P 7 Organic photovoltaics and related electrochemical models (K. Fellner, G. Friesecke) → NS, IS

Organic Photovoltaic (OPV) devices are a high-potential solar power technology whose advantages of cheap materials and possible ink-jet like printing production are currently still outweighed by their lacking efficiency. Modern Li-Ion batteries are highly complex multi-scales devices with huge impact for the current car and airplane industries.

OPV devices combine different conducting organic materials. The generation of free charge carriers (e.g. electrons and holes) occurs (in contrast to classical photovoltaic devices) indirectly through the light-induced generation of quantum-bound pairs of charges, so-called excitons. Effective exciton dissociation (and thus production of electric current) only occurs near interfaces between materials with suitable electro-affinity (HOMO-LUMO) gaps. In Li-Ion batteries, interfaces between solid particles and the surrounding electrolyte play a similarly important role.

A simplest OPV device consists of a bilayer of two polymers with opposite electron-affinity (i.e. an electron acceptor and a hole acceptor). Close to the polymer-interface, the change in electron-affinity will align and stabilize the excitons into a dipole layer, which allows to effectively dissociate excitons by means of a suitable applied external voltage/field.

State of the art. In the physics literature, several drift-diffusion-recombination type models are proposed for OPV bilayers (see e.g. [1, 3]). The following stationary state equations are considered in [2] in one space dimension ($x \in [0, L]$) for the excitons density X, the electrons and holes densities n and p and the electric potential V:

$$\begin{aligned}
-\mu_x X_{xx} &= c_r\, np + G - (k_d(E) + k_r)X, && X_x(0) = 0, && X_x(L) = 0,\\
-[\mu_n(E)(n_x - n(V+U)_x)]_x &= -c_r\, np + k_d(E)X, && n(0) \approx 0, && n(L) = n_L,\\
-[\mu_p(E)(p_x + p(V+U)_x]_x &= -c_r\, np + k_d(E)X, && p(0) = p_0, && p(L) \approx 0,\\
-\lambda^2 \Delta V &= p - n + \varepsilon \nabla X, && V(0) = V_{\text{app}}, && V(L) = 0,
\end{aligned}$$

where the exciton dissociation rate $k_d(E)$ and the mobilities $\mu_n(E)$ and $\mu_p(E)$ depend on the electric field $E = -V_x$. Moreover, G denotes the light-dependent exciton generation, k_r the exciton recombination rate, c_r the binary recombination rate, μ_x, μ_n and μ_p the mobilities of excitons, electrons and holes, U denotes the electro-affinity workfunction, λ the Debye length and $\varepsilon \approx 0.01$ is related to the small width of the polymer-interface.

An asymptotic analysis (using that the applied voltage V_{app} is large in a working device) discusses in [2] the so-called *IV-curve*, i.e the produced current as function of the applied voltage in terms of the workfunction U and the rates G, $k_d(E)$, k_r (see also [12, 9] for a related analysis). Moreover in [2], a 2-D HDG finite-element scheme was developed to numerically calculate IV-curves. The mathematical theory for such nonlinear drift-diffusion-recombination models poses still many open problem (in particular in 3D), which should benefit from recently developed tools for nonlinear reaction-diffusion systems, see e.g. [4, 6, 5, 10].

Thesis project to be supervised by Klemens Fellner. A first goal for applying recent duality- and entropy methods to electrochemical OPV and Li-Ion models is the derivation of an entropy entropy-dissipation inequality for a prototypical drift-diffusion-recombination systems with self-consistent electric field. Promising preliminary results are work in progress by IGDK student Michael Kniely, see also [7]. A second aim are asymptotically-derived, effective OPV models, where the bilayer interface is modeled by a hyperplane rather than a thin layer. This interesting limit, which in the above model leads formally to the evaluation of non-linear rates like $k_d(E)$ for measure valued fields E, is currently under investigation.

