INFLUENCE OF THE AMBIENT ATMOSPHERE ON THE DEGRADATION OF P3HT:PCBM SOLAR CELLS

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1. Introduction

An important requirement for successful implementation of organic solar cells (OSC) is an improvement of their lifetime by elimination of formation and influence of defects. The defects and related defect states may lead to the trapping and recombination of photo charge resulting in the drop of power conversion efficiency (PCE). The defect states can have different origin and may be induced by OSC preparation processes but also induced by ambient atmosphere, radiation, and elevated temperature during OSC lifetime.

The harmful effect of ambient atmosphere on OSC relates mainly to the oxygen and water molecules. Various influence of oxygen-related states were reported including absorbance decrease [1], charge trapping [2], and charge mobility decrease leading to space charge formation [3]. The diffusion of oxygen molecules from the ambient air into the OSC leads to reversible and irreversible OSC degradations [2] and reversible degradation is caused by formation of $P3HT^+:O_2^-$ complexes [1]. The formation of localized states with the activation energy of 0.1-0.15 eV above the HOMO level of P3HT was reported [3,4]. The irreversible degradation is related to chemical reactions of oxygen molecules with organic semiconductors. These reactions are typically stimulated by UV/Vis radiation (photooxidation) or elevated temperature (thermooxidation) [5]. Several photooxidation pathways were simulated. The photooxidation was found to start at P3HT alkyle chains from which radical formation spreads towards the polymer backbone where it disrupts the π-orbital conjugation [6]. The influence of humidity on the active layer was much less studied and such an impact was reported on the metal electrode [7,8].

We used the charge DLTS (Q-DLTS) to study the influence of ambient atmosphere on P3HT:PCBM solar cells. The advantage of this method resides in its high sensitivity ($\Delta Q \sim 10^{-16}$C) enabling the correlation of defect states and OSC electrical parameters degradation [9,10]. The information about the influence of these states on photovoltaic processes and the electrical parameters of OSC was obtained from dark and light I-V curves and external quantum efficiency (EQE) measurements.

2. Preparation and characterization of samples

Our samples consisted of glass substrate with ITO layer (front electrode), P3HT:PCBM active layer (110±10 nm) and back electrode (12±3 nm Ca and 110 nm Ag). The OSC preparation was described in ref. [4]. The OSC with 1:1, 1.5:1 and 2:1 P3HT:PCBM weight ratios were investigated. The optimized ratio is 1.5:1 P3HT:PCBM. The ratios of 1:1 and 2:1 were chosen because of the similar photocurrent in OSCs before their degradation, which is determined by the area of the active bulk heterojunction.

We measured both the isothermal and temperature Q-DLTS scans in order to determine the information about concentration and the activation energy of observed defect states in the active layer. The isothermal scans were measured at room temperature 295±3 K.

Also, we measured both the dark and illuminated I-V curves to find the influence of defect states on OSC electrical parameters. The OSC were illuminated at an intensity of 1000 W/m^2 with AM 1.5G spectrum. We determined the exciton generation rate (G_{max}) and the short-circuit exciton dissociation probability (P_{sc}) [11] from I-V measurements using Eq. (1)

(1) $$G_{max} = \frac{J_{sat}}{qL} \qquad\qquad P_{SC} = \frac{J_{SC}}{J_{sat}} \quad ,$$

where J_{sat} is a saturated value of photocurrent density in reverse bias region (measured at V = -500 mV), L - active layer thickness, q - elementary charge, and J_{SC} - short-circuit current density. The product of G_{max} and P_{SC} is proportional to J_{SC}.

EQE spectra were measured in the wavelength interval of 300-800 nm without bias light to get the information about the influence on photocurrent spectral dependence.

3. Experimental results and discussion

The measured isothermal Q-DLTS spectra of OSCs with different P3HT:PCBM weight ratios are shown in Fig. 1. The peak at 20 μs corresponds to the oxygen-related states with an activation energy of about 0.15 eV determined by temperature Q-DLTS measurements as discussed in ref. [4]. As shown in Fig. 1, the Q-DLTS signal, and hence the concentration of observed defect states, increases with the proportion of P3HT in the active layer. It suggests that these states are located above the HOMO level in P3HT phase. Besides the defect state concentration, the Q-DLTS signal could be affected by morphology of the active interface. The higher proportion of PCBM (1:1 weight ratio) could lead to formation of isolated P3HT domains, which did not enable the charge release to the external circuit and therefore drop of the Q-DLTS peak is observed.

