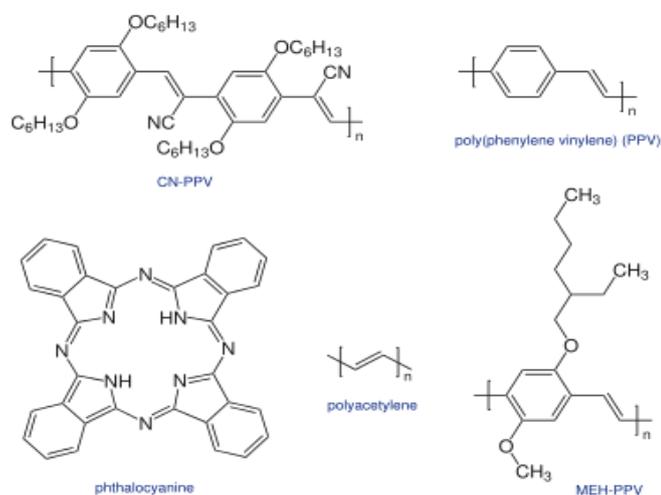


Figure 1.1 example of organic photovoltaics materials

For organic solar cells, once it is illuminated, the electron from the HOMO level is excited, but the hole and the electron remain bonded in what we call an ‘exciton state’. The latter comes before the free charge separation. In order to reach this state, the exciton needs to migrate to a charge transfer interface. Otherwise, it will just recombine and produce another photon [12]. In organic semiconductors, the diffusion length of the exciton is about 10nm. The charge transfer area is the interface between two organic materials, a donor that gives the electron. It has the highest LUMO level, and the acceptor has the lowest HOMO level. For instance, the electron in the LUMO of the donor goes to the LUMO of the acceptor, and the hole remains in the donor (Figure 1.3): this process is called the charge transfer state. In this state, the charges can easily be separated with an external electric field. The electric field is due to the difference of the work function of the two electrodes.

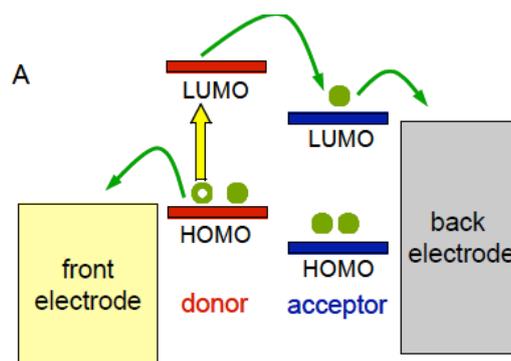


Figure 1.2 the Organic solar cell concept

III.2. The development of OPV:

The first attempts to create an all-organic solar cell were made by sandwiching a single layer of an organic material between two dissimilar electrodes. This structure is called a ‘mono-junction’. These solar cells showed extremely poor power conversion efficiencies which go up to 0.3% [12]. This low efficiency is due to the strong bonding energy of the exciton. In 1986, Tang introduced the double layer structure to the OPV (organic photovoltaic). This one was similar to the pn junction for the inorganic materials, where the donor and the acceptor have the same roles as the n and p type materials. The power conversion efficiency remained below 1% because the exciton had

to travel to the p-n interface to dissociate. In order to get a working device, one had to make thin films below 10nm, so that the thickness may limit the absorption.

The real breakthrough for OPV was made with the bulk heterojunction. Instead of having two separated layers of donor and acceptor, in this structure, we mix the two, which optimises the interface surface. With this structure, we reach nowadays more than 11% in terms of efficiency [14]. In fact, during the last few decades, OPV cells have seen their efficiency get 10 times higher, which is mainly the results of using the bulk heterojunction structures, but also thanks to the use of new materials.



Figure 1.4 Bulk Heterojunction structure

Moreover, the best efficiencies reached in the OPV field have been achieved using PIN structure. The PIN structure is common for inorganic solar cells, and it combines an intrinsic layer with two doped layers of wide gap materials to ensure charge extraction [15].

III.3. PIN concept in OPVs:

The PIN structure consists in placing an active absorber between two doped layers to enhance the charge extraction. One of the layers is n-doped in order to ensure a good conductivity for the electron and a low one for the holes; the other is p-doped resulting in a large whole conductivity and a poor one for the electrons. These two layers are meant to have a wide gap so that they would transmit all the incoming photons.

The PIN structure may be adapted to organic solar cells as we can easily dope organic semiconductors by adding organic or inorganic molecules to the mix. This doping technic is mainly used for vapour-deposited cells, as it allows easy staking and controlled mixing of layers [16]. The use of doped materials as transport layer presents several advantages, the more important ones being the following [17; 18]:

- High conductivity which ensures a good transport of the majority charge carriers;
- Decoupling the energy levels of the active layer and the electrode;
- Optimising the optical field in the absorber layer for precise wavelengths;
- Reducing recombination in the transport layer.

III.4. Tandem cells:

Another way to tackle the issue of exciton diffusion lengths for flat heterojunction is the use of tandem cells. In order to absorb all the light, two or more cells stacked upon each other can be used. To connect these sub-cells, a thin interlayer is needed between contacts to enhance recombination. Moreover, this parallel setup raises the constraint that the current going through the entire sub cells need to be equal but the voltage will be the sum of the voltage created by the sub cells. The stack of such a tandem cell is described in figure 1.5.

The working principle of this structure is as follow: the photon with high energy gets absorbed within the A heterojunction and the B heterojunction. Thus, the band gap of the A absorber would be higher than the one of the B's absorber. Then, the hole produced at the A heterojunction reaches the electrode through the hole transport layer, but the electron goes through the electron transport layer to recombine with the hole produced at the B heterojunction. The main advantage of this tandem cell is the use of materials that absorb in different spectral regions, improving the overall absorption of the cell and thus, its efficiency [20].

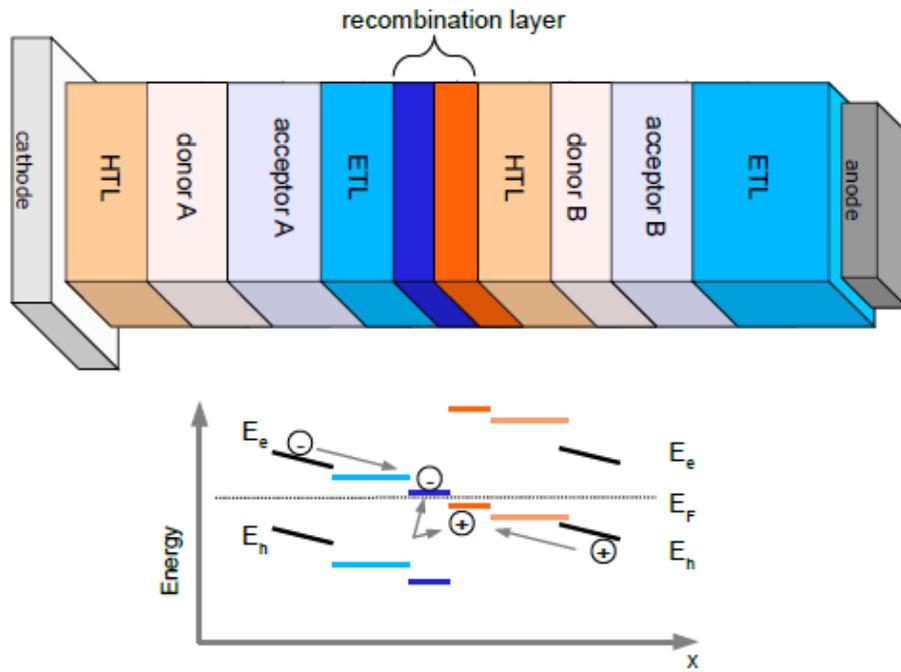


Figure 1. 5: Tandem cell stack: The electron produced within the A heterojunction goes through the ETL and recombines with the hole produced at the B heterojunction [19].

Chapter 2 – Degradation of organic solar cells

This chapter gives a broad description of the different degradation mechanisms which may occur within an organic solar cell. We shall first look into the listing of the degradation mechanisms and their causes, before taking a deeper look at the degradation within the active layer and at the electrodes.

I. Degradation mechanisms

The term ‘degradation’ refers to a change in the properties of a material or devices affecting negatively its efficiency over time. For solar cells, degradation leads to the reduction of specific cell parameters such as the J_{sc} (short circuit current), V_{oc} (open circuit voltage), FF (fill Factor) or simply the PCE (power conversion efficiency). Different agents, *ie* different environmental condition, can enhance this reduction. Therefore, we need to identify each degradation mechanism and its cause.

Literature has identified several degradation mechanisms [21-24]. These may be listed along with their causes as following:

- Mechanical: delamination, electrode failure and packaging failure. Problems within the fabrication or handling the cells can cause this type of degradation.
- High temperature: may cause morphological changes within the cells and enhance the diffusion of different materials. Some materials, such as aluminium, are known to diffuse through the other layer, causing electrical failures such as shunts. The temperature may help some chemicals to diffuse through the cell and induce some chemical reactions.
- Oxygen or water can cause the oxidation of the active layer as well as the electrodes or the HTL (hole transport layer) or ETL (electron transport layer). This chemical reaction can cause several changes within the material such as increasing the trap states, reducing the mobility, changing the work function of some materials, causing some interface failures.

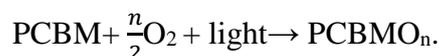
- Light can enhance some other degradation, and their effect is mainly coupled with the presence of oxygen. The main degradation due to light is the photo-oxidation of the active layer.
- Electrical: some electrical failures may cause localised heating, thus inducing localised failures within the cell. These failures can either be due to problems within the fabrication or shading effect. In fact, when a cell is shaded in a module, it gets biased by the other cells, thus inducing a hot point within the module, which results in losses in efficiency.

Organic solar cells are subject to different degradation mechanisms, but it is essential to determine the most influent ones so that we can improve their stability drastically. In the following section, we shall describe in more details the degradations that occur at the active layer and at the electrodes and interfaces.

II. Degradation of the active layer

One of the main factors that degrades the active layer in an organic solar cell is the combination of oxygen and light. In fact, these two agents induce the photo oxidation of the organic material which may result in different chemical reactions. In fact, oxygen can react with either the donor or the acceptor to create oxidized chemicals which result in a change within the energy levels of the absorber. This leads to the creation of trap states that limit the conductivity, thus the short circuit current [25].

For instance, the widely used acceptor (PCBM) is known to react with oxygen under light through the chemical reaction that can be described as the following:



The oxidized PCBM has a lower LUMO level that induces traps within the active layer [26]. This mechanism is described in the following schematic illustration (Figure 2.1).

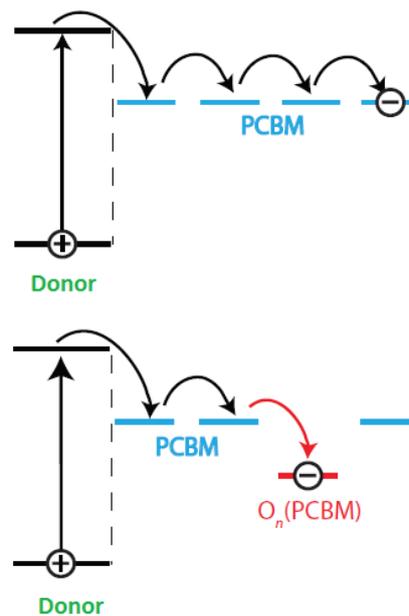


Figure 2.1: Schematic illustration of how the introduction of traps would inhibit mobility in PCBM domains.

III. Degradation of the electrodes

The choice of the electrodes is essential to obtain highly efficient organic solar cells. Indeed, the work function of the electrodes is primarily responsible for the built-in potential and optimal charge extraction. Moreover, the electrodes play a major role in the cells' stability. Thus, a good understanding of their degradation is essential to ensure a long-term stability of the organic solar cells.

III.1. Metal electrode

Metal electrodes are commonly used in organic solar cells due to their high conductivity; the most common ones being Aluminium and Silver. Both materials show a high reactivity with oxygen and water, thus leading to a reduction of the solar cell performance. The degradation that occurs within the metal electrode can be divided in three main degradation mechanisms: the oxidation of the metal layer at its interface with the organic material, the chemical interaction between the metal electrode and the organic material, as well as its diffusion into it. The latter mechanism is much weaker than the first one, as the degradation of organic solar cells in an N₂ atmosphere with or without heat is insignificant. On the other hand, the oxidation of the electrode/organic interface induces the creation of barriers that reduce the FF or the solar cell, thus its

PCE. In fact, oxygen reacts with metal and creates an oxidised layer: the latter layer hinders the charge selectivity of the electrode.

III.2. Electron and hole transport layers

The use of ETL and HTL does not solely enhance the charge extraction: it has as well an impact on the cell's stability. In fact, these layers can either play a role of a barrier for the oxygen (reducing the oxygen or water ingress through the cell), or inducing instable interfaces which react with oxygen. For example, the use of PEDOT:PSS is known to increase the degradation within other layers, thus shortening the devices' lifetime [27].