A second direction of this projects will use such effective OPV models in order to optimize the shape of the IV-curve, in particular to maximize the so-called *Fill-Factor*, which denotes the relation of the power output of an ideal OPV device to the maximum power point of the IV-curve. As controls we shall use i) the material parameters (i.e. the rates $k_d(x, E)$, $k_r(x)$ and/or the mobilities $\mu_n(E)$, $\mu_p(E)$) and ii) the geometry of the material-interface. These optimization problems which hitherto seem not to have been addressed mathematically are relevant to the technological goal of designing high efficiency OPV devices, see e.g. [13].

A third direction shall study homogenization limits to derive effective mathematical models for OPV heterojunction devices (e.g. [11]) or Li-Ion electrolytes layers (see [8] for a first result). In a similar way, we shall aim to derive models for fullerene-based, dye- or perovskite-based OPV devices, where the later hold the current world efficiency record. Here, the research will be supported by a university assistant to be hired by K. Fellner at the KFU Graz.

Further topics. Possible extensions may address multiple species of excitons or ions, more realistic models for material interface and near-interface exciton stabilization.

Bibliography

[1] J. A. Barker, C. M. Ramsdale, and N. C. Greenham. Modeling the current-voltage characteristics of bilayer polymer photovoltaic devices. *Physical Review B*, 67(7):75205–1–9, 2003.

[2] D. Brinkman, K. Fellner, P. Markowich, and M.-T. Wolfram. A drift-diffusion-reaction model for excitonic photovoltaic bilayers: asymptotic analysis and a 2-D HDG finite-element scheme. *Math. Models Methods Appl. Sci.*, 23(5):839–872, 2013.

[3] G. A. Buxton and N. Clarke. Computer simulation of polymer solar cells. *Modelling Simul. Mater. Sci. Eng.*, 15(2):13–26, 2007.

[4] J. A. Cañizo, L. Desvillettes, and K. Fellner. Improved duality estimates and applications to reaction-diffusion equations. *Communications in Partial Differential Equations*, 39(6):1185–1204, 2014.

[5] L. Desvillettes and K. Fellner. Entropy methods for reaction-diffusion equations: Slowly growing a-priori bounds. *Revista Matemática Iberoamericana*, 24(2):407–431, 2008.

[6] L. Desvillettes, K. Fellner, M. Pierre, and J. Vovelle. Global existence for quadratic systems of reaction-diffusion. *Advanced Nonlinear Studies*, 7(3):491–511, 2007.

[7] M. Di Francesco, K. Fellner, and P. A. Markowich. The entropy dissipation method for spatially inhomogeneous eaction–diffusion-type systems. *Proc. R. Soc. Lond. Ser. A Math. Phys. Eng. Sci.*, 464(2100):3273–3300, 2008.

[8] K. Fellner and V. Kovtunenko. A discontinuous Poisson–Boltzmann equation with interfacial transfer: homogenisation and residual error estimate. *Preprint IGDK-2014-08*, 2014.

[9] J. Foster, J. Kirkpatrick, and G. Richardson. Asymptotic and numerical prediction of current-voltage curves for an organic bilayer solar cell under varying illumination and comparison to the shockley equivalent circuit. *Journal of Applied Physics*, 114(10):1–15, 2013.

[10] A. Glitzky. Analysis of electronic models for solar cells including energy resolved defect densities. *Mathematical Methods in the Applied Sciences*, 34(16):1980–1998, 2011.

[11] I. Hwang, C. McNeil, and N. Greeham. Drift-diffusion modeling of photocurrent transients in bulk heterojunction solar cells. *Journal of Applied Physics*, 106:094506, 2009.

[12] G. Richardson, C. P. Please, J. Foster, and J. Kirkpatrick. Asymptotic solution of a model for bilayer organic diodes and solar cells. *SIAM Journal on Applied Mathematics*, 72(6):1792–1817, 2012.

[13] R. B. Ross and et al. Endohedral fullerenes for organic photovoltaic devices. *Nature Materials*, 8:208–212, 2009.