Degradation Analysis and Parameter Extraction of Organic Semiconductor Devices

Investigation by means of Complementary Measurement Techniques combined with Numerical Simulation

Zur Erlangung des akademischen Grades

Doktor der Ingenieurwissenschaften

von der Fakultät für
Elektrotechnik und Informationstechnik

des Karlsruher Instituts für Technologie (KIT)

genehmigte

Dissertation

von

Dipl.-Phys. Simon David Züfle

geb. in Pforzheim

Tag der mündlichen Prüfung:	20. Juli 2017
Referent:	Prof. Dr. Uli Lemmer
Korreferenten:	Prof. Dr. Sebastian Randel
	Prof. Dr. Beat Ruhstaller

ABSTRACT

The understanding of the electrical properties of organic semiconducting materials is crucial for achieving efficient and stable devices. While organic light-emitting diodes (OLEDs) already succeed as industrial consumer products in displays, organic solar cells (OSC) are still a step behind. Yet both technologies share the common potential of low-cost mass production of light-weight, flexible opto-electronic devices making them attractive for a wide range of applications.

The electrical function of both OLEDs and OSCs is governed by the physical processes of charge carrier injection/extraction, transport, recombination, light absorption and emission. The assessment of these processes requires a thorough understanding of the related material and device parameters.

Establishing reliable measurement methods and numerical models to determine these parameters is crucial for the organic semiconductor industry. 30 years after the invention of OLEDs still new active and functional materials are being developed and devices are being optimized.

In this work we present a novel synoptic approach that combines a variety of electrical characterization techniques in the steady-state, transient and ac-mode. The use of complementary techniques and analytic methods as well as the qualitative analysis of signatures in the data allows us to draw conclusions about the underlying physical processes as well as to determine specific material parameters. Hereby the various measurements are only comparable because they can be performed with the same measurement setup in a short time and under the same environmental conditions.

By marrying this combinational measurement process with numerical drift-diffusion device simulation we are for the first time able to model the whole range of electrical experiments. This enables us to evaluate the reliability of common parameter extraction routines and examine their limitations. In fact, we find that the most accurate and reliable way to determine the set of material and device parameters is a global fitting routine of the full range of measured signals with a drift-diffusion simulation.

It can be advantageous for parameter extraction to fabricate dedicated devices where only one carrier type is present, thereby avoiding recombination and other bipolar charge transport effects. Here, we demonstrate that bilayer OLEDs comprising a polar electron transport layer show a voltage regime where only holes are present in the active layer. Such devices are therefore an easy-to-fabricate alternative to metal-insulator-semiconductor (MIS) devices in order to deliberately analyse the hole injection and transport properties of the hole transport layer, or any material with suitable molecular energetic levels. By varying the device temperature we can determine the thermal activation and disentangle the charge transport from the charge injection properties.

We further apply the synoptic approach to study device degradation. A multitude of physical and chemical processes are triggered by external stress factors such as light, temperature, humidity or electrical current, and impair the performance and stability of organic electronic devices. For our investigations we perform extensive measurement routines at various points during the ageing process. Again combined with simulation as well as by analysing the specific signatures of some effects we are able to distinguish between similar processes and to identify the dominant degradation mechanisms. We also find that in many cases the full layer stack, consisting of encapsulation, various functional layers and the active materials, has to be considered in stability tests.

To conclude, the combination of various experiments and simulation allows to extract valuable information about the physics behind degradation, and represents a valid and attractive approach for further characterization of organic electronic materials and devices.

ZUSAMMENFASSUNG

Das Verständnis der elektrischen Eigenschaften von organischen Halbleiter-Materialien ist von enormer Bedeutung, um stabile und effiziente Bauelemente zu erreichen. Während organische Leuchtdioden (OLEDs) bereits industriell hergestellt werden, sind organische Solarzellen (OSCs) noch nicht so weit. Beide Technologien eint jedoch das Potential dass sie kostengünstig in grossen Massen, dabei in flexiblen und leichten Bauformen hergestellt werden könnten, was sie interessant für eine ganze Reihe von Anwendungen macht.