The transport layers play a major role in the cells' charge selectivity [34]. Indeed, the use of wide gape semiconductors enhances the extraction of electron, and blocks the holes or the other way around. Therefore, a change in the energy levels of those layers can induce the formation of a barrier or reduce the charge selectivity of the contact. Changes in the energy levels of such layers may be induced by different mechanisms: it may either be due to their oxidation, or by injecting current upon them, which triggers chemical reactions [35].

Chapter 3 – Methods for device characterisation

This chapter presents the use of different characterisation technics to follow the degradation of the cells and to understand its mechanisms. The first method is the most common one, with the J-V characteristic which provides information about the working behaviour of the cell. The other methods are imaging technics which give more localised information of the degradation.

I. J-V characteristic

The density of current voltage is the measure of the current density that goes through the cell depending on the potential difference. This characteristic is either measured in the dark or in the light. The measure in the dark serves to define the diode characteristic of the cell. The J-V under light is the most common measure for the solar cell field as it gives the most important information about the device performance. We often measure this characteristic when beaming a solar-like light (AM1.5) onto the cell, the power of such beam is 1000W/m^2 .

The light J-V measurement serves to determine the main characteristic of the solar cell. The J_{sc} represents the current density at short current, while the V_{oc} represents the voltage at open circuit. The Fill Factor (FF) is the ratio of the actual maximum obtainable power to the product of the open circuit voltage and short circuit current. This Fill factor consists as well in the area under the curve. Multiplying it by the product of V_{oc} and J_{sc} provides the efficiency of the cell η . Figure 3.1 shows a light J-V and how to read the main characteristics from the latter.

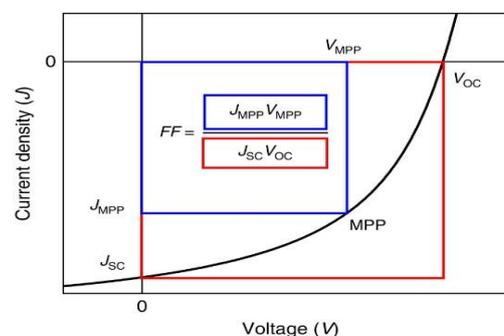


Figure 3.1 Example of a J-V characteristic

II. Microscopy and optical scanning

Optical microscopy consists in the classical way of imaging an object through yielding magnification. This technique provides relevant information regarding the degradation patterns. In fact, for organic solar cells, the degradation patterns take place within several hundred-micrometre regimes. On the other hand, its use for solar cell characterisation is very limited, especially for encapsulated cells. This is due to the reflection of the foil layer which limits the microscope magnification, thus the information we may obtain from the latter [28].

A microscopy image of a degraded cell is presented in Figure 3.2. In this picture, there is a clear difference between the degraded (green) and non-degraded areas (yellow, black), although it is difficult to ascertain in which layer this degradation occurs, as well as its nature. We may infer that this degradation originates from the crystallisation of some organic materials or the oxidation of the electrodes.

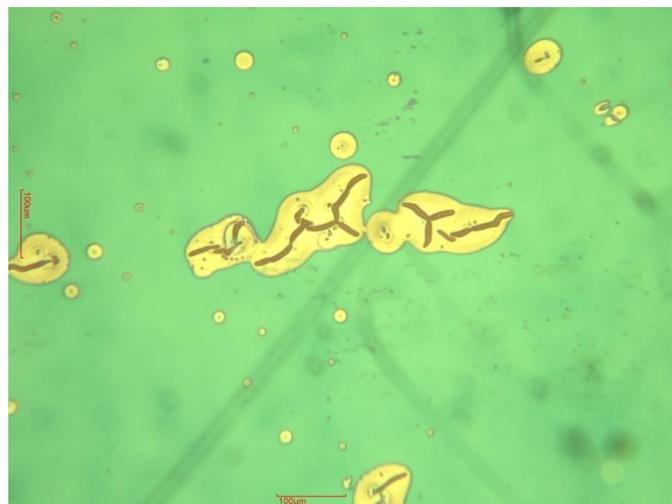


Figure 3.2: Microscopy image of a degraded solar cell

III. Electroluminescence imaging

Electroluminescence (EL) relies on the same principle as a light emitting diode (LED). Current is fed into a solar cell (essentially a large diode), and radiative recombination of carriers causes light emission. Electroluminescence provides plenty of

data about the energy levels of the device. Based on the amount of charge injected in the solar cell, we may observe a light emission coming from a specific excited level. In this work, we focus mainly on the first excited level in order to guarantee a charge transfer state in our cell [29], hence the constant injection of current around the short circuit current (I_{sc}) of the cell.

Electroluminescence imaging (ELI) relies on detecting luminescence radiation emitted by the active layer using a CCD camera. Furthermore, electroluminescence is the reciprocal action of the photovoltaic effect, thus providing vital information about the solar cell such as recombination, resistive and optical losses. The latter gives local information about the major mechanisms happening within the solar cell. The use of ELI to study degradation is extremely common in silicon solar cells, and is considerably useful for organic cells as well. The setup used for the ELI measurements will be described in Figure 3.3.

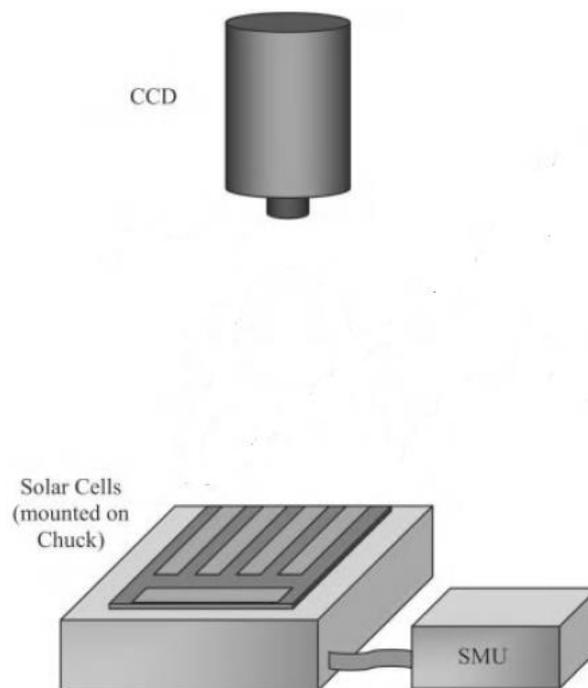


Figure 3.3: Schema of the Electroluminescence imaging setup. The SMU injects current into solar cells, and the latter emits lights detected by the CCD camera.

Several recombination mechanisms occur within a solar cell, and they have different rates of occurrence. The most interesting ones for ELI measurement are the radiative recombinations which emit lights within the range of our CCD camera. In fact, for

silicon solar cells, the use of this type of measurement provides an insight of the defects in the modules: a difference in intensity would mean a lower injection in that spot or a defect within the active layer.

The emission does not always have the same wavelengths. In fact, small changes in the chemical structure induce changes in the energy levels. This phenomenon is very important within organic solar cells due to their instable chemical structure. Thus, degradation may cause, as mentioned in the previous chapter, changes in the energy levels which may be perceived with an electroluminescence measurement.

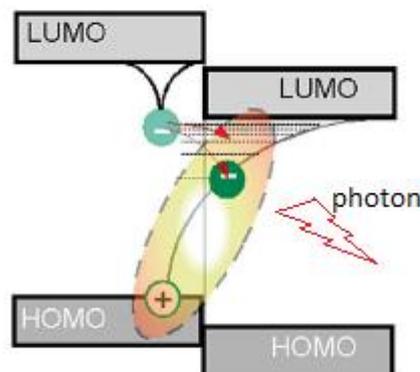


Figure 3.4: The CT state emission in an organic solar cell

IV. Lock in thermography imaging

The previous imaging technics employ the visible or near infrared parts or the electromagnetic spectrum. Another way of obtaining two-dimensional information from a photovoltaic device would be to image thermographic information. Thermography imaging relies on heat dissipated when a current drives through the solar cell. There are many mechanisms which dissipate heat in a solar cell – a description of these mechanisms being presented in Figure 3.5 [30]. Pth corresponds to the thermalisation heat of the photo-generated charge, while PDA+ and PDA- consist in the heat dissipated from diffusing or transferring carriers from the p region (donor) to the n region (acceptor). The PME and PBM correspond to losses occurring within the injection due to the Peltier effect. PA and Pdr correspond to heat dissipation due to radiative

recombination. In addition to these power sources, Joule heat dissipation is an important additional power source, the most important sources for Joule heat being the shunts and horizontal current flow in the layers. Thermography can detect these small heat dissipation mechanisms. Therefore, it is unquestionably a suitable method to complement the information retrieved by optical microscopy and ELI.

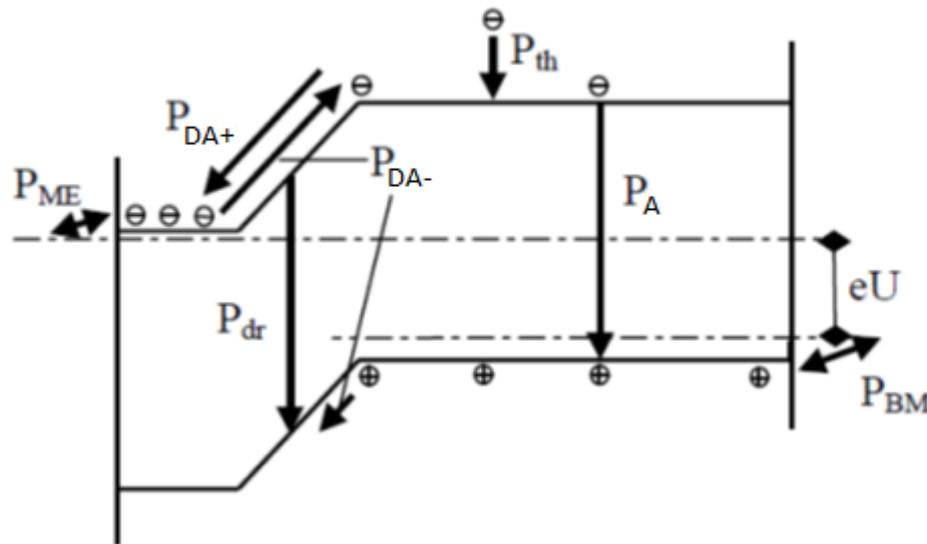


Figure 3.5: Heat dissipation mechanism in a solar cell.

However, the sensitivity of IR cameras is about 10mK or 20 mK, values which are not suitable for photovoltaic device testing. Therefore, the lock-in principle is used to increase the signal-to-noise ratio. The principle of lock-in-based imaging is defined as the following: the dissipation power of a sample is periodically amplitude-modulated by an external excitation source. Each pulse induces a thermal wave inside the solar cell which interacts with discontinuities, thus leading to detectable heat dissipation. For each period of excitation, pictures are taken with the infrared camera. These time-dependent pictures (or signals) are then convolved with $\sin(t)$ and $-\cos(t)$, and summed over all the frames to get the in-phase signal and the $S0^\circ(x,y)$ and the out of phase signal $S90(x,y)$. Figure 3.6 provides a schematic illustration of this process.

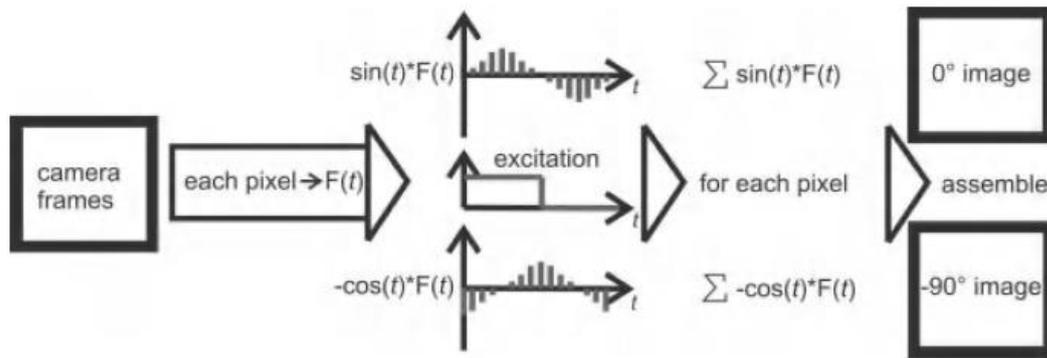


Figure 3.6: Lock-in measurement principle

These calculated signals may be perceived as the real and complex imaginary part in the analysis used to calculate the amplitude and phase signal of the surface temperature by applying the equations below:

$$A(x, y) = \sqrt{S^{0^\circ}(x, y)^2 + S^{-90^\circ}(x, y)^2} \quad \text{Eq.1}$$

$$\varphi(x, y) = \arctan\left(\frac{-S^{-90^\circ}(x, y)}{S^{0^\circ}(x, y)}\right) \quad \text{Eq.2}$$

V. Loss analysis of organic solar cells using different imaging technics:

V.1. ELI

Electroluminescence imaging can be used to detect several losses within a solar cell, as the working principle of a light-emitting diode is extremely similar to a solar cell. Moreover, the high resolution of the CCD cameras provides extremely precise information. The different features we may obtain from an ELI picture are presented in Figure 3.7, where an ELI picture of a non-encapsulated solar cell is illustrated after 300 hours in dry heat conditions. The circles correspond to dark spots which may be caused by a shunt at this precise point, or a degraded active layer. The diamonds are very bright spots which may be explained by a blue shift in the EL within that region – in fact, the camera’s quantum efficiency is very sensitive to a change in the emitted wavelength, hence the appearance of the blue shift as a bright spot. The square spots emit less light than the other parts of the cell. This may be caused by a decrease in the radiative

recombination in these pixels. Furthermore, the EL picture in Figure 3.7 is very inhomogeneous: the source of this inhomogeneity is unclear, and the EL image can provide us an answer to this question.

