

A DYNAMIC MONTE CARLO AND
EXPERIMENTAL STUDY OF ORGANIC
SOLAR CELLS

By

Krishna Feron
BSc (Cum Laude)

A THESIS SUBMITTED TO THE UNIVERSITY OF NEWCASTLE
FOR THE DEGREE OF
DOCTORATE OF PHILOSOPHY IN PHYSICS
SEPTEMBER 2013



THE UNIVERSITY OF
NEWCASTLE
AUSTRALIA

Declaration

Statement of Originality This thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying subject to the provisions of the Copyright Act 1968.

Acknowledgement of Collaboration I hereby certify that the work embodied in this thesis has been done in collaboration with other researchers, or carried out in other institutions. I have included as part of each chapter in this thesis a statement clearly outlining the extent of collaboration, with whom and under what auspices.

Acknowledgement of Authorship I hereby certify that the work embodied in this thesis contains substantive components of published papers of which I am a joint author. I have included as part of each relevant chapter in this thesis a written statement attesting to my contribution to the joint publications.

Krishna Feron

Acknowledgements

A research project is never a one-man show and my PhD project is no exception. For this reason, I dedicate this section to thanking everyone who had a significant contribution to my development as a researcher or directly to my PhD project.

I had the pleasure to work with two research groups, the Solar PV team at CSIRO Energy Technology and the Priority Research Centre of Organic Electronics at University of Newcastle. These two groups have a fruitful collaboration and established the Joint Research Centre for Organic Photovoltaics (JRCOE). The expertise and facilities of each group were invaluable in the realisation of this PhD project. I would like to thank CSIRO Energy Technology for giving me the opportunity to work with the JR-COE through their PhD internship programme. Through this programme I not only received financial support, but the programme also enhanced my PhD experience by allowing me to be an employee of CSIRO in addition to being a student at University of Newcastle.

I am grateful for the guidance that I received from my supervisors Dr Chris Fell, Prof Paul Dastoor, Dr Warwick Belcher and Dr Xiaojing Zhou. Chris and Paul not only guided me through the PhD research process, but also looked beyond the PhD period and helped me to grow as a scientist. Paul's enthusiasm and inherent desire to help people in their professional and personal development have made my PhD journey an enjoyable one. In addition to my four official supervisors, I would also like to acknowledge Tim Nagle for his help and guidance in developing the photocurrent mapping system. I am also grateful for the helpful discussions that I had with members

of either research groups.

Several factors contribute to a person's success. In addition to all the professional help I received, I was also fortunate to be surrounded by a supporting family. I thank my sister for her moral support throughout my PhD. Finally, I would like to express my endless gratitude to my mother and father who have helped me in every aspect of my life including this PhD project. Their guidance and support were key to my success and allowed me to be the best that I can be.

List of Publications

- K. Feron, X. Zhou, W. J. Belcher and P. C. Dastoor, *Exciton transport in organic semiconductors: Förster resonance energy transfer compared with a simple random walk*. Journal of Applied Physics **111**, 044510 (2012)
- K. Feron, C. J. Fell, L. J. Rozanski, B. B. Gong, N. Nicolaidis, W. J. Belcher, X. Zhou, E. Sesa, B. V. King and P. C. Dastoor *Towards the development of a virtual organic solar cell: An experimental and dynamic Monte Carlo study of the role of charge blocking layers and active layer thickness*. Applied Physics Letters **111**, 193306 (2012)
- K. Feron, T. J. Nagle, L. J. Rozanski, B. B. Gong and C. J. Fell *Spatially-resolved photocurrent measurements of organic solar cells: Tracking water ingress at edges and pinholes*. Solar Energy Materials and Solar Cells **109**, 169-177 (2013)
- K. Feron, W. J. Belcher, C. J. Fell and P. C. Dastoor *Organic solar cells: Understanding the role of Förster Resonance Energy Transfer*. International Journal of Molecular Sciences **13**, 17019-17047 (2012)

Contents

Declaration	iii
Acknowledgements	v
List of Publications	vii
Abstract	xv
1 Context	1
2 Organic Photovoltaics	5
2.1 Introduction	5
2.2 Photoconversion mechanism	6
2.2.1 Organic semiconductors	6
2.2.2 Optical properties	7
2.2.3 Exciton creation and transport	9
2.2.4 Exciton dissociation mechanisms	12
2.2.5 Charge-transfer state	15
2.2.6 Charge transport	15
2.2.7 Charge extraction	17
2.2.8 Overview of the photoconversion mechanism in organic solar cells	18
2.3 Device architectures	19
2.3.1 Bilayer structure	19