Die elektrische Funktionsweise von OLEDs und OSCs ist bestimmt durch die physikalischen Prozesse Ladungsträger-Injektion/Extraktion, Transport, Rekombination, Lichtabsorption und -emission. Die Untersuchung dieser Prozesse erfordert ein gutes Verständnis der damit zusammenhängenden Material- und Bauteil-Parameter.

Die Etablierung von zuverlässigen Messmethoden und numerischen Modellen zur Bestimmung dieser Parameter ist für die organische Halbleiterindustrie entscheidend, werden doch auch 30 Jahre nach der Erfindung von OLEDs stetig neue organische Halbleitermaterialien entwickelt und Bauelemente optimiert.

In dieser Arbeit präsentieren wir einen neuen synoptischen Ansatz, welcher eine Reihe von elektrischen Charakterisierungs-Methoden im stationären Zustand sowie im transienten und AC-Modus kombiniert. Die Verwendung von komplementären Messungen und analytischen Methoden sowie die qualitative Analyse von spezifischen Charakteristika in den Messungen lässt Rückschlüsse auf die zugrunde liegenden physikalischen Prozesse zu und erlaubt es einzelne Materialparameter zu bestimmen. Dabei sind die verschiedenen Messungen direkt vergleichbar weil sie mit dem selben Messaufbau in kurzer Zeit und bei konstanten Messbedingungen durchgeführt werden.

Indem wir diesen kombinatorischen Prozess mit numerischen Drift-Diffusions-Simulationen zusammenbringen, sind wir erstmalig in der Lage die gesamte Bandbreite der elektrischen Experimente zu modellieren. Dies erlaubt uns die Zuverlässigkeit von gebräuchlichen Parameter-Extraktions-Routinen zu testen und ihre Grenzen zu bestimmen. Es zeigt sich, dass der genaueste und zuverlässigste Weg zur Bestimmung des ganzen Parameter-Satzes eine globale Fit-Routine von Drift-Diffusions-Simulationen über die gesamte Reihe an Experimenten ist.

Es kann von Vorteil sein, für die Parameter-Analyse spezielle unipolare Bauteile herzustellen, womit Rekombination und andere bipolare Ladungstransport-Effekte vermieden werden. Hier zeigen wir, dass Zwei-Schicht-OLEDs, welche eine polare Elektronen-Transportschicht enthalten, in einem gewissen Spannungsbereich unipolares Verhalten aufweisen. Solche Bauelemente können daher anstelle von Metall-Isolator-Halbleiter (MIS) Bauteilen verwendet werden, um die Loch-Injektion sowie den Loch-Transport in der Loch-Transportschicht, oder in einem beliebigen Material mit passenden molekularen Energieniveaus, zu untersuchen. Durch Variation der Temperatur können wir die thermische Aktivierungsenergie bestimmen, und in Beiträge für den Transport und die Injektion zerlegen.

Wir wenden den synoptischen Ansatz weiter an, um Degradation zu untersuchen. Eine Vielzahl von physikalischen und chemischen Prozessen, ausgelöst durch Licht, Temperatur, Feuchte oder elektrischen Strom, kann die Leistung und Stabilität von organischen Halbleiter-Bauelementen beeinträchtigen. Für unsere Studien führen wir ausführliche Messroutinen zu verschiedenen Zeitpunkten während des Alterns durch. Durch die Kombination mit Simulationen sowie durch die Analyse der Signaturen spezifischer Prozesse ist es uns möglich, zwischen verschiedenen Effekten zu unterscheiden und die dominierenden Alterungsmechanismen zu identifizieren. Hierbei zeigt sich, dass in vielen Fällen der gesamte Schichtaufbau, bestehend aus Verkapselung, funktionellen Schichten und dem aktiven Material, in Stabilitäts-Untersuchungen berücksichtigt werden muss.

Zusammenfassend lässt sich sagen, dass die Kombination von verschiedenen Experimenten in Verbindung mit Simulationen es ermöglicht, wertvolle Informationen über die Physik hinter Degradationsprozessen zu erhalten. Dieser Ansatz stellt damit einen gültigen und attraktiven Weg für die weitere Charakterisierung von organischen Halbleiter-Materialien und Bauteilen dar.