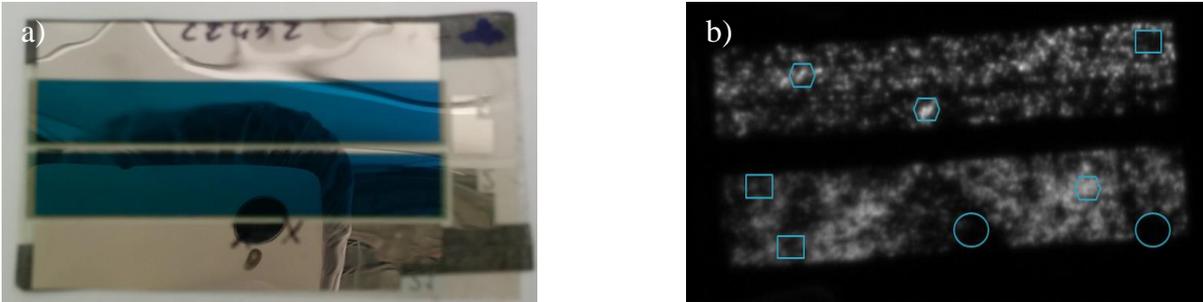


Fig 3.7: Image of the sample (a) and its EL image with a 20 mA injection current (b).

Moreover, EL imaging may be used to quantify the losses within a solar cell, and relate these to the overall efficiency of the cell. From these pictures, we may extract information such as the amount of photon emitted by the cell and the signal's disparity. The use of histograms to quantify the degradation is extremely useful. In fact, Figure 3.8 presents two histograms of samples from the same run degraded in two different ways: the first samples have been aged under light, and the other one in dry heat condition at 85°C. These two histograms are very different: the cell degraded under light shows a quick drop in the electroluminescence intensity, while the other cell mainly shows a decreasing number of emitting spots. This shows the different response of the EL to the degradation mechanisms.

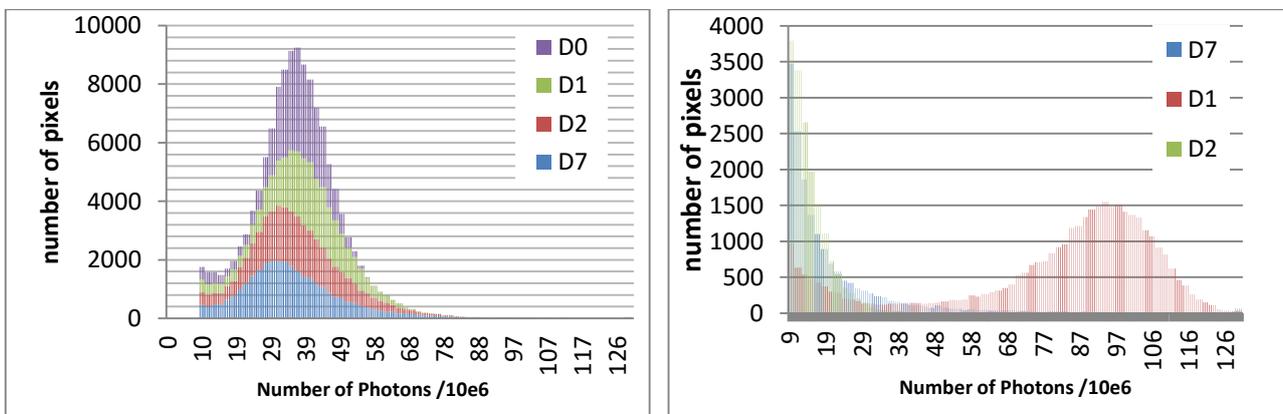


Fig 3.8: Histograms of the EL pictures' intensities of a degraded organic tandem cell

As each pixel corresponds to a small solar cell, the EL signal may be correlated to the local electrical characteristics of the cell, such as the local voltage, local current or the series resistance. For this matter, the method used by Fuyuki and al [30] and described below shall be applied. As the reciprocity principle relates the local Voltage to the EL quantum efficiency, the detected EL can be written as the following, with $Q_{cam}(E)$ being the energy sensitivity of the detector, $Q_e(E,x,y)$ the local quantum efficiency, and Φ_{bb} the spectral photon density of the black body:

$$S_{cam}(x,y) = \int Q_{cam}(E) * Q_e(E, x, y) * \Phi_{bb}(E) * dE * \exp\left(\frac{q*V(x,y)}{kt}\right) \quad \text{Eq. 3}$$

In order to calculate the V_{oc} using this equation, the local quantum efficiency of the cell is required. However, the latter is not available. Thus, we will try to approach this value with two parameters: $C(x,y)$ being a calibration value independent from the local voltage, and the other being the radiative recombination efficiency $\eta(V)$. The first parameter would be deduced from a low injection EL picture, where we presume that the local voltage is the same as the global one. Further difficulties arise for the second parameter, as it should take into account the increases of the radiative recombination efficiency with the voltage – a phenomenon routinely observed for organic solar cells. It is difficult to ascertain and determine the dependence, hence the use of a quadratic dependence to approach it. Therefore, equation 3 becomes as the following:

$$S_{cam}(x,y) = C(x,y) * \eta(V) * \exp\left(\frac{q*V(x,y)}{kt}\right) \quad \text{Eq. 4}$$

Based on two El pictures at low and high injection current, we may deduce the local voltage of the cell. For the local current, a one-diode model shall be used to measure approximately the local current density based on the following equation:

$$I(x,y) = I_0(x,y) * \exp\left(\frac{qV(x,y)}{kt}\right) \quad \text{Eq. 5}$$

The approach demonstrated by Breitenstein and Al[31] and detailed below shall be applied to calculate the local dark saturation current. It is presumed that the pixel

intensity of the calibration image $C(x,y)$ is proportional to the effective diffusion length and thus, to $I_0(x,y)^{-1}$. The result may be reduced as the following:

$$I_0(x, y) = \frac{f}{C(x, y)} \quad \text{Eq. 6}$$

The scaling factor is chosen in a way that the mean value of the local series resistance equals the global one. To calculate the local series resistance, the solar cell is modelled as a two-dimensional network of parallel nodes which consists in a diode and a resistance. According to ohms' law, the local series resistance is determined as the following with U_{app} as the applied voltage when measuring the El:

$$R_s(x, y) = \frac{U_{app} - U(x, y)}{I(x, y)} \quad \text{Eq. 7}$$

Figure 3.9 presents an example of the application of this method for a module of 24 tandem cells connected in series. The upper image represents the Electroluminescence images of the module at two different current injections (20mA and 120mA). The first one revolves around $0.1 \cdot I_{sc}$, while the other is around I_{sc} . Picture c represents the calculated local voltage of module; and picture d represents the local series resistance. For this module, it is essential to emphasise on the very high series resistance, which is mainly due to the sheet's resistance of the bottom electrode

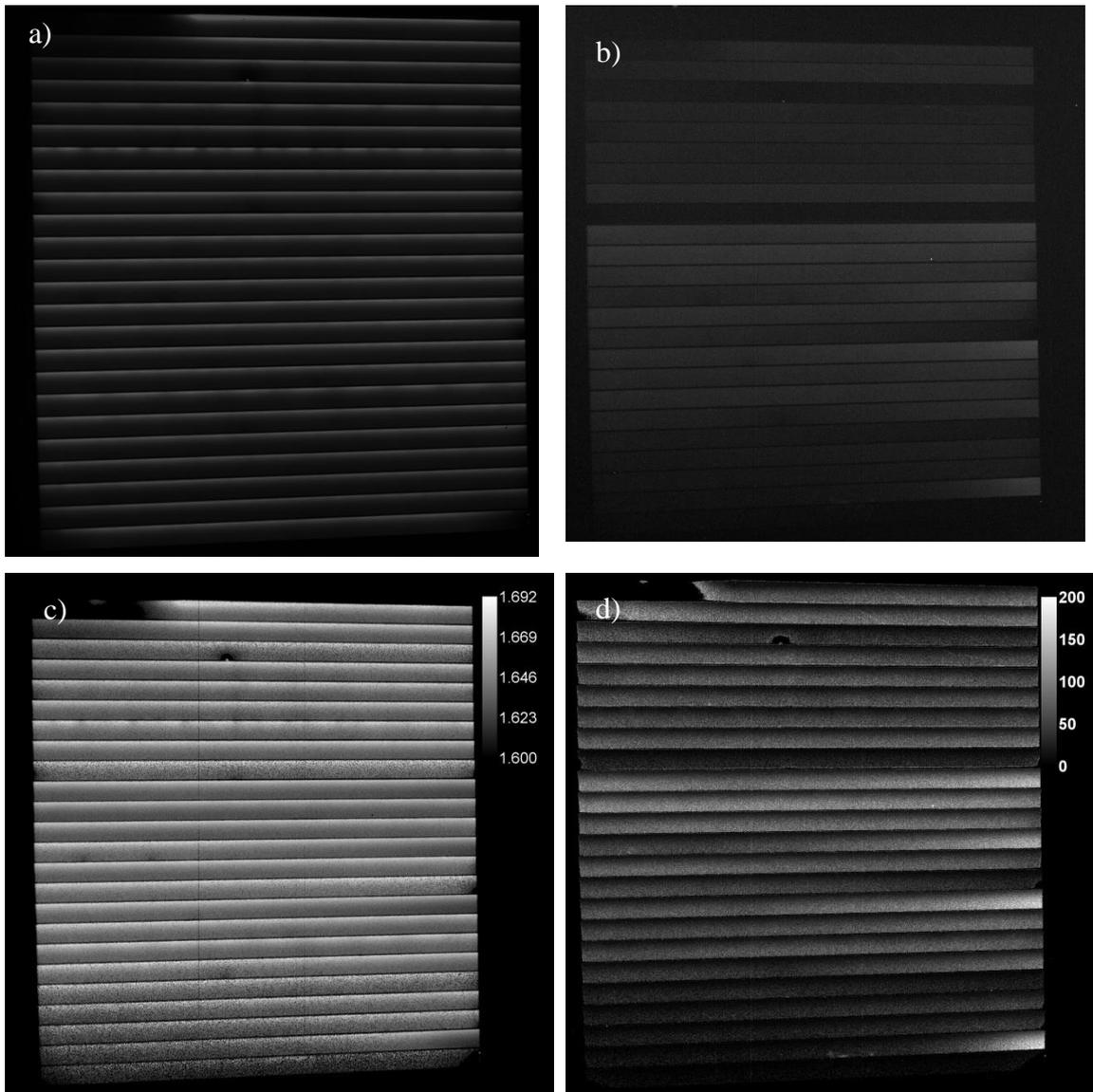


Fig 3.9: Picture a: Electroluminescence of the module at 120mA. Picture b: Electroluminescence of the module at 20mA. Picture c: Calculated local voltage. Picture d: Calculated local series resistance

v.2. Thermography

Dark lock-in thermography is a powerful tool for loss and defect analysis in a solar cell. As previously mentioned, the thermography signal is directly related to the power dissipation in a cell, thus to its losses. The DLIT is often measured in forward and inverse bias to get a full understanding of the heat dissipation. The forward-biased signal is related to the heat dissipated when the current is flowing through the diode, while the inverse bias is related to the current going through the shunts and defects. Therefore, coupling both signals would give a better insight of the losses. Figure 3.10

illustrates a thermography signal from a degraded solar cell both in forward and inverse bias. One can clearly see the shunts in the inversed-bias picture, as they are the only ones emitting pixels. Analysing the forward-biased image is more complicated as there are more heat dissipation mechanisms to deal with. However, we can clearly see a contacting problem for the second pixel in the forward biased picture.

