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Analytical and numerical study of photocurrent transients in organic polymer solar cells

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ABSTRACT

This article is an attempt to provide a self consistent picture, including existence analysis and numerical solution algorithms, of the mathematical problems arising from modeling photocurrent transients in organic polymer solar cells (OSCs). The mathematical model for OSCs consists of a system of nonlinear diffusion–reaction partial differential equations (PDEs) with electrostatic convection, coupled to a kinetic ordinary differential equation (ODE). We propose a suitable reformulation of the model that allows us to prove the existence of a solution in both stationary and transient conditions and to better highlight the role of exciton dynamics in determining the device turn-on time. For the numerical treatment of the problem, we carry out a temporal semi-discretization using an implicit adaptive method, and the resulting sequence of differential subproblems is linearized using the Newton–Raphson method with inexact evaluation of the Jacobian. Then, we use exponentially fitted finite elements for the spatial discretization, and we carry out a thorough validation of the computational model by extensively investigating the impact of the model parameters on photocurrent transient times.

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1. Introduction and motivation

A continuously growing attention has been paid over the last years by the international community and government authorities to monitoring the effect of the increase of global concentrations of carbon dioxide, methane and nitrous oxide on the quality of our everyday life. The results of the investigation carried out by the Intergovernmental Panel on Climate Change [1] have brought the European Union (EU) to the decision that carbon dioxide emissions should decrease by 20%, and that 20% of the energy produced in EU should originate from renewable energy sources, such as wind, water, biomass, and solar, not later than 2020 [2].

In this perspective, research and design of third generation (3G) photovoltaic devices [3] for solar energy conversion into electrical and thermal energy turns out to be a central topic in the wider area of renewable energy sources. Roughly speaking, 3G photovoltaic devices can be divided into two main classes: electrochemical cells [4–6] and organic polymer cells [7–9] which are the topic of the present article. Most of investigation activity in solar cell design is devoted to the experimental study of innovative materials for efficient and flexible technologies, and is not presently accompanied by a systematic use of computational models to predict and optimize their performance.

This article is an attempt to fill this gap by introducing the numerical engineering community to the mathematical problems that arise in the context of modeling and simulation of OSCs. With this aim, we try to provide a reasonably self-contained picture of the topic, including a discussion of the peculiarities of the model, an analysis of the existence of a solution, and the description of a robust computational algorithm to compute such solution. In particular, we focus on a special class of OSCs, namely that of bulk heterojunction (BHJ) devices, that currently represent the most promising technology in terms of energy conversion efficiency [8,9]. Charge transport in BHJs is described by a set of nonlinear PDEs of diffusion–reaction type with electrostatic convection coupled with a kinetic ODE for the temporal evolution of exciton concentration in the cell [10–13].

Section 2 is devoted to the description of the structure and working principles of BHJs while in Section 3 the mathematical model is introduced and the connection between its features and the physical phenomena involved in photocurrent generation is drawn. Some effort is also put into highlighting the main differences between the problem at hand and the case of more standard crystalline inorganic semiconductor devices. In Section 4, under suitable assumptions on the model coefficients, *i*) we prove the existence of a solution of the problem in stationary conditions; and *ii*) we derive a simplified model in transient conditions, that is amenable for a qualitative analysis of the time response of the device, and for which we again prove existence of a solution.

For the numerical treatment of the problem, which is the topic of Section 5, we carry out a temporal semi-discretization using an implicit adaptive method, and the resulting sequence of differential

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subproblems is linearized using the Newton–Raphson method with inexact evaluation of the Jacobian. Then, we use exponentially fitted finite elements for the spatial discretization, to ensure a stable approximation of the internal and boundary layers arising in the distribution profile of the photogenerated carriers. The numerical experiments of Section 6 are meant, on the one hand, to illustrate the complex interplay among different physical phenomena determining the photocurrent turn-on transient time of a realistic BHJ cell in different regimes and, on the other hand, to characterize the range of applicability of the reduced model introduced in Section 4. In Section 7 we address some concluding remarks and indicate possible future research directions.