13 SUMMARY

This thesis investigates charge carrier transport in organic semiconductor devices. For this purpose we employ a novel approach of combining experiment and simulation and a variety of characterization techniques. We use this approach to investigate and formulate parameter extraction methods, and to analyse and determine degradation mechanisms in organic solar cells and polar OLEDs. The tools for our investigations are the measurement setup *Paios* and the modelling software *Setfos*, which are developed and commercialized by the company Fluxim AG.

13.1 COMBINATORIAL APPROACH

The measurement setup *Paios* unites a large variety of electrical characterization techniques in the dc, ac, and transient mode for solar cells and OLEDs. It allows to perform these experiments in an automated, consistent and reproducible way. There are several advantages to this approach:

- The measurement errors which are due to the measurement instrument are the same for all techniques, leading to a higher comparability.
- The automation of the measurement routines leads to unprecedented data acquisition speed.
- Performing all experiments with the same device under the same environmental conditions and without re-contacting gives a highly increased comparability and consistency of the data, as it excludes device-to-device variation and minimizes degradation in between measurements.
- The specific hardware used (*Paios*) further comes with a sophisticated graphical user interface, additional functional modules (e.g. stress-test, temperature), and the possibility to include numerical modelling by the drift-diffusion solver *Setfos* and fitting directly in the same user interface.

Most of the devices we investigated are small-area research devices fabricated in academic laboratories mainly by hand and mostly with solution-processing of the active layers. Therefore, device-to-device as well as sample-to-sample variations can be high and the reproducibility of measurements is impaired. Thus, it is difficult to obtain identical devices in the first place. This obviously can strongly influence the results, especially when investigating degradation, or for quantitative parameter determination.

This problem has lead to the current situation that solar cell efficiency values are often reported as a statistical mean over a series of nominally identical devices, that is, devices which have been produced in one batch with the same fabrication process and parameters. While this allows to estimate the reliability of the data and numbers, this strategy is not applicable to the investigation of degradation by complementary techniques. The time and effort needed to sequentially degrade and characterize a series of identical devices without an automated stress and measurement setup is very high. Furthermore, any re-contacting and transfer between different measurement equipments represents a potential error source, and uncontrolled time delays between stress and measurement may also distort the consistency of the data. Hence, for a degradation analysis that does

not focus only on one measurement technique it is much more suitable to employ one device at a time, and therefore automate the stress and measurement process as far as possible.

With the *Paios* Stress-Test Module it is possible to apply an electrical, light or thermal stress to the device and sequentially measure the whole measurement routine, making it a highly suited tool for stability analysis.

We base our work on both the combination of various electrical experiments in the steady-state, transient and impedance modes, as well as the combination of measurement with simulation. In general, the steady-state measurement of an IV-curve conceals a lot of important information, as it depicts only the equilibrium situation. Transient and modulated methods are much better suited to investigate the dynamics of charge transport in organic electronic materials.

Charge transport in all solar cells and light-emitting devices is governed by electric fields (drift) and density gradients (diffusion). While in most inorganic devices diffusion currents dominate, due to the employment of doped layers , in organic semiconductors the transport is mainly governed by drift. The drift-diffusion modelling approach is in principle suited for all semiconductor devices, and specific models for charge carrier mobility, injection, excitons and furthermore have been developed to account for the individual peculiarities of the different technologies.

The possibility to for the first time simulate all these different experiments allows to qualitatively understand the influences of the various material and device parameters on the experiments. Hereby the qualitative shape of a characterization signal can give valuable information without the need for being quantitative. Furthermore, this approach helps us to relate specific features in different experiments to each other. For example, the occurrence of an S-shaped IV-curve can, but does not need to be correlated with a current overshoot in the TPC signal, depending on the underlying mechanism. Thus, a synoptic view of several experiments allows us to identify the underlying process.

The numerical modelling furthermore is very useful to test analytic parameter extraction formulas. It turns out that they are usually not applicable for the complete parameter space, but their accuracy is limited to specific conditions and parameter regions. Being able to model the experiments, we can specify these parameter regions and the accuracy of the extracted values. From this we are able to give advise for more appropriate experimental conditions, and it is also possible to design new parameter extraction routines and analytical models.