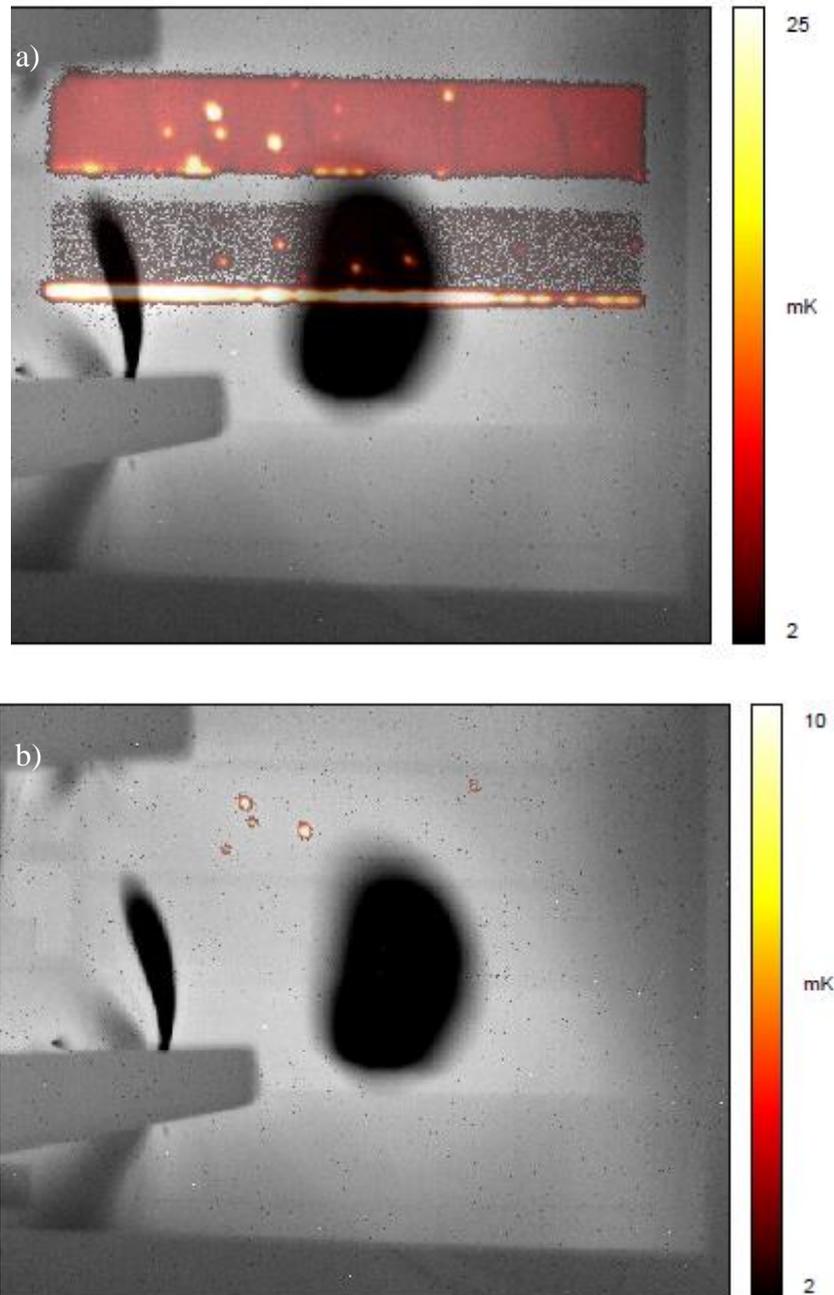


Fig 3.10: Thermography image of an organic tandem cell in forward bias (a); and inverse bias (b).

Moreover, quantitative values about diode parameters such as the ideality factor and the dark saturation current can be extracted from the DLIT experiments [32]. To do so, Breitenstein and some co-workers defined the local power dissipation P_{loc} of a solar cell in the dark as the following:

$$P_{loc}(x, y) = \frac{S_{DLIT}(x, y) * P_{tot}}{\int S_{DLIT}(x, y) dx dy} \quad \text{Eq 8}$$

With S_{DLIT} as the camera signal and P_{tot} as the applied electrical power. From the local power dissipation we can get important information about the diode; in this work we will mainly focus on extracting the local current out of this value using the local voltage measured with ELI.

V.3. Combination of both imaging techniques

Both the DLIT and ELI techniques give relevant information about the degradation of the solar cells; thus combining both techniques will allow a better understanding of the degradation mechanisms. In order to demonstrate the benefit of applying both imaging methods, we will present an example of such analysis for a degraded cell. The sample consists of non-encapsulated tandem solar cells that have been degraded for 5 days in dry heat conditions.

First of all, both the DLIT in forward bias and the EL at 20mA present the same features: they have the same bright spot. The inverse bias DLIT does not show any shunts, thus we can infer that the dark spot in the middle is not due to a shunt. Moreover the bright spots in both ELI and DLIT can be due to a barrier in an injection layer that increases the heat dissipation and the local voltage. In conclusion, it is obvious that one measurement technic is not sufficient to understand all the degradation mechanisms.

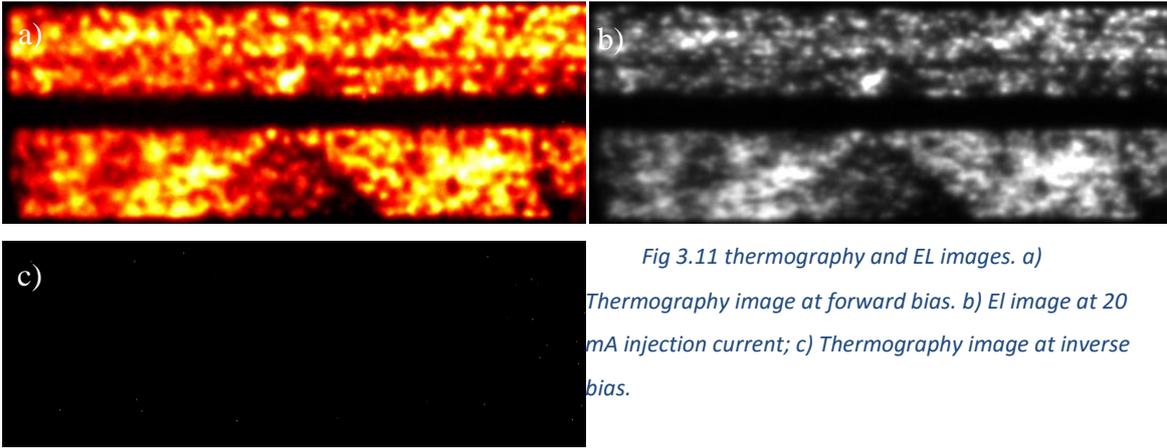


Fig 3.11 thermography and EL images. a) Thermography image at forward bias. b) EL image at 20 mA injection current; c) Thermography image at inverse bias.

Chapter 4 – Photo degradation of organic tandem solar cells

This chapter presents a study of the degradation of organic tandem solar cells under one sun and in the air. The chapter begins with a presentation of the samples used for this study, before exposing and discussing the devices' performance.

I. Device characteristics and aging conditions

The used devices for this experiment are tandem small molecules solar cells which have been evaporated on polyethylene terephthalate (PET). Their structure is similar to the one presented in the first chapter. However, the used materials are confidential. Among these samples, two groups may be differentiated: the opaque and the semi-transparent one. The only difference between these groups is the nature of the back electrode. This work shall focus on the understanding of the degradation mechanisms of the organic materials in general. The samples used have two devices connected in series, each of 3.575cm^2 . A picture of an encapsulated device is presented in Figure 4.1.

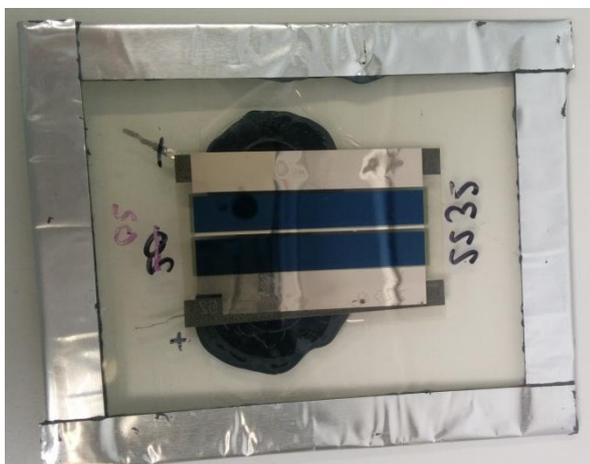


Figure 4.1 Picture of an encapsulate organic solar cell

The samples have been studied in two different situations. Some have been fully encapsulated, while others have solely been protected with a thin plastic layer. The aim is to study the degradation of fully encapsulated and non-encapsulated samples. The encapsulation of the cells is performed by gluing two barrier films over the solar cell. However, the performance of the barrier is not relevant for this study. The solar cells

were aged under a solar simulator at sun conditions ($1000\text{W}/\text{m}^2$) in ambient air, while reference cells were kept in the dark in ambient air as well.

II. Electrical characterisation

The solar cells' degradation has been investigated by measuring the J-V characteristics of the samples at different times during their degradation. The use of this electrical characterisation is extremely useful to get an insight on the overall degradation of the cells.

The performance of the fresh sample were similar to each other: the opaque cells had a power conversion efficiency around 7% and a fill factor around 70%, while the transparent cells have a lower PCE which revolves around 6% with a fill factor of 65%. The main difference between these two is the short circuit current, as it starts at 22mA for opaque cells, and only at 17 mA for transparent ones.

From the measure I-V characteristics, we extracted the normalised development of the main characteristics of the cells over time: J_{sc} , V_{oc} , FF, PCE. These results are presented in the following fingerprints (figure 4.2):

- ◆ Self Opaque
- ✕ Self transparent
- light + Encapsulated transparent
- Light Opaque 1
- ✱ Light transparent 1
- light + Encapsulated transparent
- ▲ Light Opaque 2
- light transparent 2

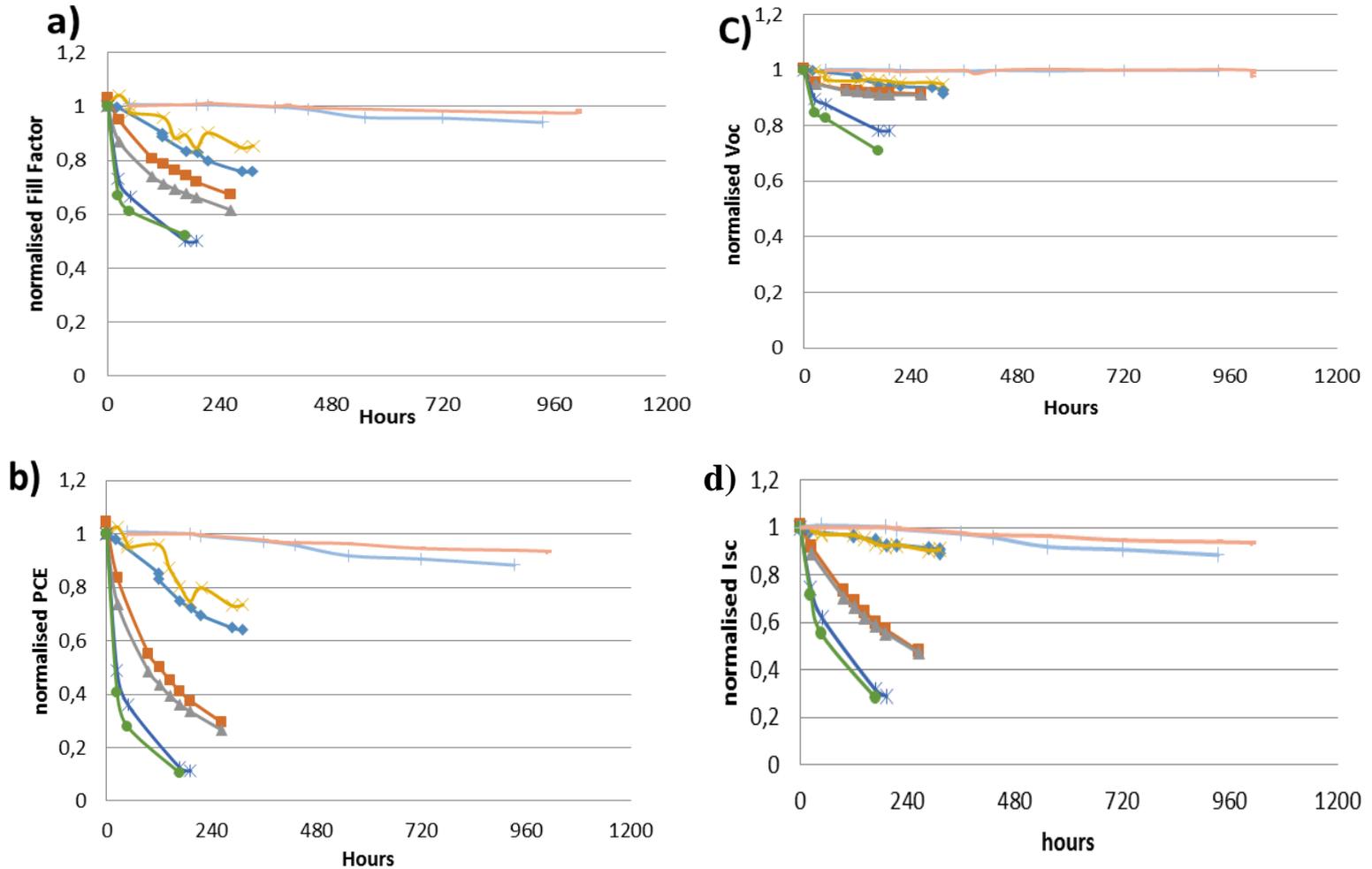


Figure 4.2: Photo aging of tandem solar cells. The graph shows the long-term temporal evolution of FF(a), PCE(b), Voc(c) and Isc(d).

