CH3NH3PBI3 IV Output Parameters Degradation Investigation

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Organic photovoltaics, based on hybrid inorganic organic optoelectronic perovskites, with structure alkali- metal- halide are the newest emerging technology in the third generation development. Despite tremendous efficiency records, more than 21 %, optoelectronic perovskites' instability prevents their commercialization and mass production. Issues with degradation are caused by various types of environmental influences. The main issues with stability and power loss in devices are linked to moisture, oxygen, temperature, and light-induced structure defects. Initial measurements are taken after long term debugging with minimal aggressive exposure to environmental conditions. In this case, preliminary degradation studies begin from measurements of light-induced effects. In this work, we will present the main trends in degradation of external characteristics during common I-V measurements, in the order of parameters which were effected the least by environmental factors. This investigation was made on fixed CH3NH3PBI3 solar cells with standard 1.5 AM testing and initial efficiencies more than 8 %.

Keywords: Organic photovoltaics, Perovskite, Power conversation efficiency, Solar cells.
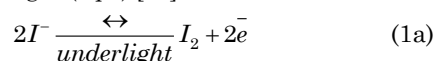
1. INTRODUCTION

Third generation of photovoltaic mostly is presented by organic solar cells, organic photovoltaics (OPV) and emerging hybrid perovskites (PS), both of devices are thin film cells. Last 5 years in this field showed big jump in growth of power conversation efficiency (PCE) up to 13 % for OPV and over 20 % for PS [1-5]. Since beginning XXI century OPV achieved traditional silicone based cells, in its turn commercialized amorphous Si:H ($\sim$ 13 %) and on the other hand PS cells moves breakthrough towards to crystalline Si, CIGS (Copper Indium Gallium diSelenide) and CdTe, to more than 20 % PCE level and now are close to Shockley- Queasier limit [6-10].

Based on competitive laboratory results next development step requires up – scaling and stable work of devices, here scientific area expands to many directions: roll-to-roll deposition techniques, resistance for environment moisture and oxygen with suitable encapsulation, long-term underlight stability [11-12].
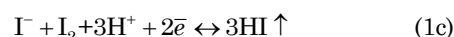
At least one direction of research is one of the main keys for PS cells development, because physics of elementary processes is still not determined in details. But though basic origins and questions of light-induced degradation are formulated:

1) Degradation due to trapped charges at abrupt organic/cathode interface;
2) Bond breaking, caused by hot polarons/hot excitons;
3) Bipolarons near cathode- semiconductors interface;
4) UV light affecting.

Firstly, it's necessary to note, that accordingly to PS advantage in film processing – low formation energy between anion (for example MAI – methyl ammonium iodide – CH3NH3I) and cation (for example PbI+), it is easy to make, but in opposite easy to pull apart by heat, electric field and light (eq.1) [13].

$$2I^- \xrightarrow[\text{underlight}]{\leftrightarrow} I_2 + 2\bar{e} \qquad (1a)$$

(on the donor – acceptor interface)

$$3CH_3NH_3^+ \leftrightarrow 3CH_3NH_2^+ \uparrow + 3H^+ \qquad (1b)$$

$$I^- + I_2 + 3H^+ + 2\bar{e} \leftrightarrow 3HI \uparrow \qquad (1c)$$

Equation 1 showed only one of possible routes of perovskite dissociation during degradation. Main factor of chemical structure stability lies in optimal crystal compatibility of composing atoms radiuses. Perovskite structure is ABX3 (A-alkali, B- metal (Pb, Sn, Ge), X – halide). Goldschmidt in 1927 formulated special stability factor, depending on atom radius ratio (Eq.2):

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \qquad (2)$$

For most stable molecules, this factor is 1, while for perovskites it is nearly 0.8. For summary of this description of perovskite instability, reports about long-term study shows decreasing of peak characteristics after few days or weeks (depends on structure and composition) and degradation measurement are no longer, then 10 000 hours. Although, promising progress is reported in Snaith and Graetzels groups in different works with using of metal oxides, mesoscopic structures, small radius cations doping [14-15].

Influence of degradation on *I-V* parameters doesn't decrease all parameters at the same time. Absorption may be stable, while quantum efficiency decreases, exciton quenching by polarons creates trap-states and sub-bandgaps [16]. In this work, series of periodical measurements on widely-known MAPbI3 PS solar cell under standard 1.5 AM light conditions was made. Light-induced degradation firstly decreases quantum efficiency with resulting maximum power decrease was showed. Than C-H bonds starts to break, that causes shunt resistance losing and leaks increasing. Finally dissociation of perovskites leads to absorption loss and impairment of cathode- semiconductor interface, as result – J_{sc} fall and R_s rise.