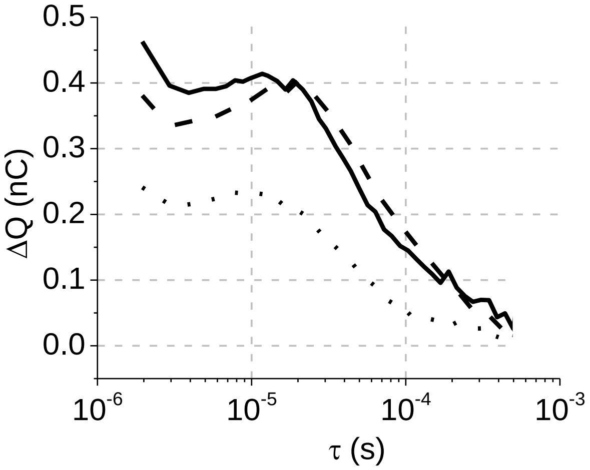

Fig. 1: *The isothermal Q-DLTS spectra of OSCs with different P3HT:PCBM weight ratio after 20 days of degradation in ambient air. P3HT:PCBM weight ratios: 1:1 (dot), 1.5:1 (dash), 2:1 (solid).*

The time evolution of PCE of OSCs with different P3HT:PCBM weight ratio during degradation is shown in Fig. 2. The OSCs were the most stable with optimized P3HT:PCBM weight ratio of 1.5:1. The results suggest the two dominant stages of degradation. The OSC with higher proportion of PCBM degraded faster in the first stage (during first 5 days) while the samples with higher proportion of P3HT degraded faster in the second stage (after 10 days). The P3HT:PCBM weight ratio could influence the oxygen diffusion into P3HT as well as the impact of oxygen-related states on PCE.

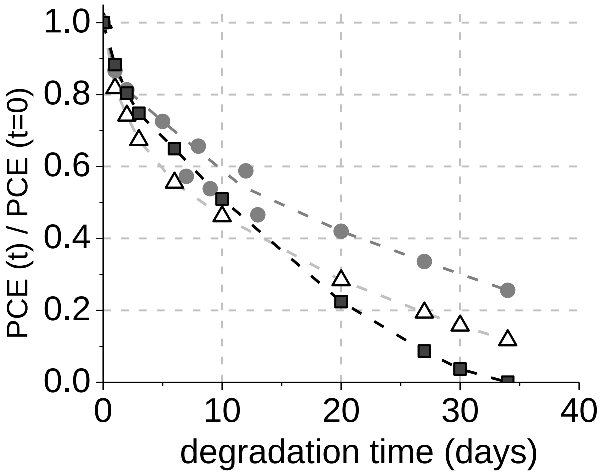

Fig. 2: *Time evolution of PCE of OSCs with different P3HT:PCBM weight ratio during degradation in ambient air. P3HT:PCBM weight ratios: 1:1 (triangles), 1.5:1 (circles), 2:1 (squares). Lines are eye-guide* only.

The degradation had the strongest influence on the decrease of J_{SC} as was discussed in ref. [4]. The presence of two degradation stages is more obvious from the correlation of J_{SC} with the ΔQ (proportional to defect state concentrations) as shown in Fig. 3. Interestingly, the first section of the correlation is the same for all weight ratios, implying the OSC degradation is induced by these states. The second stage of the degradation is affected by additional effects probably related to the active interface, since the correlation of OSCs with lower area of active interface (i.e. 1:1 and 2:1 weight ratios) had steeper slope.

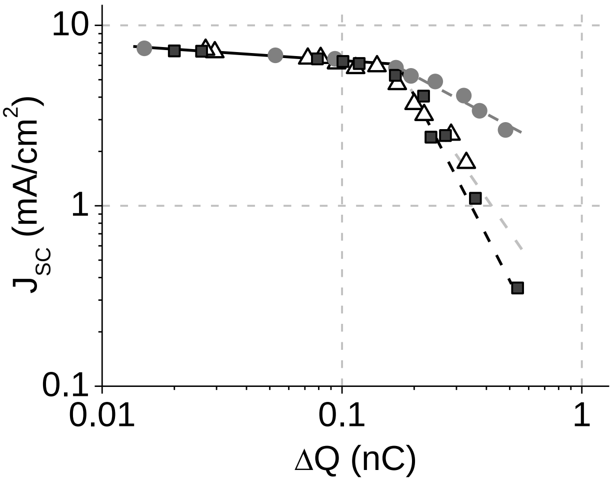

Fig. 3: *The correlation of J_{SC} with isothermal Q-DLTS signal at rate window 62.5 ms^{-1} and room temperature for different P3HT:PCBM weight ratios: 1:1 (triangles), 1.5:1 (circles), 2:1 (squares). Lines are eye-guide* only.