First of all, the graphs above stress the importance of encapsulation for these solar cells' lifetime. Indeed, the encapsulated solar cell did not degrade by more than 10% after 1'000 hours under illumination, while the non-encapsulated one got totally degraded after less than 200 hours. This observation demonstrates the role of external agents in the degradation of organic solar cells such as oxygen or water.

The illuminated cells degraded mainly in terms of Isc, in comparison to dark degraded cells. In fact, the Isc drops to less than 60% for both transparent and opaque cells after 150 hours of illumination. This significant drop in Isc may be at the origin of the drop in Voc. The drop in Isc may have been caused by several factors, such as

charge extraction limitation as well as the increase in trap state. The fill factor of every non-encapsulated cell drops relatively quickly, and tends to stabilise after some time. Thus, we may infer that this drop is not solely due to photo degradation, but is related as well to the presence of air, as we do not observe any drop for encapsulated cells. Overall, the losses in PCE for the illuminated solar cells are mainly determined by the I_{sc} , as well as a modest decay of fill factor.

Overall the losses in PCE for the illuminated solar cells are mainly determined by the I_{sc} and a modest decay of Fill Factor.

In order to deepen our understanding of the mechanisms behind this photo degradation, we have analysed the J-V characteristics of the illuminated cells in order to find similarities between their electrical behaviour and known defects in solar cells. The development of the I-V characteristics of the cells is presented in Figure 4.3:

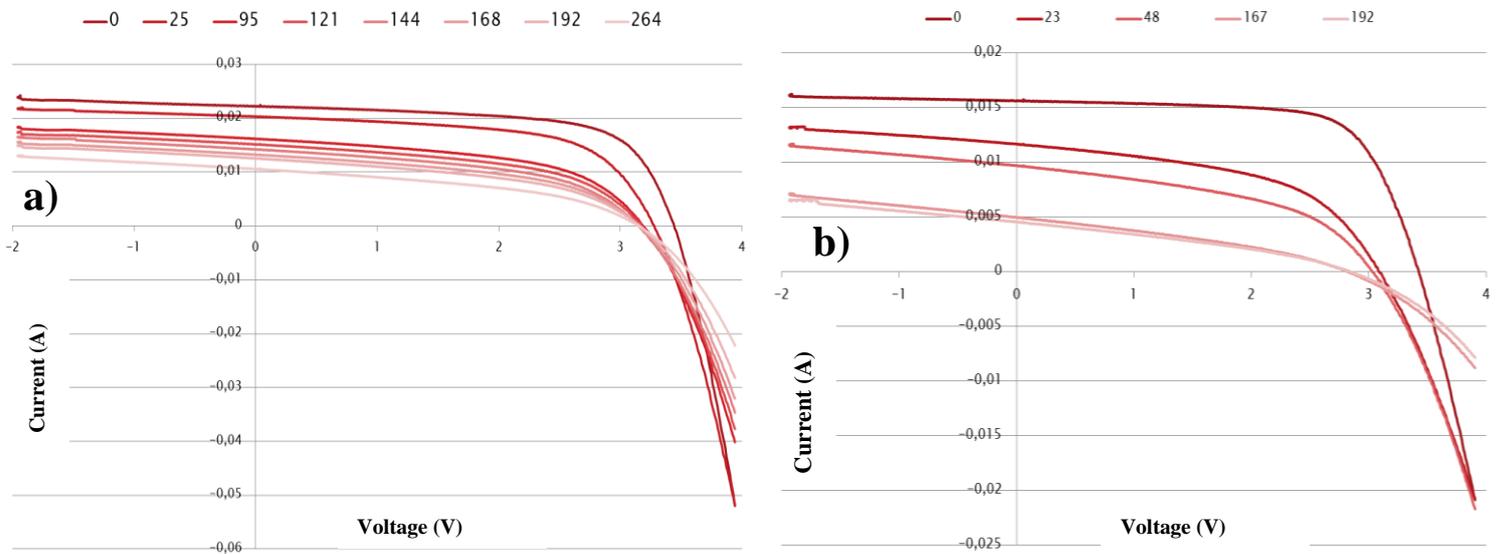


Figure 4.3: I-V characteristics of the photo degraded opaque cell (a) and a transparent cell (b)

The J-V characteristics of the photo-degraded cells show an initial drop of V_{oc} after 24 hours. Then, the V_{oc} remains constant. On the other hand, the short circuit current drops continuously, with a clear decrease of the shunt resistance. These J-V characteristics are similar to organic solar cells with an increased trap state density. Indeed, the increase of trap states would explain the losses of current extraction and the

increase of leakage current. Moreover, these trap states can be induced by the photo-oxidation of the active layer [26].

Figure 4.4 presents the modelled J-V characteristic of an organic solar cell with different electron trap states density. This model has been performed using the program General-purpose Photovoltaic Device Model (GPVDM) [33]. This program uses a finite difference approach to solve both electron and whole drift-diffusion equation. To model the different electron trap state, we use the electron tail slope. An increase of this slope is linearly related to an increase in the trap states.

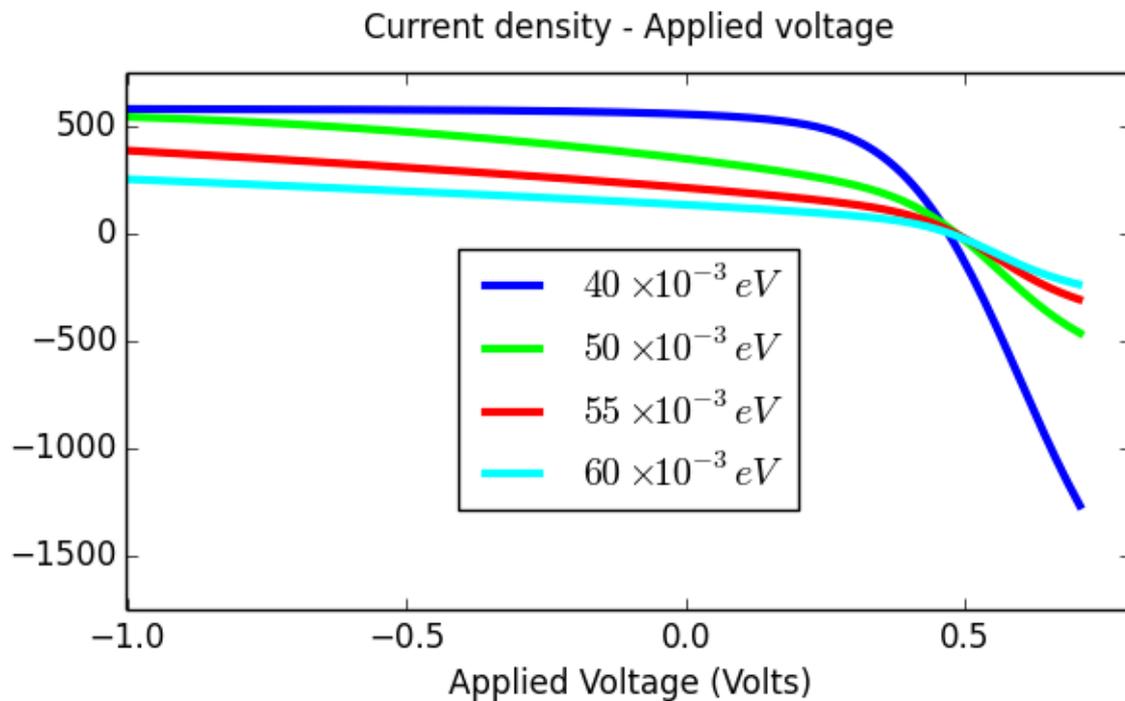


Figure 4.4: Simulated J-V characteristics with different trap densities.

The model shows a similar behaviour as the photo degradation of the cells. This supports the previously cited effect of the photo degradation upon the active layer. The light induces the photo oxidation of the active layer, thus increasing the amount of trap states.

III. Electroluminescence imaging of photo degradation:

The data presented in the previous section show the global change of the solar cell's specific parameters. However, it would be highly desirable to correlate the loss in device performance with local changes in device behaviour. To further elucidate the effect of photo degradation on local change of OPV device performance, ELI and DLIT were applied on the devices.

At first, the ELI measurement of the opaque non-encapsulated cells (Figure 4.5) will be discussed. It has previously been discussed and stated that EL irradiation originates from charge transfer state luminescence. Therefore, the signal retrieved by the camera is correlated to the CT state recombination occurring at the given current. The images below were taken at 20mA ($\approx I_{sc}$) forward bias with one-minute exposure time. All pictures are at the same scale.

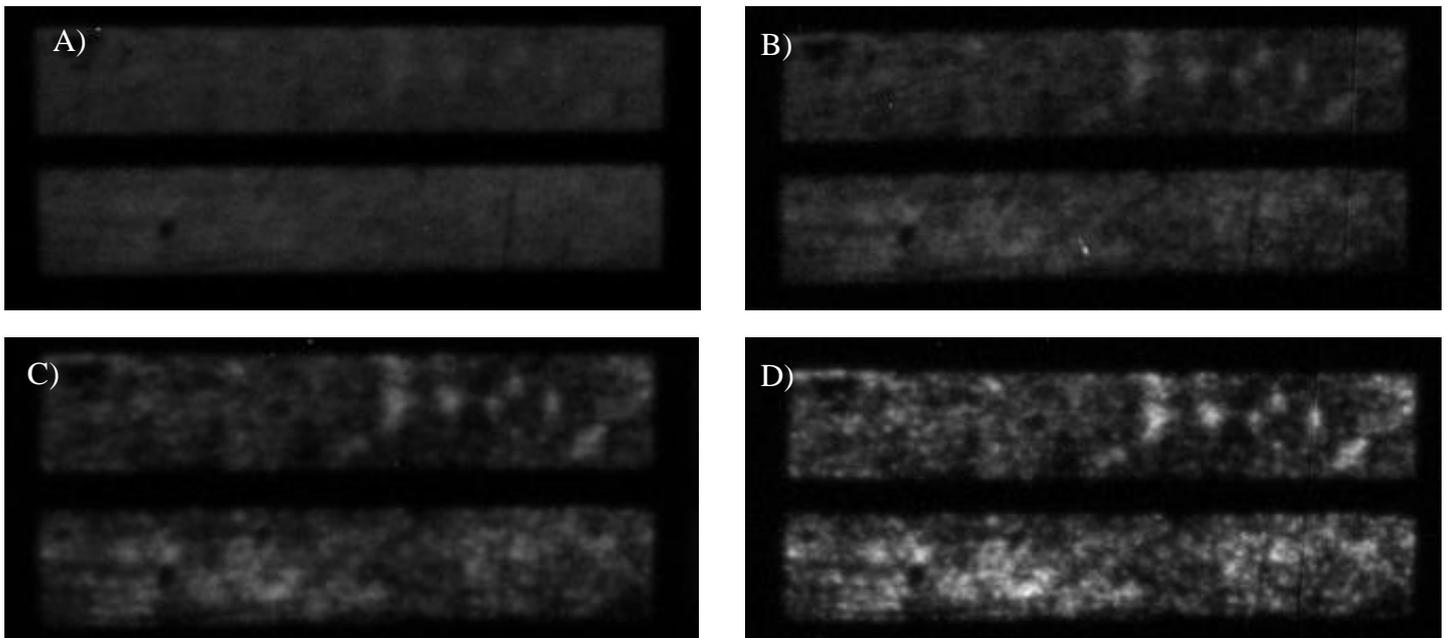


Figure 4.5: EL images of a photo degraded opaque cell at different times. A: Fresh sample, B: After 72hours of light exposition; C: after 168 hours; D: After 240 hours.

The images above show a homogenous decrease of luminescence at first, before the appearance of some bright spots. The first phenomenon may have been caused by an increase of non-radiative recombination which would have decreased the radiative one.

The aforementioned explanation may be applied to justify the increase in the trap states' density. The degradation's homogeneity could be explained by the homogeneous penetration of oxygen into the cell, and the homogeneous illumination. An overall calculation of the illumination coming from the cell is presented in table 4.1: this calculation serves as a quantification of the cells' luminescence.