Another way to obtain material parameter values is the full drift-diffusion modelling of the experiment combined with a fitting procedure. Hereby the experiment is simulated with the correct measurement settings, and the deviation between simulation and measurement is minimized by an algorithm which is stepwise adapting the model parameters. However, multiple local minima of the error may exist due to the multi-dimensional parameter space, and depending on the starting values different solutions may be obtained. We have shown that this ambiguity can be avoided by fitting several different experiments at the same time. This leads to a strongly changed error landscape in the multi-dimensional parameter space, and it is much more likely to find the global minimum of the error, and therefore the correct parameters.

13.2 PARAMETER EXTRACTION

In order to determine specific material parameters like the charge carrier mobility, often unipolar, single-layer devices are fabricated. In this configuration only one carrier contributes to the current, and the analysis is not complicated by a second carrier type or by bimolecular recombination. The simplification of the system usually yields higher success for parameter determination using analytic formulas. This approach comes, however, with a fundamental drawback, namely that the direct transfer of the results to a full device is often not correct.

There are several reasons for this:

- Analytic models for single-carrier devices are often only valid for and applied to thick films, while in fully functional devices the layer thicknesses are much smaller. Layers of different thicknesses need different fabrication conditions, which can lead to a different morphology and changed material properties.
- The surrounding functional layers can influence the determined as well as the effective parameters. For example the nominal barrier for carrier injection from the electrode into the active material is strongly reduced by an injection layer.
- In a bipolar device bimolecular as well as Shockley-Read-Hall recombination can strongly affect parameter analysis. The determined effective mobility can be lower than the one in a unipolar device by orders of magnitude.

On the other hand, because in bipolar devices electron and hole parameters can not be distinguished, it can still be useful to employ unipolar devices. Layer stacks comprising an insulating layer have been introduced as an alternative, as they keep the active layer processing parameters while being strictly unipolar. They are, however, non-functional devices. Yet, under specific circumstances, also regular devices show a regime where the signatures of only one carrier type are observed. This condition will probably yield the most accurate parameter estimation, as it does not require an unusual film thickness or preparation.

One class of devices that shows a unipolar regime are polar bilayer OLEDs. Due to the polarity of the ETL there is a voltage regime where holes are already injected and the layers are still empty of electrons. Thus, there is no steady-state current, but transient and impedance techniques can be performed to investigate hole transport and injection. In the voltage regime between the hole injection voltage and the built-in voltage the device can be understood as a metal-insulator-semiconductor (MIS) device, where the ETL is still insulating and the HTL is already semiconducting. In this work we have investigated these polar OLEDs and elaborated new ways to determine parameters by exploiting the MIS character.

The MIS-CELIV experiment was originally developed for "real" MIS-devices. We show for the first time that it can be employed also in polar bilayer OLEDs to determine the hole mobility in the HTL. Hereby the thickness ratio between ETL and HTL defines the available experimental voltage region for the measurements, and whether the small-charge regime or the space-charge limited case can be evaluated. We find values of the hole mobility in α-NPD of $\mu_h \approx 10^{-4}$ cm^2/Vs at room temperature, using voltages just above the hole injection voltage.

The temperature dependence of the charge mobility is a second topic that we have addressed. Assuming an exponential increase of the mobility with temperature, we employ simulation to

investigate how well the mobility activation energy can be obtained using an Arrhenius analysis. We find that a large hole injection barrier can influence the determined values. Furthermore, we show that the temperature dependent transition frequency between the two capacitance plateaus in C-f-T data can also be analysed by an Arrhenius fit, however giving an effective activation energy which depends on both the mobility activation and the injection barrier. The combination of C-f-T and MIS-CELIV therefore has the potential to allow distinguishing between the two contributions of injection and transport to the thermal activation. We find in an α-NPD/Alq_3 device that the combined activation energy of $\approx$ 0.5 eV is composed of two nearly equal contributions of the hole injection barrier and the charge mobility activation energy. Furthermore, the use of simulation allows us to better understand the limitations of the analysis methods. The main reasons for the inaccuracies found in the self-consistency study are the inhomogeneous charge density profiles which contradict with the assumptions of the analytical model.

