

# **MODELLING THE EFFECTS OF THE ANODE WORK FUNCTION IN PPV LED**

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Transparent conducting oxides are widely used as the transparent electrode in polymer light emitting diodes (PLEDs). The physical properties of these materials and consequently device performance strongly depend on their processing and surface treatment. The injection of charge from the transparent electrode into the polymer layer occurs by tunnelling through a potential barrier from the electrode to molecules close to it. This barrier is influenced by the difference in the relevant energy levels of electrode material and polymer molecules, the external applied potential, the Coulomb potential of the charges present in the polymer layer and the potential of their image charges on the electrodes, and may also be altered by electrode degradation effects. A better understanding of the effect of varying this potential barrier on the functioning of PLED is necessary to achieve further improvements in these applications. Here we present a theoretical study of the influence of changes in the potential barrier at the transparent electrode, on bipolar charge evolution through thin polymer layers, in the absence of defects and impurity states, while the other electrode functions as an ohmic contact. Results of a mesoscopic model provide insight into bipolar charge injection, charge and recombination distribution throughout the polymer layer, and may suggest new materials and processing methods to optimize these optoelectronic devices.

**Keywords:** Mesoscopic modelling, Indium tin oxide, anode work function, polymer LED, injection and recombination efficiency, PPV

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## 1. Introduction

One of the most usual optoelectronic devices using a semi-conducting polymer as an active layer is a polymer light emitting diode (PLED). This device uses a polymer thin film sandwiched between two electrodes where the injecting electron-contact, cathode, is a metal or a combination of metal layers, and the injecting hole-contact is a transparent conducting oxide like indium tin-oxide (ITO). The reason for the choice of this kind of electrodes is related to the similarity between their Fermi energy ( $E_F$ ) levels and the conducting levels of the polymer chains that form the active layer. One of the problems with this type of device is related to the mismatch between the contact energy levels, that is, Schottky barrier height, which can reduce the internal quantum efficiency by reducing the ratio between the formed excitons and the injected carriers. In the case of the anode contact, that problem has its origin in the difference between the Fermi level of the anode and the highest occupied molecular orbital (HOMO) of the polymer chains. The barrier height at the electrode/polymer interface depends, among other factors, on the physical properties of the electrode (e.g. texture, presence of impurities, work function, etc) and the polymer chains (e.g. intra-molecular charge mobility, ionization potential, electron affinity, etc), which can influence the operation of PLEDs [1].

ITO is a conductive electrode and transparent to visible light, and so it is widely used as anode. However, ITO is not an ideal anode because its physical properties depend on the fabrication process and its stoichiometry is not well defined [1]. On the other hand the

morphology and texture of the polymer network near the electrode contact can depend on the process chosen for the deposition of the polymer layer. While there have been attempts to investigate experimentally the influence of these factors on hole injection into polymer layer, a clear picture has not emerged because of the difficulty in determining (and impossibility of controlling) the exact morphology near the electrode/polymer contact and the anode work function [2, 3]. In the work presented here we use computational techniques, in particular mesoscopic modelling and simulation, to gain insight into how modifying the anode work function influences bipolar charge injection and recombination, particularly near the electrode/polymer interfaces, within a polymer film with controlled morphology.

## **2 . Device model and simulation method**

The present simulations are based on an improved version of the mesoscopic modelling technique developed by us over the past few years. A detailed description of the original model can be found in refs. [4, 5]. In this section we will only describe the modifications that were made to account for the electrodes, which were not included originally. Assuming perfect electrodes with no impurities or defects near their surface, we consider that the injection process occurs by tunnelling. To calculate the potential barrier near the electrodes we modelled the polymer sample as a network of stiff-chain segments with different lengths. Each segment has its own physical properties that depend on its length [4] and that consequently will limit the potential barrier near the electrode/polymer interface. The same physical properties will also limit the thermally activated hopping process of charge carriers between polymer strands, and in this way will rule charge distribution in the polymer layer.

As a consequence, the space charge distribution in the polymer network will influence the electric potential near the interface, and thus the potential barrier height. Since both electrodes are perfect, the only physical property that we need to consider for each one of them is its work function. Since the electrodes are conductors we have to regard how the charge distribution in the polymer layer influences them, by taking into account the effect of image charges in the electric potential near the electrode/polymer interfaces due to the polarization of both electrodes. In our model we allow that once a charge has been injected into a monomer of a strand near the electrode, the influence of charge distribution in the polymer film and the image charges can allow that the charge returns to the electrode, a process known in the Onsager Theory [6]; when this happens we have a backflow current. By considering the influence of all these aspects we can conclude that near the electrode/polymer interface we will have a cascade of potential barriers that can only be understood at the mesoscopic scale.