Table 4.1 Electroluminescence numerical analysis

Hours	El current (mA)	Measured Voltage	EL count	Normalised EL count
0	20	3,4	2,78E+08	1
72	20	3,5	2,09E+08	0,75
120	20	3,63	2,51E+08	0,9
168	20	3,7	2,72E+08	0,98
240	20	3,87	3,52E+08	1,16

It is clear from the table above that luminescence drops due to photo degradation, before increasing due to bright spotting. The bright spots that appear in the cells are due to a slower degradation mechanism. The latter is not solely related to illumination – in fact, the bright spots are present as well in the EL images of the dark degraded cell (Figure 4.6). This phenomenon will be discussed more in detail in the chapter about heat-triggered degradation.

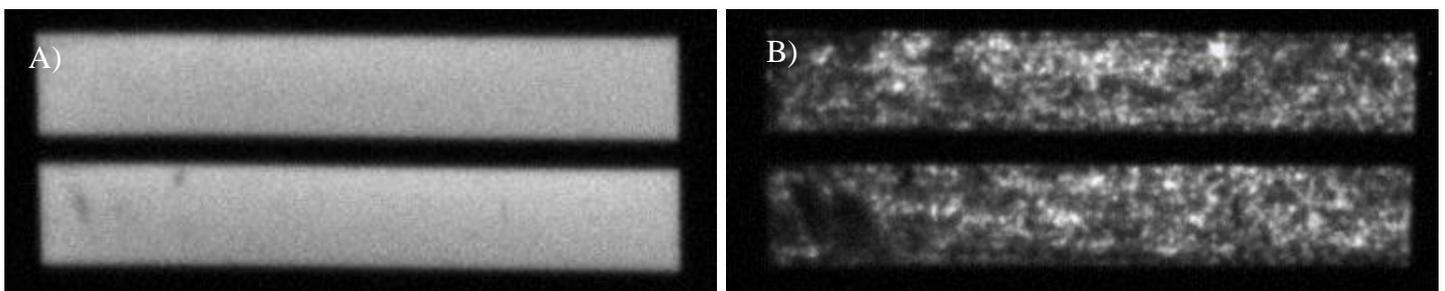


Figure 4.6: El images of a self-degraded opaque cell at different times. A) Fresh, B) After 212 hours.

Transparent cells are more affected by light than opaque cells. The EL images of the photo-degraded transparent cells show a bigger drop of luminescence (Figure 4.7). This can be explained by the permittivity of the electrode used in both cases. In fact, the metallic electrode constitutes a better barrier against oxygen than the transparent one.

Thus, oxygen ingress into transparent cells is more important than the opaque ones, hence a larger photo oxidation for the transparent sample.

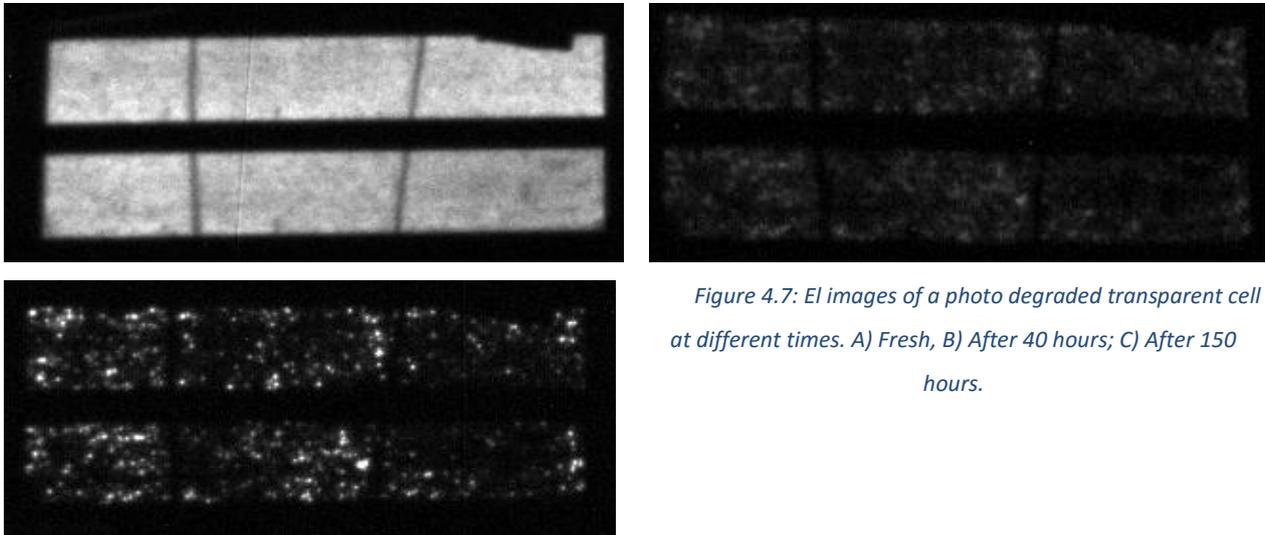


Figure 4.7: EL images of a photo degraded transparent cell at different times. A) Fresh, B) After 40 hours; C) After 150 hours.

IV. Thermography imaging:

In order to have a better understanding of the localised degradation happening in the solar cell, a thermography measurement has been performed on the samples. The thermography provides complementary information about energy losses within the cells. The images were very similar to the electroluminescence images, but they help perceive the issue from another point of view: while electroluminescence is mainly related to radiative recombination happening within the cell, thermography provides a better understanding of energy losses within the cell.

The thermography image of the non-encapsulated opaque cell degraded under one sun (Figure 4.8) demonstrates the same features as the cell on Figure 4.5. Bright spots can clearly be distinguished, as they appear as hot spots in the thermography. However, effects of the drop of luminescence in the thermography images are not observable. Therefore, while thermography constitutes a powerful tool to distinguish heat-related losses, it lacks in terms of featuring changes in radiative recombination.

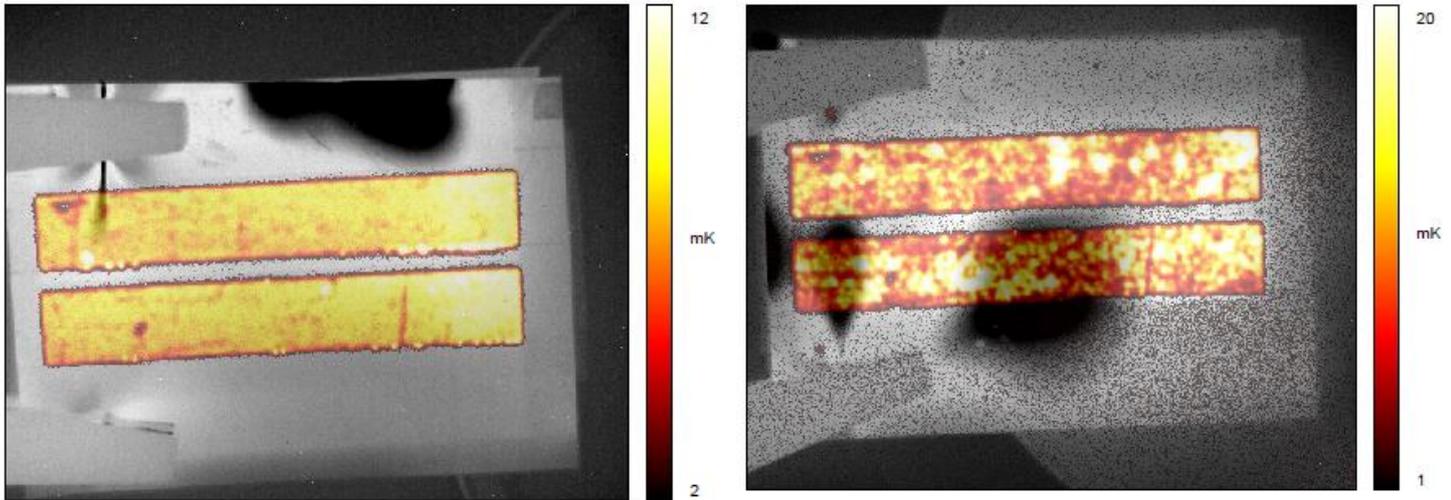


Fig 24: Amplitude Thermography images of a photodegraded cell at different degradation. A fresh sample, B after 167hours

V. Conclusion

In a nutshell, short circuit current is the fastest degrading parameter for non-encapsulated cells. Alongside, encapsulation helped improving the solar cell's lifetime. Thus, the presence of oxygen or water in the air has a great effect on the degradation as well. Taking into account the I-V characteristic evolution, we could infer that the main degradation is due to the increase of trap states in the active layer; these trap states being introduced by photo-oxidation of the active layer. Furthermore, based upon the imaging technics, we could presume that two main degradation mechanisms happen with the exposure to sun and air. The first constitutes the photo-oxidation of the active layer, which increases the amount of trap states, thus reducing the short circuit current. The second corresponds to the oxidation of transport layers, which results in an injection or extraction barrier.

This work helped identifying the main degradation path for the cells under light; as a further step to improve the understanding of the phenomena, one could look at what happens at a molecular scale, and determine what are the reaction that causes the trap formation or the barrier formation.

Chapter 5 – Heat and oxygen-related degradation of tandem cells

This chapter presents a study of the degradation of organic solar cells under dry heat condition. It begins with a presentation on the evolution of electrical characteristics of the cells with the degradation, before attempting to understand the degradation's origins with medialisations and imaging technics.

I. Device characteristics and aging conditions

The used devices for this experiment are similar to the ones used for the photo-degradation experiment. The samples correspond to a tandem small molecule cell deposited on PET with encapsulated and non-encapsulated ones. In order to study the effect of heat and oxygen on the cells, we aged them on dry heat conditions at 85°C. This aging condition is similar to the fast aging setup used to certify the lifetime of a solar cell.

II. Electrical characterisation

V.1. The experimental results

The degradation of solar cells is investigated by measuring the J-V characteristics of the samples at different times of their degradation. The fingerprints of the relevant characteristics are presented in Figure 5.1. The measurements were done at 1'000W/m² intensity.

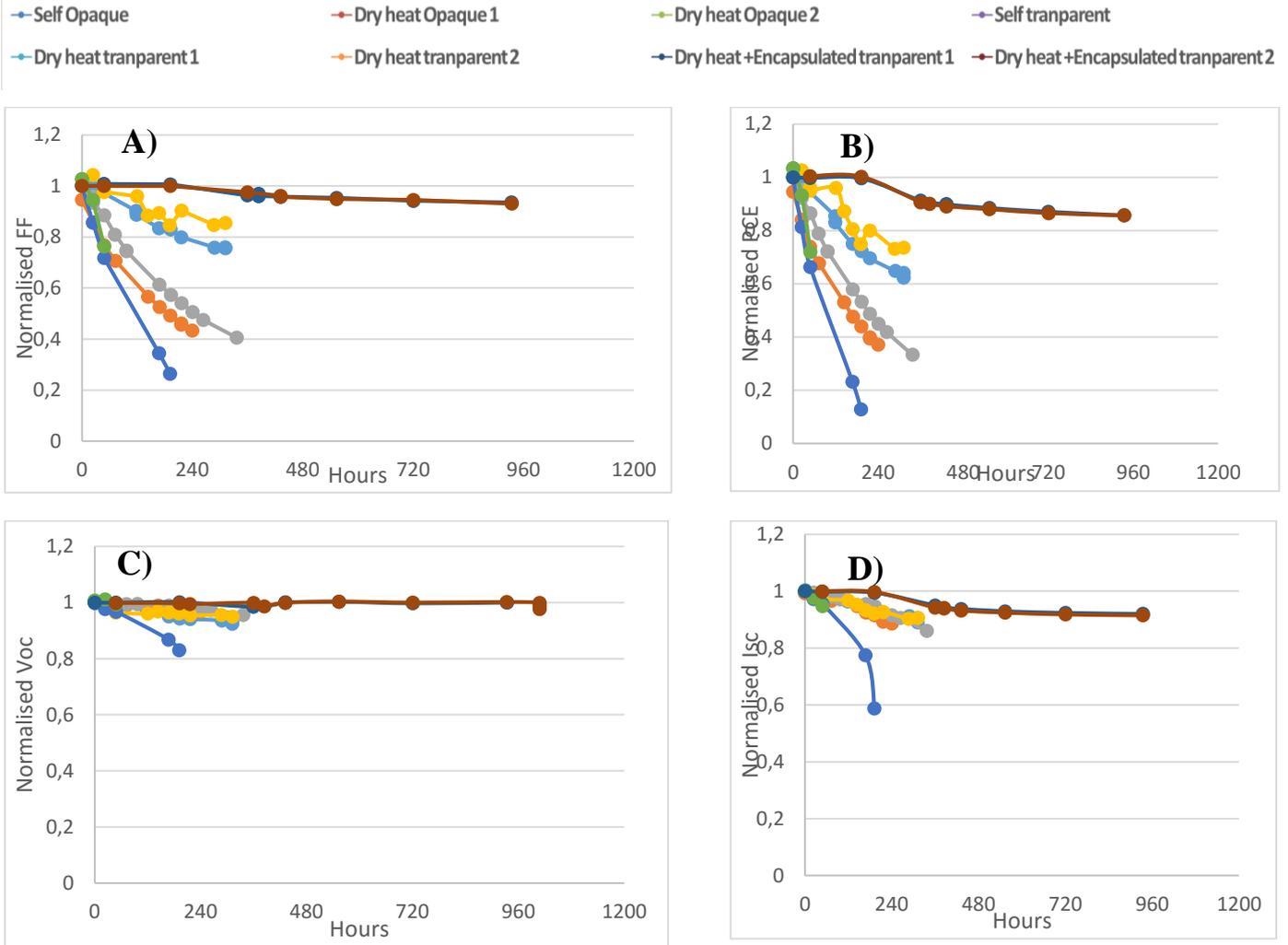


Figure 5.1: Dry heat aging of tandem solar cells. The graphs show the long-term temporal evolution of FF(a), PCE(b), Voc(c) and Isc(d).