There are other devices that show both a second capacitance plateau and a peak in the dark-CELIV signal - doped organic solar cells. While the doping is basically a loss mechanism and usually due to degradation, these devices also allow to consider only one carrier type in some measurements. The dark-CELIV peak contains only carriers of one type, therefore the extracted mobility is more reliable than the one from photo-CELIV. Using drift-diffusion simulation allows for fitting the dark-CELIV with only one mobility, and then keeping this mobility while fitting the photo-CELIV signal with the other mobility and the recombination prefactor as the only fit parameters. Furthermore, the temperature dependence of the capacitance-frequency in doped devices also yields an activation energy which depends mainly on the mobility activation.

Thus, in order to accurately determine material parameters one needs to distinguish between different processes. This can be done by simplifying the layer stack, or by exploiting the specific operating regimes of some layer stacks and by utilizing specific signatures of physical processes. Often already the distinction of electron and hole parameters is not possible, and at one point an arbitrary assignment is made. In the cases presented here the assignment of the respective carrier type is straight-forward, however.

13.3 DEGRADATION ANALYSIS

The second part of this work deals with the degradation of organic semiconductor devices by various factors such as humidity, oxygen, light or electrical current. Traditionally degradation mechanisms are studied by monitoring the gradual performance decrease of a series of devices during prolonged operation. What we propose in this thesis is to intermittently and repeatedly carry out a series of diagnostic techniques in AC, DC and transient mode on the same device. Thereby a rich and comprehensive data set is acquired that enables a systematic analysis and an understanding of the underlying mechanisms that goes beyond the standard stability lifetime measurements. The studies we have performed are in principle similar to other studies done before, which however included further, rather time-consuming, expensive and sometimes invasive, experimental methods. We show the same conclusions can be obtained by our approach in a far more elegant way.

The first study we present underlines the role of hole transport materials in the degradation of the cathode. We investigated the solar cell stack ITO/HTL/P3HT:PC_{61}BM/Al with different

solution-processed hole transporters: PEDOT:PSS, MoO_3, V_2O_5 Oxopolymer and V_2O_5 Xerogel. The devices were not encapsulated and exposed to air in the dark under three different temperature and humidity conditions.

The dominant degradation mechanism is the oxidation of the aluminium cathode triggered by an ingress of humidity, leading to the formation of a thin insulating aluminium oxide layer and thus a loss in effective area for charge extraction. The most prominent signature of this effect in the IV-curve is therefore the strong loss of short-circuit current and at the same time a stable open-circuit voltage. In transient photocurrent measurements a short-lived transient current is observed, as the active material and with it the photogeneration is still unchanged. However, the electrons cannot be extracted at the organic/insulator interface barrier, leading to a space-charge build-up and a complete loss of the driving electric field, giving a steady-state photocurrent of zero. In this fully degraded state the whole device area is oxidized and the device has become a MIS-device, which is confirmed in capacitance-voltage and MIS-CELIV measurements.

The effect is accelerated by humidity as well as temperature, and its speed is governed by the choice of the HTL. We find that PEDOT:PSS, which is hygroscopic, strongly enhances the diffusion of water into the device. In contrast, the alternative HTLs can slow down the process by a factor of up to 380.

From modelling the water concentration inside the stack we could compute the loss in effective area which is proportional to the measured short-circuit current over time. The diffusion simulation gives a squareroot-of-time dependence for diffusion from the edges, which agrees well with the measured behaviour. The 2D modelling thus confirms the proposed lateral progress of degradation, and further allows us to give an estimate of the water diffusion constant in the different hole transport materials.

Another study was performed using encapsulated devices with the structure ITO/HTL/PCDTBT:PC_{71}BM/LiF/Al where PEDOT:PSS and evaporated MoO_3 were used as hole transport layers. The encapsulation prevents water and oxygen ingress and with it the oxidation of the aluminium electrode. The devices were stressed by illumination, thus most of the degradation is expected to stem from the active material. However, in the PEDOT:PSS devices a strong initial voltage loss was observed, in contrast to the MoO_3 devices. This burn-in effect is thus related to the PEDOT:PSS/organic interface energetics. This initial instability leads to a large drop in V_{oc} of around 100 meV. At later times the main degradation mechanism is the photodegradation of the absorber layer.