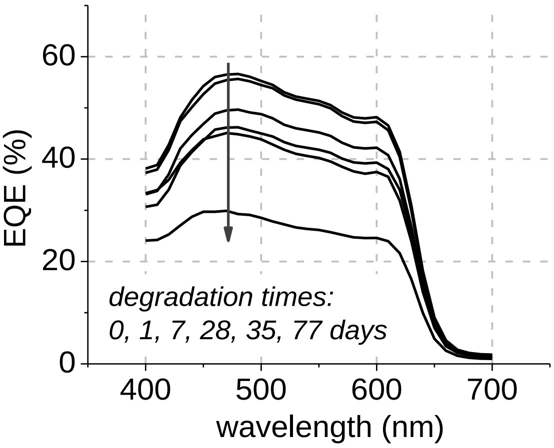

Fig. 4: *The evolution of EQE spectra of OSC with P3HT:PCBM weight ratio 1.5:1 during degradation in ambient air.*

As seen from EQE measurements in Fig. 4, the EQE spectra decreased with degradation time without changes of the shape. Therefore, we suppose that the exciton generation by photon absorption was almost unaffected during degradation.

The degradation of exciton generation rate (which involves also exciton recombination) is much faster compared to that of exciton dissociation probability (Fig. 5). It means that the decrease of J_{SC} is dominantly determined by the exciton recombination in P3HT, which corresponds to EQE measurements. Thus, the excitons recombine prior reaching the donor/acceptor interface. The exciton recombination does not have to take place directly at observed defect states because of low activation energy of these states. However, it can be caused by exciton mobility decrease resulting in shortening of exciton diffusion length due to the charge trapping at these states. In the case of the highest proportion of P3HT, the sudden decrease of P_{SC} after 20 days of the degradation may be caused by the back contact oxidation.

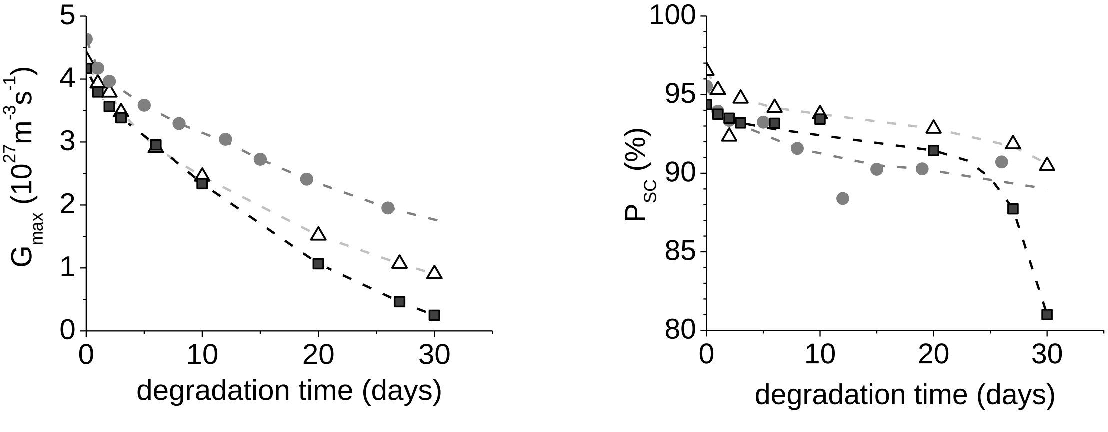

Fig. 5: *Time evolutions of G_{max} and P_{SC} for OSCs with different P3HT:PCBM weight ratio during degradation in ambient air. P3HT:PCBM weight ratios: 1:1 (triangles), 1.5:1 (circles), 2:1 (squares). Lines are eye-guide* only.

4. Conclusions

The presented results show the influence of the ambient oxygen on the creation of defect states localized about 0.15 eV above the HOMO level in P3HT phase. Two degradation stages were observed. The first stage, which takes place in first 5 days of the degradation, seems to be caused by the oxygen-related defect states. This degradation was the fastest in the OSC with the lower proportion of P3HT. The second stage is probably determined by other defect states, which were not observed with Q-DLTS. Here, the defects related to donor/acceptor interface may have played the dominant role. This degradation stage was the most pronounced in the case of the highest proportion of P3HT, where the back contact oxidation could also influence the degradation. The results from I-V measurements show the ambient air degradation in dark mainly influences the exciton recombination in P3HT in both stages of degradation.

Acknowledgement

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