2.3.2	Bulk heterojunction structure	20
2.3.3	Interdigitated structure	22
2.3.4	Nanoparticle structures	24
2.4	Modelling organic photovoltaic devices	25
2.4.1	Electrical equivalent circuit model	25
2.4.2	Drift-diffusion based modelling	26
2.4.3	Dynamic Monte Carlo model	27
2.5	Stability	28
3	Experimental	29
3.1	Device fabrication	29
3.1.1	Substrate preparation	30
3.1.2	Spin-coating thin films	31
3.1.3	Evaporative deposition	32
3.1.4	Encapsulation	33
3.2	Device and materials characterisation	33
3.2.1	UV-VIS absorption spectroscopy	33
3.2.2	Photoluminescence measurements	33
3.2.3	Profilometry	33
3.2.4	Atomic Force Microscopy	34
3.2.5	X-ray photoelectron spectroscopy depth profiling	34
3.2.6	Current-voltage characteristics	34
3.2.7	External Quantum efficiency measurements	37
4	Monte Carlo modelling	39
4.1	Introduction	39
4.2	Monte Carlo method	41
4.3	Setting up the morphology	47
4.4	Light absorption	50
4.5	Energy considerations	51
4.5.1	The Gaussian energetic disorder model	52

4.5.2	Built-in electric field	54
4.5.3	Coulomb interaction	55
4.5.4	Surface charge induced at the electrodes	56
4.6	Exciton transport and recombination	56
4.6.1	Förster Resonance Energy Transfer	59
4.6.2	Random Walk	61
4.7	Charge Transport	62
4.7.1	Miller-Abrahams expression	63
4.7.2	Marcus theory	63
4.8	Charge extraction and injection at electrodes	68
4.9	Charge recombination	74
4.10	Determining performance parameters from simulations	76
5	Förster resonance energy transfer theory compared to a simple random walk	81
5.1	Introduction	81
5.2	Simulation Methodology	84
5.3	Results and Discussion	86
5.3.1	Validation of the implementation of FRET	86
5.3.2	Impact of fabrication process on energetic disorder	86
5.3.3	FRET compared with a random walk: exciton diffusion	88
5.3.4	FRET compared with a random walk: photoluminescence	89
5.3.5	FRET compared with a random walk: energy relaxation and long-range hopping	92
5.3.6	Exciton diffusion and sensitivity to domain size variations	97
5.4	Conclusion	99
6	Experimental validation of the dynamic Monte Carlo model: thickness dependence of organic photovoltaic performance and the impact of charge blocking layers	101
6.1	Introduction	101

6.2	Experimental and modelling aspects	102
6.3	Results and Discussion	109
6.3.1	Thickness dependence of IQE and J_{SC}	109
6.3.2	Charge blocking layers	109
6.3.3	Recombination mechanisms	111
6.3.4	XPS analysis of interfaces	112
6.4	Conclusion	117
7	Anomalous current-voltage behaviour	119
7.1	Introduction	119
7.2	Simulation methodology	123
7.3	Results and discussion	128
7.3.1	Effect of energy traps on exciton transport	128
7.3.2	Traps in the bulk compared with traps at the electrode interfaces	132
7.3.3	Injected charge carriers vs photo-generated charge carriers	135
7.3.4	Charge recombination and s-shape severity	137
7.3.5	Isolating the effect of the compositional donor-acceptor distribu- tion at electrodes on I-V curves	141
7.4	Conclusion	144
8	Assessing nanoparticle morphologies	147
8.1	Introduction	147
8.2	Experimental and modelling aspects	148
8.2.1	Device fabrication and characterisation	148
8.2.2	Simulation parameters	149
8.3	Results and discussion	149
8.3.1	STXM imaging	149
8.3.2	Constructing the 3D morphology	153
8.3.3	Photovoltaic performance and nanoparticle size	157
8.4	Conclusion	162