We also addressed photodegradation by concentrated sunlight, thereby investigating the PCDTBT:PC_{71}BM solar cell stack as well as a second batch of samples based on a HBG1:PC_{61}BM blend. In the first case an increased illumination intensity basically just accelerates the degradation. The burn-in behaviour is always observed, and later trapping probably becomes the dominant mechanism. Therefore, in this material system concentrated light may be used to accelerate the degradation and to predict device stability lifetimes.

In the HBG1-based devices, however, a clear difference is observed for devices aged at 1 sun and devices aged with 50 or 100 suns. Under high illuminations the devices show signatures of doping building up, additionally to trap-related signatures which are observed under all intensities. We furthermore find that the photodoping part is fully reversible after storage in the dark for 30 days. Therefore, in this BHJ material, accelerated ageing by concentrated sunlight is not a valid tool to predict the cell stability.

Based on the degradation studies shown here we conclude that it is crucial to look at the complete stack when investigating stability of organic solar cells. It would have been grossly incorrect to ascribe the short-circuit current loss of uncencapsulated devices to a change in the active material. It is also wrong to relate the burn-in observed in the PCDTBT-based cells only to the PCDTBT. In both cases the role of the functional layers (hole transport layers) and the encapsulation cannot be underestimated. Thus, variations of the experiment are indispensable in order to learn about the contributions of the various layers to the overall degradation, and we suggest to:

- Compare encapsulated to non-encapsulated devices
- Vary the material(s) of the functional layer(s)
- Vary the ageing conditions temperature, humidity, current, illumination intensity

The second conclusion we can draw from the degradation experiments is not to focus only on the IV-curve parameters. Basically every degradation mechanism leads to a decrease of the device performance (PCE) over time. While recording this curve may allow to determine a lifetime, and to compare different materials or ageing conditions, it is not possible to determine the dominant ageing mechanism from this data alone.

Only by the combination of several experiments a full picture of the processes going on in the device may be obtained. While a huge range of other experimental techniques has been employed for this purpose, we have demonstrated that also the combined analysis of various electrical measurements is equally useful. Finally, the postulated degradation mechanisms can be tested by numerical modelling of the full device, and the picture can be completed.

14 OUTLOOK

We have shown that simulation-based analysis of transient electrical measurements can give deeper insight into the underlying physical processes in organic semiconductor devices. This approach also allowed us to test commonly used models and develop new analytic routines for parameter extraction.

In fact, this procedure may be applied to a large range of analytical models and parameter extraction routines:

- The CELIV formula has been demonstrated to be not always reliable, as the assumptions made are usually not correct. Also the improved equations based on more appropriate models, partly even based on (simplified) drift-diffusion modelling, turn out to be not suited to accurately determine the charge carrier mobility in relevant stack architectures. Therefore, based on our tools, a new parametrized CELIV formula dependent on ramp rate, peak position and peak height may be developed in the future.

- As we show in the Appendix C.5, also other techniques like the transient photocurrent rise may be suited to determine the mobility. Here as well a simulation-based development of a dedicated formula and the investigation of its limitations would be a very useful effort.

- The modulated photocurrent techniques IMPS/IMVS also offer new ways to gain information on mobility and recombination. As they have just become available for simulation now, they surely should be investigated in more detail.

- We find that the transient photovoltage decay commonly used to analyse the recombination behaviour is problematic. First of all the basic theory of minority carrier recombination is usually not fulfilled in organic solar cells. Secondly the influence of the measurement resistor as well as non-ideal shunting behaviour can distort the signal and render it useless. In our opinion time-delayed charge extraction methods like OTRACE-CELIV or Delaytime Charge Extraction are much better suited to really measure the recombination kinetics.