Under dry heat condition, the non-encapsulated cells lose more than 50% of efficiency after 200 hours. A drop in the fill factor mainly affects the loss in power conversion efficiency. In fact, both the Voc and the Isc remain stable, but the fill factor dropped to 70% in less than 100 hours. The effect of encapsulation is evident: the latter improves the lifetime of cells by order of magnitude. Moreover, regarding these cells, a drop in the FF, Isc and PCE is observable after 240 hours of aging; before then stabilising again. This drop may be due to a layer which reacts quickly with oxygen: as soon as oxygen is reached, a more stable layer is formed. A drop in the Isc and Voc after 48 hours of exposure is observable. This drop may be associated to the important loss in fill factor, as it reaches values of less than 40%.

Figure 26 shows the J-V characteristics of the non-encapsulated solar cell at different degradation times. These graphs show the formation of an S-shape near the Voc, thus justifying the drop in fill factor. The presence of this kink in the characteristics was mainly due to injection problems. In fact, the observed phenomenon may be explained by an injection barrier.

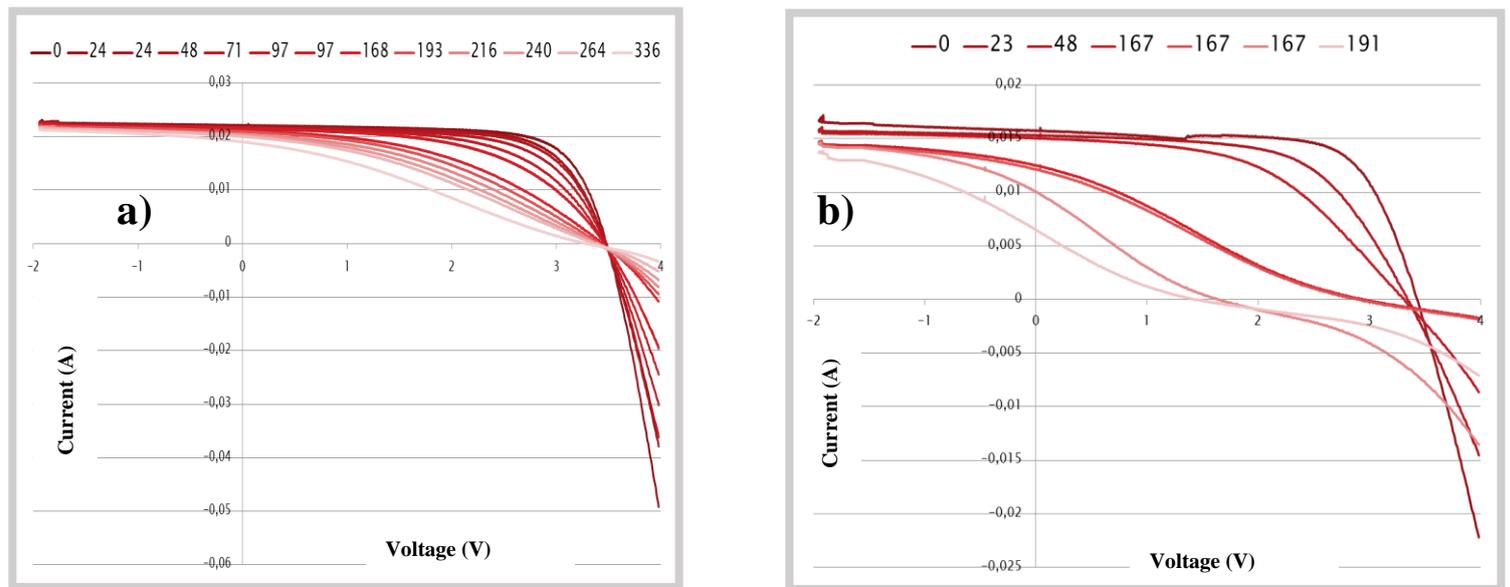


Fig 5.2: I-V characteristics of the dry heat degraded opaque cell (a) and transparent cell (b)

The transparent and opaque cells degrade at different rates, as the transparent cell degrades much faster. The kink in the I-V characteristic is more significant in the transparent cells. The degradation does not solely affect the fill factor of the transparent cell, but the Voc and Isc as well. Moreover, a drop in the photocurrent is observable, which is more pronounced for transparent cells. This phenomenon is not solely related to injection failures, but accounting other degradation mechanisms as well.

V.2. I-V characteristic simulation

In order to clarify the origins of the observed S-shape on the J-V characteristic, we modelled different injection failures which can induce the same behaviour using the GVDM program. The degradation that fitted the most our observation was an injection barrier, either at the whole transport layer, or simply the electron transport one. This barrier could be due to a mismatch in the energy level between the bulk heterojunction

and one of the aforementioned layers. To model this mismatch or the change in the energy level of those layers, the charges at the back electrode have been changed.

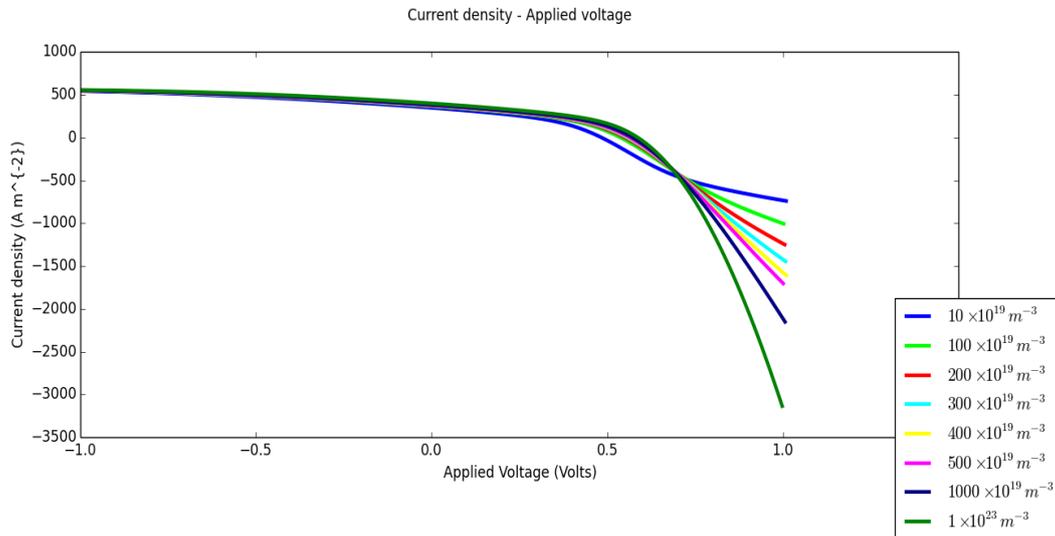


Figure 5.3: Simulated J-V characteristic with different barriers at the back electrode

Figure 5.3 shows the model used to understand the origin of the S-shape. This model confirms that the origin of the losses in the fill factor is due to a deterioration of the transport layers, and more accurately a change in their energy levels. The oxidation of one of these layers induced a change in the energy levels, and the high temperature had activated oxidation. The oxidation of the transport layer does not explain all the features observed in the J-V characteristic: the drop in the photocurrent is not observed in the model. Thus, we may infer that other degradation mechanisms occur in the cell, but at a slower rate.

V.3. Extraction, or injection barrier?

Using the simulated I-V characteristic, we determined that the drop in the fill factor's origin for the dry heat-degraded sample is an injection or extraction barrier. Having a knowledge on which barrier is causing the observed S-shape would be extremely useful to identify the degrading layer. In fact, identifying and determining the barrier type would very much assist to understand if the defect is present at the electron transport layers, or the whole-transport ones.

To differentiate the extraction from the injection barrier, the method proposed by Tress and Al is used. The latter lies upon measuring the I-V characteristic of the cells at different light intensities. The authors discovered that the barriers behave differently when changing the light intensity. In fact for the injection barrier, the main parameter that changes with light intensity is the Voc; but for the extraction barrier, the main change is due to the S-shape that gets more pronounced with higher intensities. Furthermore, one may use the simulated data presented in their paper to further characterise the barrier.

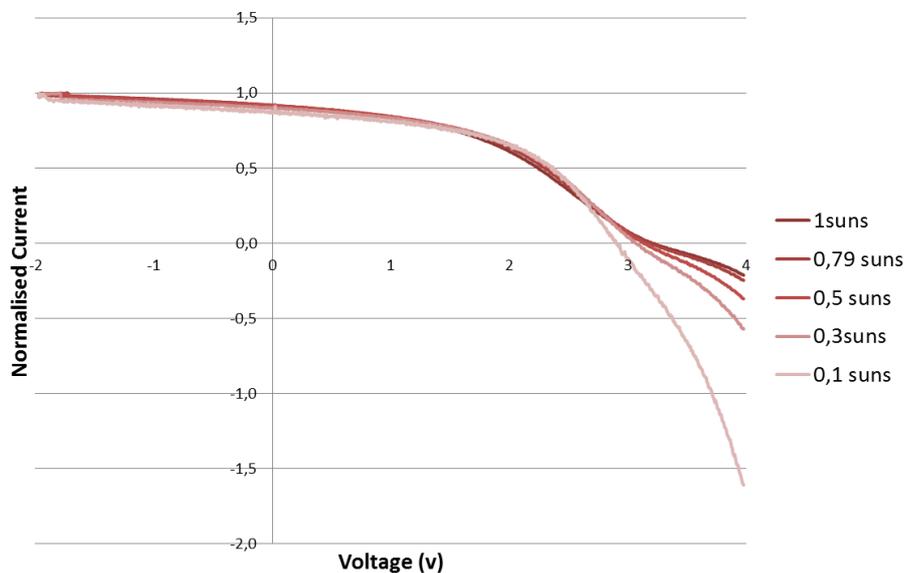


Figure 5.4: Normalised I-V characteristic for degraded opaque cell at different light intensities

Figure 5.4 presents the I-V characteristic of an opaque cell degraded under dry heat conditions. The observed behaviour is very comparable to cells with an injection barrier. In fact, the I-V characteristics are extremely similar, except when they are close to the Voc, where there is a very particular behaviour of cells with injection barriers. We may therefore conclude that aging organic solar cells at dry heat condition cause the formation of an injection barrier.

The fact that the encapsulating increases the solar cells' lifetime proves that oxygen plays a major role in the injection barrier formation. Moreover, it is known that oxygen can p-dope organic materials. Presuming that the main degradation is due to the p-doping of a transport layer within the cell, we may infer that the degrading layer is an

electron transport layer. Indeed, the p-doping of a semi-conductor would cause its conductive band (or LUMO level) to get lower, thus creating a barrier for the electron injection. The p-doping for a hole-transport layer would then cause an extraction barrier.

VI. Electroluminescence imaging of dry heat degradation:

The images presented in Figure 5.5 show the local behaviour of the opaque cell upon aging in dry heat conditions. The images show an inhomogeneous degradation of the cell, as we observe spots that get darker, and others that get brighter. The difference between the bright and the dark spots gets bigger with time. Finding the origin of this inhomogeneity is extremely challenging: in fact, based upon the previous chapter, degradation comes from the transport layers. Therefore defects in the deposition of these layers or defects within the barrier performance for oxygen of the other layers could lead to these features.

