

Organic solar cell aging

As the efficiencies of polymer solar cells have steadily improved over the last years, we are reaching a point where stability rather than efficiency is becoming one of the major impediments for commercialization. Polymer solar cells degrade via several chemical and physical pathways that affect different parts of the device, namely the donor and acceptor materials, the active layer morphology, as well as the interlayers and electrode materials. Water and oxygen, often in combination with light, play a key part in many of the degradation processes. The active layer components are known to be susceptible to photo-degradation in combination with oxygen or water that has leaked into the device. Hence, encapsulating the devices to protect them from the ambient atmosphere is necessary. So far, the degradation mechanism behind the morphology of the active layer is not clear. Due to the presence of water and oxygen in the air it is difficult to extract the morphology degradation through common characterizations during the device aging. Thus, in our group we have used in-operando techniques which can achieve the morphology tracking in the operation process without chemical degradation.

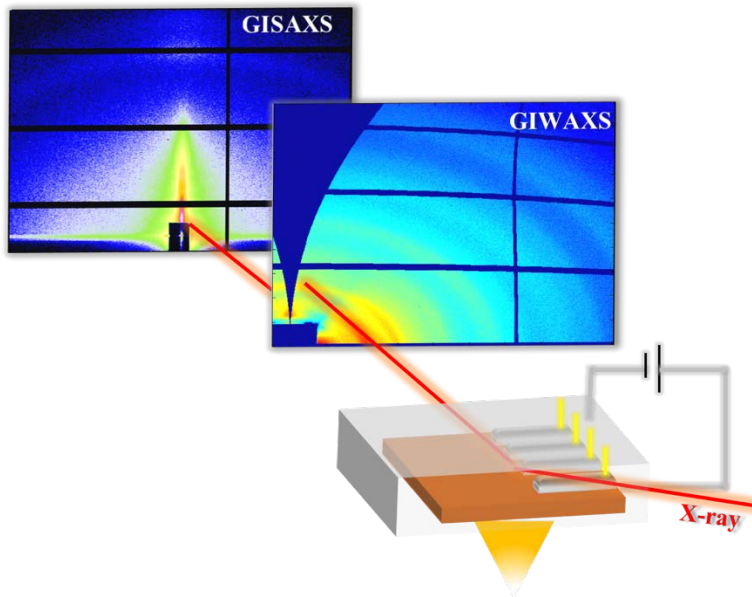


Figure 1. Sketch of in-operando GISAXS/GIWAXS measurements set-up

In our group, we are focusing on studying the morphology degradation of organic solar cells during operation. We intend to figure out the temporal evolution of the active layer morphology under illumination. Thus, an in-operando set-up was developed which allows measuring the current-voltage (IV) characteristics under illumination and following the morphological changes simultaneously. In situ grazing incidence small/wide angle X-ray scattering (GISAXS/GIWAXS) are the methods of choice for characterizing the morphology evolution (as shown in Figure 1). The measurement is performed under vacuum conditions to avoid chemical degradation via oxygen and water. A lamp is used to simulate a sun radiation spectrum illuminating the solar cells, and the photovoltaic performance is recorded.

In the last decades, P3HT:PCBM based solar cells have been the prominent model system in organic photovoltaics. We used in-operando GISAXS and GIWAXS measurements to detect the morphology changes of the P3HT:PCBM active layer during device degradation. Firstly, P3HT:PCBM based solar cells in standard geometry were investigated by in-operando GISAXS measurements. Growing polymer domains and domain distances were observed and correlated to the device degradation. The coarsening of the morphology resulted in a decay of the short-circuit current density (J_{SC}) as the probability that excitons are reaching the donor (D)/acceptor (A) interface decreased¹. Figure 2a shows the temporal evolution of photovoltaic parameters. The decay of the J_{SC} (Figure 2a) which dominates the degradation of the solar cell performance is correlated to the morphology coarsening observed with GISAXS (Figure 2b). Besides, in-operando GIWAXS measurements were applied to probe the polymer crystallinity evolution during the aging of P3HT:PCBM based devices. The results show that the open circuit voltage (V_{OC}) has a strong correlation with the polymer crystallinity². Moreover, the in-operando GISAXS measurements were carried out on P3HT:PCBM based devices with inverted architecture as well. The results show that these solar cells are more stable than the standard geometry devices. The photovoltaic performance and the morphology of active layer were found to be quite stable during the time scale of the in-operando GISAXS experiment³.