- The assessment of trap parameters - density, energetic distribution, capture rates - constitutes a huge task. Especially in the context of photodegradation trapping and dispersive transport play an important role. Therefore dedicated experiments for quantitative parameter determination need to be found and understood. Deep-level transient spectroscopy might be such a technique, as well as temperature-dependent low-frequency impedance measurements (thermal admittance spectroscopy). For this effort, however, also the simulation side may need some extensions, as currently not all combinations of mobility, injection, and trapping models are supported.

While the idea of comparing several experiments as well as comparing measurement and simulation is not new, only now we are for the first time able to pursue this idea with respect to electrical techniques, and bring it to a quantitative level. For this achievement it was necessary to have a measurement setup where complementary experiments can be performed in a short time, enabling a synoptic approach. And only due to the improved computation speeds in *Setfos* it has become possible and realistic to simulate all experiments and to perform global fitting routines.

The polar bilayer OLED stack was identified to be well-suited for specific parameter extraction routines borrowing from the theory of MIS-devices. One of our conclusions for reliable parameter determination is that for the investigation of new materials there is probably no way around fabricating dedicated devices to determine specific parameters. Now, apart from purely unipolar devices and "real" MIS structures, also devices with a polar layer implement carrier selectivity. This concept enables new layer combinations, and in principle allows to separately address both electron and hole parameters of a material.

For our experiments we employed very standard materials and layer stacks which have been available for us. This leads to various consequences: Simple stacks are easier to understand and therefore more suitable for degradation as well as parameter extraction studies. Common active layer materials such as P3HT:PCBM or α-NPD/Alq_3 are useful in order to compare the results to previous studies. They do, however, only offer limited efficiencies as well as stabilities. Therefore it is unclear whether the results obtained can be directly transferred to more efficient or very stable devices. Today's record cells probably do not suffer from the same loss and degradation mechanisms, otherwise they wouldn't be that efficient.

The hand-made and mainly solution-processed devices show only a low reproducibility. Thus fully quantitative studies do not always seem meaningful, as a different device from the same batch will behave slightly different. Therefore qualitative behaviour of different experiments versus a parameter variation are more informative. The variation may be a measurement parameter like light intensity, a device parameter like the layer thickness or the used functional material, and the progress of degradation under a given stress condition. In all these cases qualitative changes in the shapes of the various measurements are observed which are signatures for specific physical (or chemical) processes. We believe that the goal should be to find a suitable model that can explain all these observed changes qualitatively. As models always contain simplifications it is unlikely that a fully quantitative picture can be found which is based on the change of only one model parameter. Especially for stability analysis several processes happen simultaneously, and the goal should be to identify the most severe one.

The current focus in OPV stability research is on photostable materials and thermally stable morphologies. Photodegradation usually contains chemical reactions that decompose the organic material and lead to the generation of charged species (doping, radicals) or sub-bandgap states (traps). Therefore the characterization of the changes in the density-of-states would be the most important task concerning (opto-)electrical measurements and simulations. For this purpose it is probably necessary to include further experimental techniques such as thermally stimulated current spectroscopy or spectral response.

During thermal stress the morphology of a bulk-heterojunction changes. It is assumed that during a de-mixing process the fullerene tends to cluster and form larger domains while simultaneously diffusing towards one side of the film. Some of the resulting effects could be tackled with our approach. The phase-segregation will lead to a change in the recombination efficiency, and may also lead to a lower effective mobility. Furthermore fullerene accumulation on one side could be simulated as a thin fullerene-only layer at the interface, mainly leading to extraction problems.

However, more complicated situations and a more direct accounting for the changing cluster sizes is not directly possible within our drift-diffusion effective medium approach. The presented effective area model using a parallel circuit of different cells might be one way to go, by simulating various cross-sections corresponding to different polymer/fullerene mixing. On the other hand, as the electrical measurements only deliver a total current of the full device, other experiments would be needed to justify a chosen parametrization. Thus, the use of a 1D effective medium model to describe thermal stability studies still needs to be evaluated.

As for the degradation issues related to oxygen and water, we are confident that good encapsulation strategies and materials are available today, also from the OLED industry, and that this will not pose a threat to device stability in a future industrial fabrication scenario of OSCs. Furthermore, the reproducibility issues can also be well handled by upscaling and automation. Therefore, the race for organic solar cells is still on!