9 Mapping photocurrent	165
9.1 Introduction	165
9.2 Experimental aspects	167
9.2.1 Light beam induced current setup	167
9.2.2 Beam profiling	168
9.2.3 Intensity considerations	170
9.3 Results and discussion	171
9.3.1 Evaporative deposition: shadowing effect	171
9.3.2 True photoactive area	174
9.3.3 Identifying the impact of visual defects	182
9.4 Conclusion	189
10 Diffusion limited degradation	191
10.1 Introduction	191
10.2 Experimental and modelling aspects	193
10.2.1 Device fabrication	193
10.2.2 Environment control	194
10.2.3 One-diode model	195
10.3 Results and discussion	195
10.3.1 General observations of encapsulated devices	195
10.3.2 General observations in non-encapsulated devices	196
10.3.3 Identifying the diffusant	198
10.3.4 Searching for an oxide layer	200
10.3.5 Degradation length	200
10.3.6 Quantifying the increase in water uptake due to PEDOT:PSS	203
10.3.7 Extracting the diffusion coefficient	204
10.3.8 Quantifying ingress at pinholes	206
10.3.9 Ingress in devices with a silver cathode	209
10.3.10 Optimising lateral design for device durability	210
10.4 Conclusion	214

11 Conclusion and Further Work	217
11.1 Conclusion	217
11.2 Further Work	222
A Random walk diffusion length relations	225
References	227

Abstract

The main focus of this thesis was to develop a dynamic Monte Carlo (DMC) model that could act as a virtual organic solar cell, which would then be used to analyse and predict OPV performance.

The photoconversion process in organic solar cells consists of several molecular processes: light absorption, exciton transport, exciton dissociation, charge transport and extraction. The optical field and thus exciton generation profile is determined using transfer matrix techniques. Exciton transport is modelled using Förster resonance energy transfer (FRET) theory. Charge transport is described using Marcus theory and charge injection is known to follow Miller-Abrahams expressions. The DMC approach provides a platform where these various theories can be combined to model the entire photoconversion process.

Exciton transport can be modelled using a simple random walk or using a more rigorous and computationally more intensive theory such as FRET theory. The DMC model was used to investigate the consequence of either theories on exciton dissociation and charge transfer state separation. A random walk is computationally more efficient than FRET and is the preferred approach when modelling single component systems as found in photoluminescence experiments. However, neglecting energy relaxation and non-nearest neighbour hops leads to an underestimation of geminate recombination and an overestimation of photocurrent up to 2 % in organic solar cells.

Experimental validation of the DMC model was provided by modelling and experimentally measuring external quantum efficiency and short-circuit current as a function

of active layer thickness. Excellent agreement was found and the model was further used to analyse charge selectivity at the electrodes, interface recombination and bulk recombination. It was found that interface recombination is dominant for thin active layers and that a substantial gain in performance is expected by improving charge selectivity at the electrodes, in particular the anode.

Full I-V curves can be calculated using the DMC model. This capability was used to investigate s-shaped I-V curves. Electron traps were only found to induce s-shaped I-V behaviour when the traps are located at the electrode interfaces. Injected charge carriers do not induce s-shaped I-V curves; photogenerated charge carriers are necessary to observe this behaviour. Simulations suggest that OPV material systems that exhibit less charge recombination are more likely to exhibit s-shaped I-V curves. The open-circuit voltage does not always coincide with the centre of the 's' and could be changed by tuning charge recombination. DMC modelling was further used to investigate why thermal annealing removes s-shaped behaviour. Results suggest that vertical phase composition at the electrodes is not the cause of inflected I-V curves, rather charge traps is the cause of this anomalous behaviour. Energy traps were also found to affect exciton transport as they reduce the exciton diffusion length.

DMC models take into consideration the three dimensional nanostructure of the photoactive layer. This capability was used to investigate core-shell nanoparticle morphologies. Annealing was found to improve the efficiency of nanoparticle devices and modelling suggests that different annealing conditions to what is commonly used for BHJ devices are needed to increase the efficiency further. In addition, simulations indicate that annealing conditions should be re-optimised when changing the nanoparticle size. The performance of core-shell nanoparticles approaches that of the BHJ morphology, when optimised for both feature size and nanoparticle size. Hence, the core-shell morphology does not necessarily severely limit charge extraction and, in theory, optimised nanoparticle devices should yield similar efficiencies as optimised BHJ devices.

A high resolution light beam induced current (LBIC) setup was developed and used to investigate lateral non-uniformities that are the result of imperfect fabrication

techniques or degradation.

The primary degradation mechanism in standard organic solar cells is water diffusion limited oxidation of the aluminium cathode. A diffusion model was applied, which allowed for the determination of the diffusion rate and also the diffusivity of water in PEDOT:PSS. Diffusion through pinholes is quantified to be significantly slower than diffusion at the cathode edge. Lateral device design was shown to substantially influence the degradation rate and pattern.