In our mesoscopic simulations we use an active layer of poly(p-phenylene vinylene) (PPV), with a thickness of 100 nm, where the stiff-chain segments with variable length are parallel to the electrodes, in the same way that happens when a polymer film is deposited by spin-coating on ITO electrodes [7, 8]. We have assessed the influence of changing anode work function values on injection and evolution of bipolar charges through the polymer layer for two different applied external electric fields. The cathode work function was chosen so that the potential barrier height at cathode/polymer interface (defined as the difference between the cathode work function and the average electron affinity of the polymer strands) is small enough ( $0.25 \times 10^{-19} \text{J}$ ) for electrons to tunnel through it easily.

Since in our model multiple charges (electrons and/or holes) can return to the electrode where they came from, the rate for injection hole – electron pairs into the polymer layer is not constant. On the other hand, the number of charges that can jump from the electrode to the polymer is limited by the barrier height. By changing the work function of the anode we alter the number of holes that can jump to the polymer film, and thus alter the charge distribution and the electric potential that they create near the anode/polymer interface. Therefore, the competition between current flow, charge accumulation and recombination can be affected. By increasing or reducing the anode work function ( $\Phi_A$ ), compared to the average ionization potential of the polymer chains ( $\bar{I}$ ), we alter the height of the potential barrier near the anode/polymer interface. When  $\Phi_A < \bar{I}$ , there is a potential barrier formed for hole injection near the anode/polymer interface. When the opposite occurs ( $\Phi_A > \bar{I}$ ), hole encounters negative potential barrier (ohmic contact) and hole injection will just be limited by space charge distribution in the polymer network. In this paper we concentrate our study on the effect of changing the anode work function compared to the average ionization potential of the polymer strands and since we will not study other effects we will call this difference the potential barrier height at anode/polymer interface without confusing the reader.

### **3. Results and discussion**

When the barrier height at anode/polymer interface is higher than  $1 \times 10^{-19} \text{J}$  the number of electrons injected is greater than the number of holes injected, but the total number of injected charges practically stays unchanged (see Fig. 1). This behaviour is mainly

determined by two effects. The first one is related to the potential barrier at the cathode/polymer interface. Although the height of this potential barrier is very small, which will allow that electrons go through it easily, percolation of electrons is limited by their accumulation near the cathode/polymer interface. As a result electron injection is space charge limited. The second is related to the height of the potential barrier at anode/polymer interface that will limit the number of injected holes. In this case, the strength of the local electric field near the anode, due to the applied electric field and the electron distribution effects, will allow that some holes tunnel through the potential barrier. The hole injection is mostly dictated by the distribution of electrons in the polymer layer, but electron injection does not depend on the changes that occur at anode/polymer potential barrier. Therefore an increase in the strength of the applied electric field will increase the number of both electrons and holes injected, as we can see in Fig.1. This will have some implications on the distribution of the recombination events through the polymer layer. Since hole-injection is limited by the presence of electrons near the anode/polymer interface, this will lead to a significant number of recombination events near the anode when the potential barrier for hole injection is higher than the potential barrier for electron injection (see Fig. 2). In this case there is a competition between electron flow towards the anode and charge recombination close to the anode/polymer interface. As the potential barrier at anode/polymer interface increase the number of holes injected will depend on the number of electrons accumulated in that region. On the other hand, the number of electrons collected by the anode will depend on the number of recombination events due to the hole injection. As a result the number of recombination events near the anode/polymer interface reaches a maximum when the barrier height for hole injection is of the order of  $1 \times 10^{-19} \text{J}$ .

The reason for this non-intuitive result lies on the properties of the polymer chains. Since the ionization potential of the polymer chains depends on their length [4] and the length of the chains within the polymer layer has a Gaussian distribution with a mean value of 5 monomers, this will lead not to one barrier but several potential barriers with different heights near the interface, as the work function of the anode changes.

When the potential barrier at anode/polymer interface tends to vanish, the number of injected charges (either electrons or holes) increases for the two applied electric fields considered on this work, as shown in Fig.1 Now, the number of electrons and holes injected in the polymer layer is similar, which gives rise to their accumulation near the injecting electrode. Fig. 3 shows the distribution of recombination events inside the polymer layer for the two different applied electric fields in presence and absence of a potential barrier at anode/polymer interface. When the potential barrier at both electrode/polymer interfaces is negligible, the region where most of the recombination events take place is shifted to the middle of the polymer layer. In this case, the injection of charge from the electrodes is limited by space charge distribution, and the way that charge is distributed in the polymer layer depends on the hopping of charges between neighbour polymer strands. Our polymer network does not have any structural defect that can lead to an effective trapping of charge, and so the hopping process is limited by the internal electric field and the properties of the polymer chains. Therefore, when an injected charge jumps between neighbour chains towards the opposite electrode, the probability of meeting a charge of opposite sign on the same chain increases in the centre of the polymer film. As a consequence, there is a maximum in the recombination efficiency on that region. When both electrode/polymer

contacts are ohmic, the number of injected charges that undergoes recombination near the anode decreases significantly, as can be seen in Fig. 2 and Fig. 3. This spatial distribution of recombination efficiency will have implications in the PLED efficiency since there is a decrease in the number of recombination events in the region close to the anode and an increase in the centre of the polymer layer which will reduce the influence of the electrodes in exciton quenching.