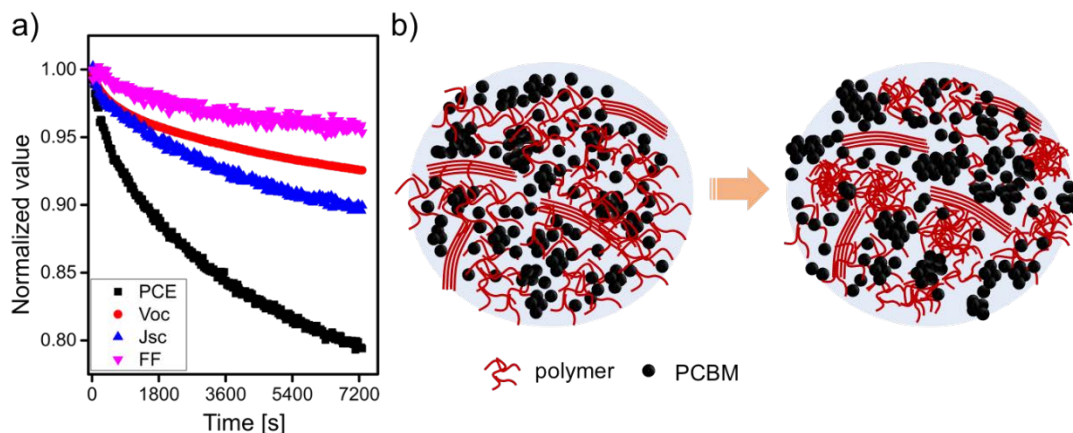


Figure 2. a) Temporal evolution of photovoltaic parameters during operation and b) schematic of the morphology coarsening under illumination.

To enhance the efficiency, doping with a solvent additive is proposed to optimize the morphology of the active layer and considered to be a more efficient and convenient approach compared to thermal annealing and solvent annealing. The solvent additives generally have a higher boiling point than the host solvent and are able to selectively dissolve specific components. These features provide the possibility to form interpenetrating networks providing larger D/A interfaces in the bulk heterojunction film which facilitates exciton separation. However, the question raises whether the solvent additive with high boiling point will affect the stability. Thus, we performed in-operando measurements on PCPDTBT:PCBM and PTB7-Th:PCBM based solar cells with and without solvent additives^{4,5}. Due to the high boiling point of the solvent additives, residual solvent additive is left in the film after the device fabrication. The evaporation of the solvent additives during operation was probed by the in-operando GISAXS measurements, which observes a shrinking of the polymer domains. Furthermore, the decrease of the polymer domain sizes provokes charge trapping in the active layer, resulting in a serious decay of the fill factor (FF)^{4,5}.

Therefore, considering the stability of the device, it is necessary to remove all the solvents during the device fabrication.

Moreover, we performed in-operando GISAXS and GIWAXS measurements on PffBT4T-2OD:PCBM based solar cells, in which thermal spin-coating and thermal annealing are contained in the device assembly. Thus, the solvent additive can be removed to a large extent. Based on the in-operando GISAXS measurements, no solvent evaporation is probed and the polymer domain sizes of the device with solvent additives are constant during the measurements. Besides, the *FF* value is the most stable value in the corresponding solar cells. However, according to GIWAXS characterization, we find that a decay of polymer crystallites in the device with DIO additive is strongly correlated with the decrease of the V_{OC} value. These studies give more information for choosing a proper solvent additive for future more efficient and more stable organic solar cells.

Despite these pioneering in-operando experiments, the morphological degradation of organic solar cells is not fully understood. More experiments are needed to understand the physical degradation pathways. Attention will be put on novel high-efficiency non-fullerene solar cells and ternary solar cells which are highly promising for a real-world application of organic solar cells. There is no doubt that our research will contribute to the marketability of organic photovoltaics by providing solid knowledge for the optimization and production of the next generation organic solar cells.

References

- (1) C. J. Schaffer, C. M. Palumbiny, M. A. Niedermeier, C. Jendrzewski, G. Santoro, S. V. Roth, P. Müller-Buschbaum: *A direct evidence of morphological degradation on a nanometer scale in polymer solar cells*; *Adv. Mater.* **25**, 6760–6764 (2014).
- (2) D. Moseguí González, C. J. Schaffer, S. Pröllner, J. Schlipf, L. Song, S. Bernstorff, E. M. Herzig, P. Müller-Buschbaum: *Codependence between crystalline and photovoltage evolutions in P3HT:PCBM solar cells probed with in-operando GIWAXS*; *ACS Appl. Mater. Interfaces* **9**, 3282–3287 (2017).
- (3) W. Wang, C. J. Schaffer, L. Song, V. Körstgens, S. Pröllner, E. D. Indari, T. Wang, A. Abdelsamie, S. Bernstorff, P. Müller-Buschbaum: *in operando morphology investigation of inverted bulk heterojunction organic solar cells by GISAXS*; *J. Mater. Chem. A* **3**, 8324–8331 (2015).
- (4) C. J. Schaffer, C. M. Palumbiny, M. A. Niedermeier, C. Burger, S. V. Roth, P. Müller-Buschbaum: *Morphological degradation in low bandgap polymer solar cells - an in operando Study*; *Adv. Energy Mater.* **6**, 1600712 (2016).
- (5) D. Yang, F. C. Löhner, V. Körstgens, A. Schreiber, S. Bernstorff, J. M. Buriak, P. Müller-Buschbaum: *In-Operando study of the effects of solvent additives on the stability of organic solar cells based on PTB7-Th:PC₇₁BM*; *ACS Energy Lett.* **4**, 464–470 (2019).