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MESOSCOPIC STUDY OF BIPOLAR CHARGE TRANSPORT IN POLYMER-BASED DEVICES

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0Abstract

We present generalised Monte-Carlo calculations of bipolar charge carrier transport in polydiacetylene to assess effects of some key factors on the properties of polymer-based light emitting diodes. Our mesoscopic model includes specific realisations of the polymer network and examines the effect of polymer structural order on current flow and charge recombination within the polymer layer. Specifically addressed are the issues concerning the fractions of polymer strands contributing to the charge injection processes at electrode interfaces and to electroluminescence. Our results suggest that radiative recombination increases as short chain concentration increases, whereas current efficiency shows an opposite behaviour. Radiative recombination decreases as charge injection efficiency decreases and its internal efficiency seems to saturate for a luminescent chain concentration greater than 30%. Our results also suggest that both current efficiency and space charge increases as charge injection efficiency decreases. Polymer disorder due to inclusions in the network does seem to contribute to reduce both current and recombination efficiencies.

Keywords: Mesoscopic modelling, conducting polymers, electroluminescence.

1. Introduction

Despite the progress to date, polymer-based light emitting diodes (LEDs) are still very much at the research stage [1]. Self–organization on many solution processable polymers results in complex microstructures. Charge carrier transport within the polymer layer is usually limited by the most difficult hopping processes and it is therefore dominated by polymer disorder. This has important consequences for the electronic and optoelectronic properties of these materials. Thus,

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improvements in device performance can be achieved by control of polymer morphology on device characteristics.

Mesoscopic modelling, which works at an intermediate scale between atomic and macroscopic scale, is suggested as an adequate technique for study the effect of mesogenic alignment on bipolar charge transport, recombination and trapping in polymer-based devices. The present work examines the bipolar charge evolution through a polydiacetylene (PDA) film as a function of charge injection efficiency and luminescent chain concentration. The effect of inclusions, which do not trap electrons or holes, is also discussed.

2. Description of the mesoscopic model

2.1. Polymer network

In order to build realizations of a polydiacetylene network we have placed individual straight strands of finite and variable length initially perfectly oriented as in macroscopic single crystal [2] and assigning randomly a small rotation to each one of them. The number of units in each chain varies from 2 to 20 and it is chosen randomly, except in those chains bound to the electrodes where that number was set to 20 in order to diminish the attraction between the electrodes and the injected charges (of either sign) through polarization. The highly oriented domains are separated by regions of about 10 Å width. Within each domain interchain distances of 7-14 Å have been used.

2.2. The rules for charge evolution

Electrons and holes are injected in the polydiacetylene film from opposite electrodes at good electrical contacts chosen randomly. The films we consider are of thickness 90 nm and have a surface area of 100 nm^2.All charge carriers are injected at same time. In the present examples we do not allow for multiple charge to be injected in a sequence of events. Our approach allows us to include the dependence on length and conformation on work functions and electron affinities of molecules using self-consistent molecular dynamics; this is not included in the present examples.

The charge injected at one end of a chain moves along the chain under the influence of the total applied field, which the sum of the applied external field of 2×10^8 Vm^{-1} [3], the field of other charges in transit or trapped within the polymer network and the field due to electrode polarization. All charges are treated explicitly, rather than through a continuum limit and the Poisson equation. Cyclic boundary conditions have been imposed, so we have also evaluated the electric field contribution from the nearest image of each charge in the film. It is straightforward to generalise to include the effects of the electric field on jump- and recombination probabilities.

A charge injected at one electrode percolates through the polymer film jumping to the neighbour chain which has the greatest hopping probability $w/(\sum w)$. Here, the sum is over all the nearest neighbour strands and w is the jump rate given elsewhere [4]. The charge stops, but continues to contribute to the space charge, when the total electrical field on the charge is zero or when $w<10^{-5}$.

The capture of oppositely charged carriers on the same chain gives rise to both radiative and non-radiative recombination depending on the chain length. Following Sixl [5], we have assumed that polydiacetylene chains with more than 8 units do not luminesce.

3. Results and discussion

Our earlier work [6] suggests that some of polymer strands at electrode interfaces may never play a part in the charge injection process. In order to study the effect of charge injection efficiency on both electrical and electroluminescence characteristics of light-emitting diodes, we have calculated charge carrier recombination and current flow efficiencies as a function of luminescent chain concentration for several charge injection efficiencies (fractions of polymer strands involved charge injection process) and five different nematic alignment structures of polydiacetylene.