2. Bulk heterojunction organic solar cells

Before presenting the mathematical model which is the main focus of this paper, a schematic description of working principle of OSCs, and in particular of those with a BHJ structure, is in order. For more details on the subject the interested reader is referred to [8,9]. The simplest possible structure for an organic-polymer based solar cell is depicted in Fig. 1: two thin films composed of a conjugated organic polymer and of a material with high electron affinity, usually referred to as a *acceptor* are sandwiched between one transparent (*e.g.* indium-tin-oxide or fluorinated tin oxide) and one reflecting metal contact (usually aluminum or silver). When illuminated, electrons in the Highest Occupied Molecular Orbital (HOMO) in the polymer are promoted to the Lowest Unoccupied Molecular Orbital (LUMO) thus forming an electron–hole pair. Such pair, which we refer to as an *exciton* (Fig. 1(a)), in contrast to what is usually the case in standard inorganic semiconductors, is electrically neutral and has very strong binding energy (of the order of 1 eV) with a radius in the sub-nanometer range. The *diffusion length* λ_X of a moving exciton in commonly used polymeric materials is of the order of a few nanometers. An exciton has a non-negligible chance of eventually reaching the polymer/acceptor interface only if it was photogenerated within a distance $\leq\lambda_X$. In case this occurs, the built-in chemical potential drop produced by the difference in electron affinity between the two materials is strong enough to *stretch* the exciton driving the electron and hole to a distance of the order of 1 nm thus reducing the strength of their Coulomb attraction. This less tightly bound electron–hole pair is referred to in the literature as a *geminate pair* (Fig. 1(b)) and the energy of the bond is low enough that it can be overcome by the electric field induced by a small voltage difference applied at the contacts. The newly separated electron and hole migrate, driven by electric field drift and diffusion forces, to the anode and cathode, respectively, where they are *harvested* thus producing a net current (Fig. 1(c)). The currently investigated most promising device technology to maximize the efficiency of the photogeneration process is the BHJ cell depicted in Fig. 2 which is produced by spin-casting both the polymer (usually rr-P3HT or MDMO-PPV) and the acceptor (usually some derivative of fullerene or inorganic nanoparticles, *e.g.* titanium-dioxide) from a common solution. This process results in a highly folded structure that has the advantage that all photogenerated excitons eventually reach an interface, at the price of reducing the *effective* carrier mobility because of the convoluted path that carriers need to travel to reach the contacts. Also, from a perspective that is more relevant to the topic of this paper, the highly disordered structure of BHJs makes it difficult to characterize model parameters, as an averaging over the highly disordered nanostructure of the device would be required. Therefore the typical approach is to estimate the parameter values experimentally and resort to numerical simulations to properly interpret the measurement results.

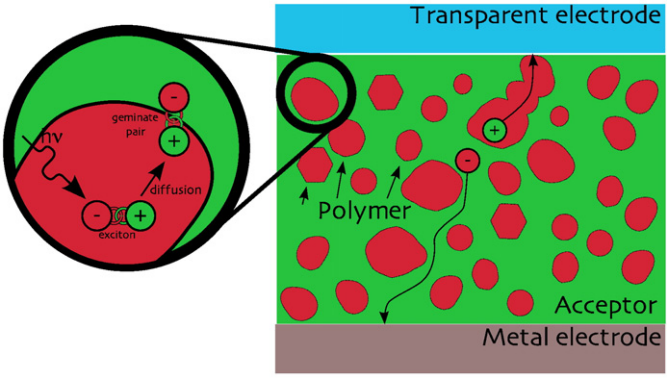

Fig. 2. Bulk heterojunction OSCs.

3. The mathematical model

In this section we illustrate the mathematical model of the photogeneration mechanisms that drive charge transport in BHJ solar cells (see [9–13]). The polymer/acceptor blend is represented by a homogeneous material filling a bounded domain $\Omega\subset\mathbb{R}^d$, $d\geq 1$, with a Lipschitz boundary $\Gamma\equiv\partial\Omega$ divided into two disjoint subregions, Γ_D and Γ_N, representing the interface between metal and polymer blend and interior artificial boundaries, respectively. We assume that $\mathrm{meas}(\Gamma_D)>0$ and $\Gamma_D\cap\Gamma_N=\emptyset$, and denote by ν the outward unit normal vector along Γ.

3.1. Governing equations

Charge transport in the device is governed by the set of continuity equations

$$\begin{cases} \dfrac{\partial n}{\partial t}-\mathrm{div}\boldsymbol{J}_n = G_n-R_n n \\ \dfrac{\partial p}{\partial t}-\mathrm{div}\boldsymbol{J}_p = G_p-R_p p \end{cases} \quad \text{in } \Omega_T, \tag{1a}$$

where $\Omega_T\equiv\Omega\times(0,T)$, $T>0$, n and p denote the *electron and hole density*, respectively. Using from now on the symbol η to indicate either of n or p, $\boldsymbol{J}_\eta$ are the corresponding *flux densities*, G_η, are the carrier *generation*

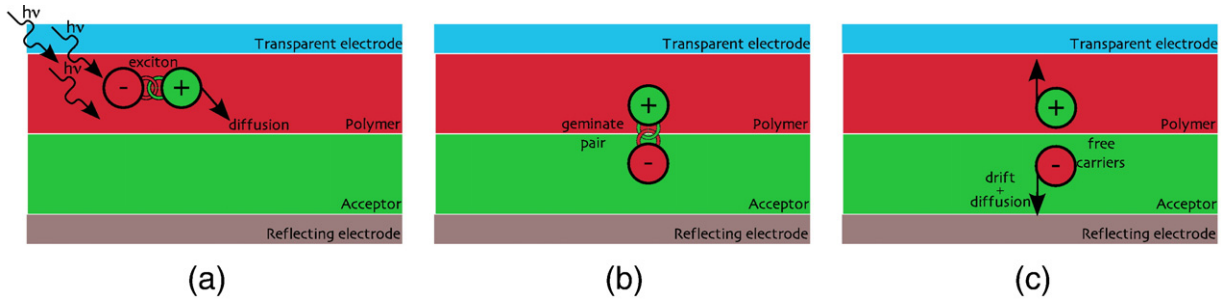

Fig. 1. Working principle of OSCs.

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