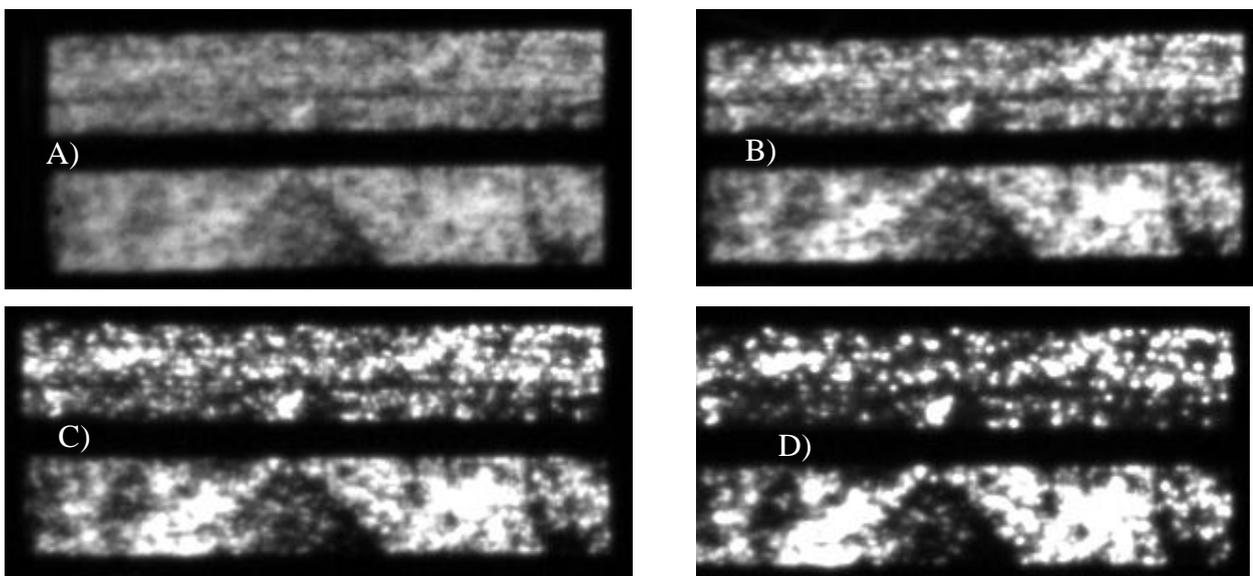


Figure 5.5: EL images of a dry heat degraded opaque cell at different times. A: Fresh sample, B: After 72 hours of light exposition; C: After 168 hours; D: After 240 hours.

The inhomogeneous degradation observed in Figure 5.4 proves the importance of a two-device model to approach the experimental data in order to obtain a better understanding of the phenomenon. Tress and Al have treated the issue of two devices with different injection barriers, and found that the cell with a higher injection barrier

has more recombination within the active layer [33]. We may then infer that these bright spots are the degraded spots. In fact, microscopic images of these spots (Figure 5.6), show a local change in the morphology of the film. These images greatly support the assertion of the degraded nature of these spots.

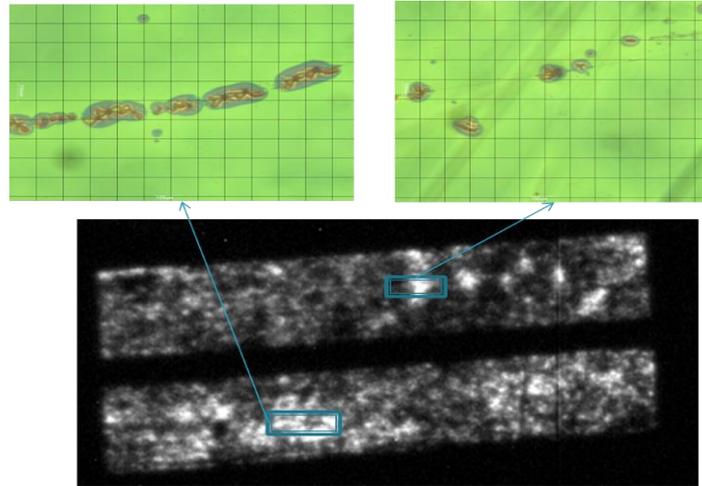


Fig 5.6: Microscopy images of the bright spots for a dry heat degraded opaque cell.

Assuming that the bright spots are caused by the degradation of one of the transport layers, we may use the electroluminescence images to follow the samples' degradation by analysing these spots. To do so, all signals greater than the maximal signal of the initial pictures have been taken out of the EL images. The results of these calculations are presented in Figure 5.7

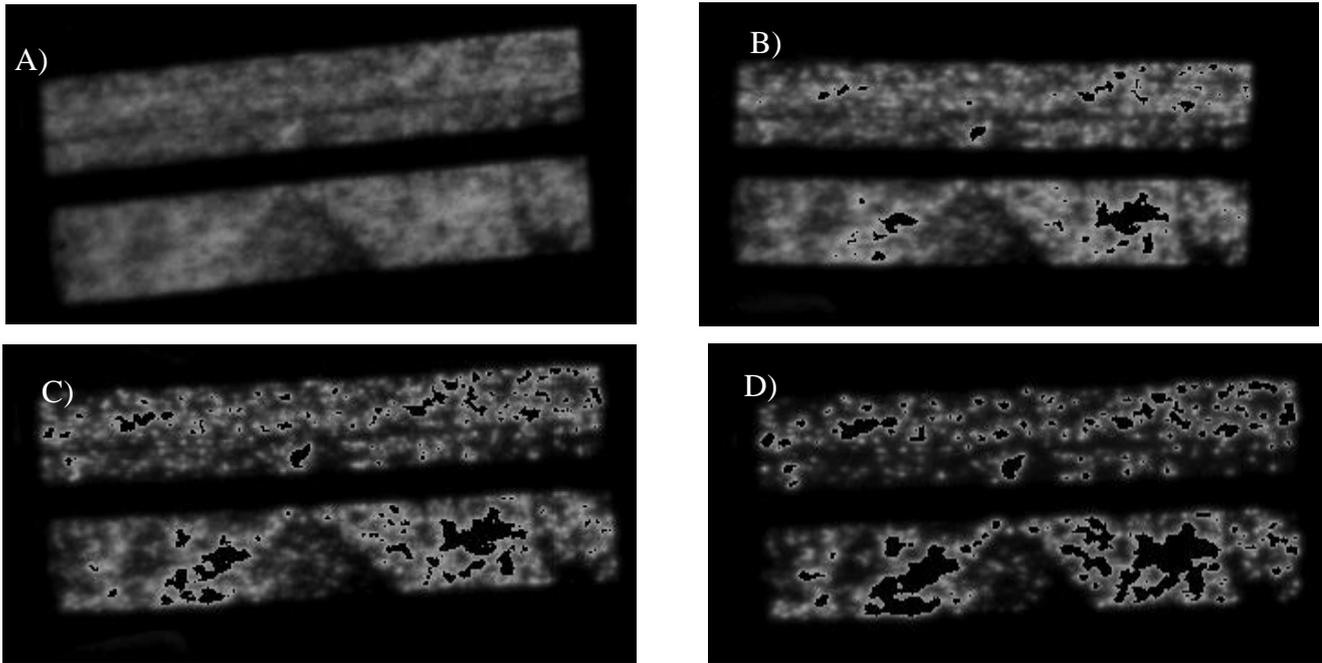


Fig 5.7: EL images of a dry heat degraded opaque cell at different times without the bright spots. A: Fresh sample, B: After 72hours of light exposition; C: After 168 hours; D: After 240 hours.

The expansion of the degradation cited above from the images of Figure 30 may easily be monitored. Indeed, the dark spots get wider with time. The defects causing the degradation, which starts from those spots in particular, could be due to a pinhole in the back contacts, which then lets oxygen flow through. Moreover, presuming that these spots are dead spots, we could correlate the overall luminescence emission to the efficiency of the cell, as demonstrated in Table 5.1.

Hours	'EL'	Normalised EL	PCE	Normalised PCE
0	317204300	1	5,4	1,00
72	315540607	1,01	4,4	0,81
96	275296190	0,88	3,7	0,69
166	204462915	0,66	2,5	0,46

Table 5.1: Analytical analysis of the EL pictures

VI.1. Spectrally-resolved EL

The electroluminescence observed in the EL picture principally originates from recombination at CT states. However, changes in energy level of the transport layer could induce an injection to the active layer at a higher energy level. Thus, the luminescence could originate from CT states at a higher energy level than those of the fresh one, or even from the exciton state. Therefore, we have been looking at the spectrally resolved luminescence of a fresh and a dry heat degraded sample.

Figure 5.8 presents the normalised spectrally resolved electroluminescence of two fresh samples and two degraded samples under 20mA forward bias. The degraded samples have been kept at dry heat condition for 48 hours. No significant difference between the degraded and fresh samples may be observed, as the emission remains at the same wavelength. Therefore, the only difference between the bright and dark spots observed before is the recombination rate.

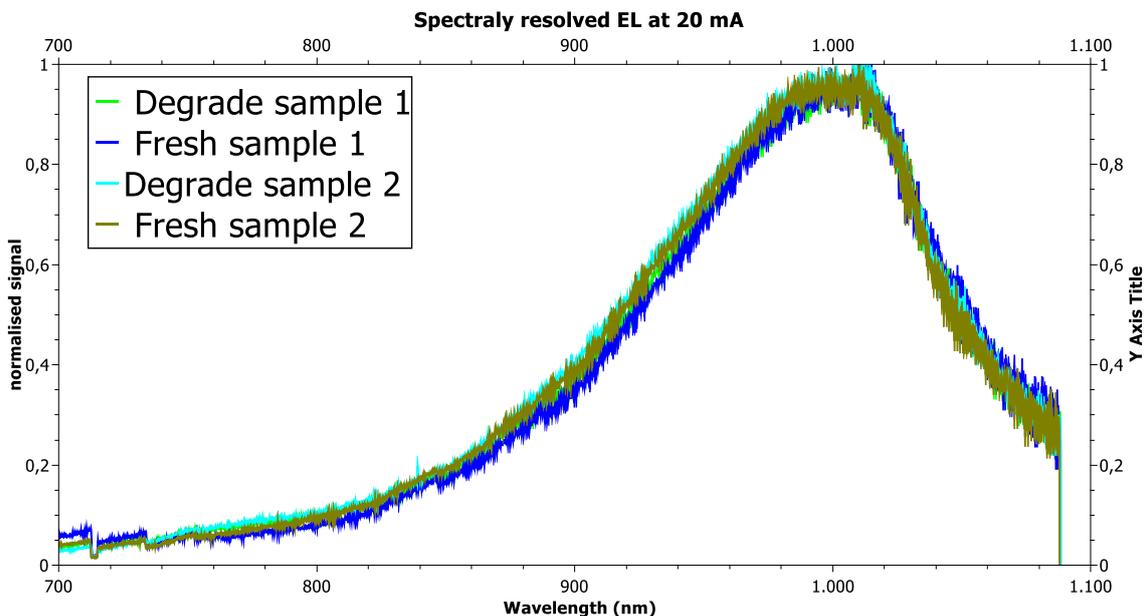


Fig 5.8: Spectrally resolved EL for fresh and dry heat degraded samples.

Moreover the peak of the electroluminescence is at higher wavelength than the gap of any of the active materials used, thus it is indeed an emission from the Charge transfer state.

VII. Conclusion

Throughout this study, we looked at the degradation of organic solar cell under dry heat condition (85°C). We used a dry heat condition to focus on the effect of oxygen and high temperature. According to electrical characterisation, we observed the effect of encapsulation on the cell's lifetime. Thus, external agents and mainly oxygen cause the main degradation.

Moreover, the major losses in PCE are due to a drop in the fill factor, which have been caused by a barrier formation at some interface. Using the model, we may infer that this barrier is either an injection or extraction barrier at the interface between the absorber and the transport layers. From the analysis of intensity dependent on I-V characteristics, we concluded that the barrier was an injection barrier, and we suspected the electron transport layer to have oxidised. Electroluminescence imaging provides a more localised view of the degradation. We observed a rather inhomogeneous degradation, meaning that oxygen does not penetrate uniformly to the cell, or that the cell does not react evenly to it. Therefore, using these technics, we can identify the weakest spots in the cell, and work on improving their stability. In order to understand the origin of this inhomogeneous degradation, we are planning to analyse the degradation of the transport layers alone. This experiment would help us characterise the weakest link and work on improving it stability.

Chapter 6 – Conclusion

To conclude, this study puts into evidence various aspects of organic solar cells' degradation. The work focuses on how to use characterisation technics to follow up and understand degradation mechanisms. To achieve this goal, local cell information about different loss processes provided from imaging methods, such as DLIT or ELI, were set in relation to electrical characterisation experiments of the investigated test samples. The combination of imaging experiments and electrical characterisation experiments as a function of different degradation stages was remarkably useful, enabling the characterisation of several degradation paths within organic solar cells.

The first step was to associate the degradation mechanisms observed in solar cells with the information provided by characterisation technics. Using the images observed in ELI and DLIT, we were able to link defects with their location. In the second part, we presented a study of light-induced degradation in a tandem small molecule solar cell. Using different characterisation technics, we found that the main degradation is related to the presence of air or oxygen in particular. Moreover, it has been observed that losses in the cells' efficiency may be due to the increasing number of trap states, which hinder the charge collection. In the third part, we studied the effect of heat and dry air on tandem small molecule solar cells. We concluded from this work that cells degraded at dry heat condition suffer from the formation of an injection barrier at the electron transport layer. Furthermore, the degradation appeared to be inhomogeneous.

All in all, this work provides an insight of the degradation paths in small molecule solar cells. However, on the other hand, our study raises many questions which remained unanswered by the end of this thesis. In fact, a better understanding of the chemical reactions, inducing the trap states' formation, remains unanswered. The origins of the inhomogeneous degradation observed in the dry heat-degraded cell remain as well a mystery, thus implying the urgent need for further research on this area as a whole in the future.

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