The Fig. 1 shows the radiative and the non-radiative recombination predicted within the polymer film, for a balance between the injection of the two charge carrier types (electrons and holes). Our results suggest that non-radiative recombination decreases as short chain concentration increases, whereas radiative recombination shows an opposite behaviour. Since radiative internal efficiency seems to saturate for a concentration greater than 30%, this is consistent with the idea that only a small fraction of short chains might be responsible for light emission. Both radiative and non-radiative recombination decreases as charge injection efficiency decreases.

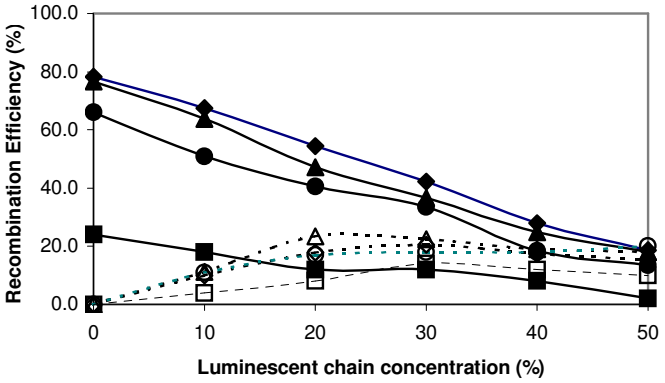

Fig. 1. Radiative (open marks) and non-radiative (close marks) recombination efficiencies within the polydiacetylene film as a function of luminescence chain concentration for the following charge injection efficiencies: (a) 10% (square), (b) 40% (circle) (c) 70% (triangle) and (d) 100% (diamonds). The marks indicate the average value of the data points that were calculated explicitly. The curves are simply a guide to the eye.

The current efficiency (charge that reaches the opposite electrode per injected charge) decreases as the charge injection efficiency increases (see Fig. 2). Besides, the current efficiency decreases as short chain concentration increases as a result of the build-up of space charge within the polymer film. Both current efficiency and space charge increases as charge injection efficiency decreases.

Polymer disorder due to inert inclusions in the network, which do not trap charges of either sign, does seem to contribute to reduce both current efficiency and recombination. In this case, an increase of space charge is predicted.

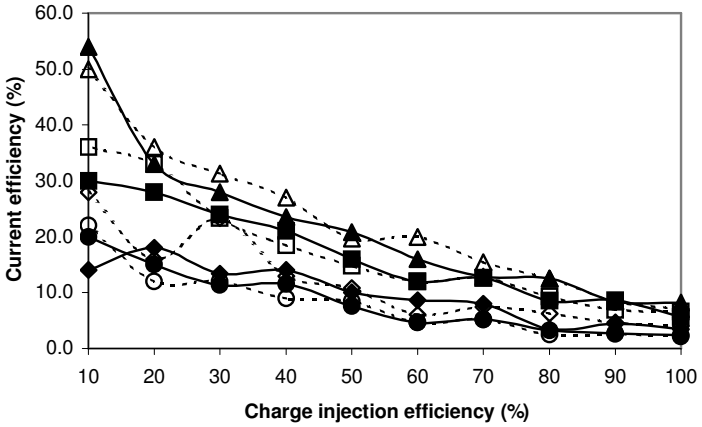

Fig. 2. Electron (close marks) and hole (open marks) current efficiencies as a function of charge injection efficiency for the following luminescence chain concentrations: (a) 10% (triangle), (b) 20% (square) (c) 30% (diamond) and (d) 40% (circle). The marks indicate the average value of the data points that were calculated explicitly. The curves are simply a guide to the eye.

4. Conclusions

Mesoscopic modelling of bipolar charge injection, transport and recombination in conducting polymers, such as those reported here, can give some insights into what limits the performance of polymer based devices at scales which can only be studied experimentally using a Scanning Tunnelling Microscope. Our results suggest a build-up of space charge within the polymer layer in relatively disordered structures due to a large concentration of short chains or the presence of inclusions in the polymer layer. We believe this is a plausible explanation for low electroluminescence efficiencies. Our mesoscopic model provides a means to design better film structures in order to improve the effectiveness of new materials and optimisation for organic electronics application.

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