#### **4. Conclusions**

Controlling charge injection into polymer layer is one of the key factors for achieving a good efficiency in PLEDs, and understanding charge behaviour at electrode/polymer interfaces is the first step to achieve this control. Using a mesoscopic modelling we have demonstrated that, controlling the work function of the electrodes can be a way for improving the efficiency of this kind of devices. Although our simulation conditions are far from real, it seems clear that a decrease in the number of charges that undergoes recombination near the electrodes can be achieved by using ohmic contacts. This will reduce the effect in exciton quenching by the electrodes and improve exciton formation in the centre of the polymer film.

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Figure 1 – Number of charges (electrons and holes) injected into the polymer layer when the potential barrier height at anode/polymer interface is changed. The lines are just a guide to the eye.

Figure 2 – Recombination efficiency (proportion of injected electron-hole pairs which recombine) near the electrodes (cathode and anode), for two different applied electric fields (200 MV/m and 300 MV/m), as a function of the potential barrier at anode/polymer interface. The lines are just a guide to the eye.

Figure 3 – The distribution of recombination efficiency along the direction perpendicular to the electrode surfaces (defined as the model axis), when the potential barrier at anode/polymer interface is  $1.72 \times 10^{-19} \text{J}$  (triangles) and for an ohmic contact (squares).

These results were obtained for an applied electric field of 200MV/m (closed marks) and 300MV/m (open marks). The lines are just a guide to the eye.

Fig.1

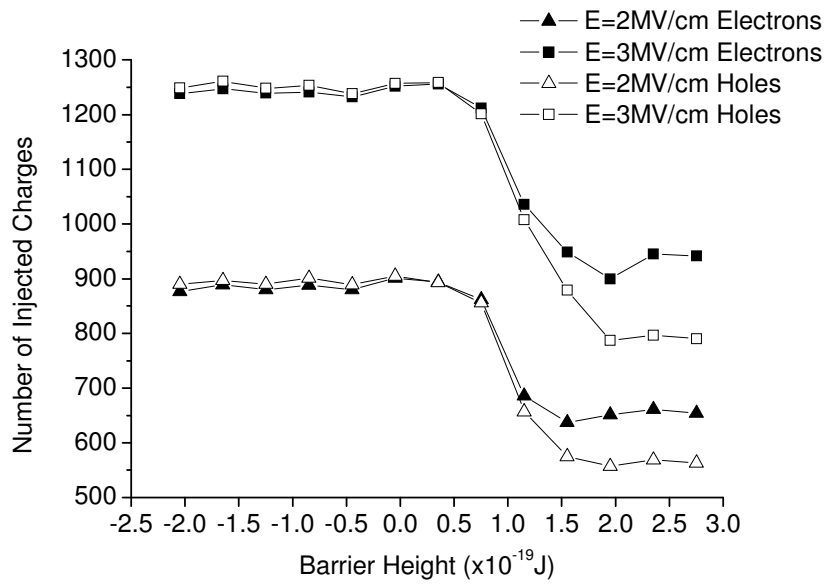


Fig. 2

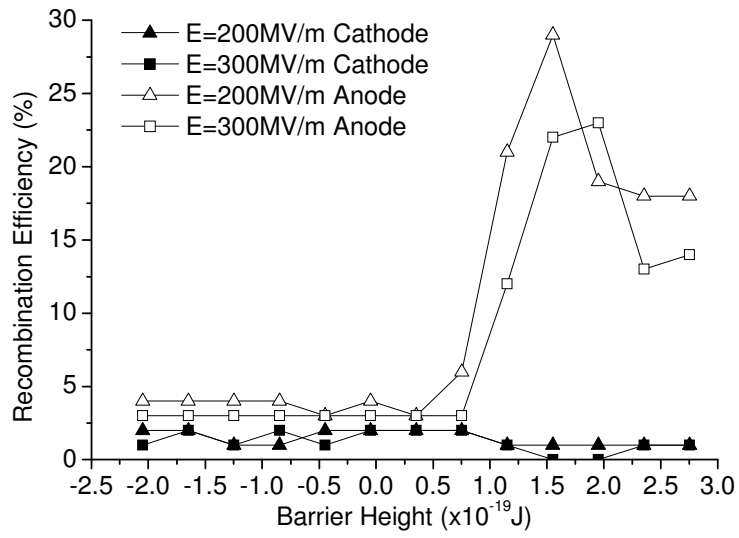


Fig. 3