2. EXPERIMENTAL PROCEDURES

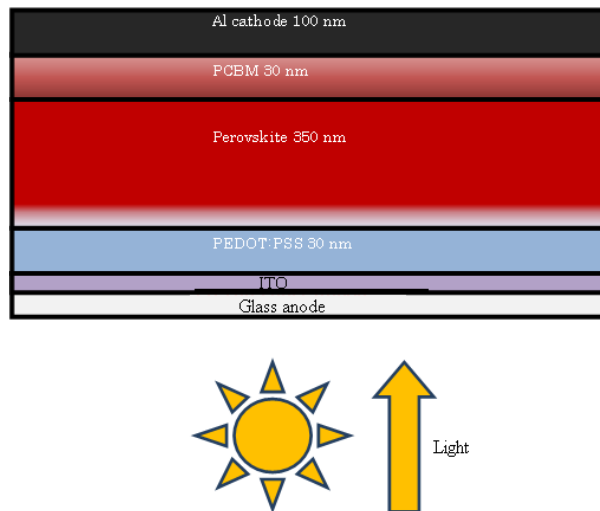Solar cells based on perovskite $CH_3NH_3PbI_3$ were produced with planar structure (Fig. 1).

Fig. 1 – Solar cells structure based on perovskite $CH_3NH_3PbI_3$

Transparent electrode profile should provide a basic functional task – to prevent the closure of the cathode to the anode. Initially, the ITO conductive layer from substrate was etched the from edge to the border of the applied photoactive polymer. However in the most cases when taking the current-voltage characteristics (*I-V*) the noise was detected, and contact was broken. For the hole-transport layer the PEDOT: PSS polymer aqueous solution was used, before application of the aqueous solution it was filtered through a 0.45 micron Teflon filter. Hole-transport of PEDOT: PSS layer was deposited by centrifugation at 3000 rpm speed of rotation / min for 60 seconds to achieve a thickness of 30 nm. Further the formed film was annealed at 150 °C for 15 minutes, after it the substrate cooled to room temperature and then was transferred for the photoactive coating on a layer. All fabrication routine was done in box with nitrogen atmosphere (Oxygen 10 ppm, water 1 ppm). Perovskite solution was mixed in 1.2 M concertation using PbI2 and MAI (both DYESOL production) previously dissolved in GBL : DMSO (7 : 3 by volume). PCBM acceptor solution was prepared in anhydrous chlorobenzene in 10 mg/ml concentration. ITO pixelated substates (Lumtec, 10 Ohm / □) were cleaned by next steps in ultrasonic bath (20 minuters on each steps) – Alkiline detergent 1 %, deionized water (18 Mohms), acetone, toluene, methanol, isopropanol (all ME grade) and final UV exposure during 15 min for surface activation.

Firstly PEDOT : PSS 1.1, % water solution (Heraeus Clevious) was spincoated on ITO substrates with 3000 rpm speed during 60 sec to grow 30 nm layer, then it was annealed at 150 °C during 10 minutes. After it perovskite film was formed with 2 steps spincoating, from 20 sec at 1000 rpm to 20 sec at 5000 rpm and toluene dripping at last step, annealing was done at 100 °C (10 minutes). PCBM (Solene) layer was spin-coated at 1000 rpm during 40 sec. Finally Al cathode layer was

thermally evaporated to achieve 100 nm thickness at $2 \cdot 10^{-6}$ Torr vacuum level. Encapsulation was done with Norlan 65 pixel square was obtained as 0.084 cm² square. *I-V* measurement was done by Newport Thermo Oriel solar simulator at 1.5 AM spectrum, 100 mW/cm² irradiation level and by using Keithley 2400 source-measure unit.

3. RESULTS AND DISCUSSION

Firstly initial *I-V* measurements were done for 4 samples for fixing "as produced" results (Fig. 2 and Table 1), then best sample (№ 3) was chosen for *I-V* parameters degradation study.

After initial testing sample № 3 was measured periodically with 12 hours interval, and it was clearly observed, that U_{oc} and J_{sc} were staying constant while fill factor (FF) is essentially a measure of quality of the solar cell start its decrease from 0.72 to 0.54 (loss of 33 %) in cause of R_s increasing up to 15 Ohm·cm² – cathode – PCBM interface degradation.
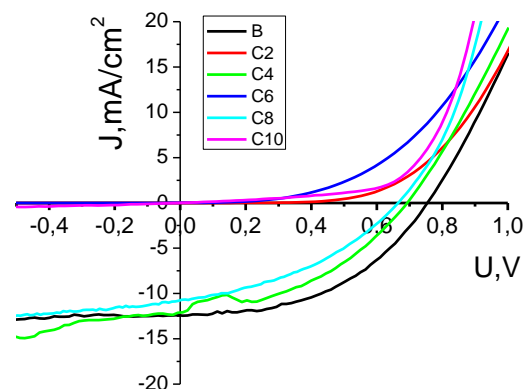

Fig. 2 – 72 hours I-V curves of № 3 perovskite cell

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Next 36 hours of measurements were obtained (fig. 3, 4. and tab. 2, 3) with continue decreasing of FF, R_{sh} and R_s and starting degradation of V_{oc} and J_{sc} , that characterizes by quantum efficiency decrease and absorbance of perovskite layer and perovskite – PCBM interface.

Thereby it is forming a clear trend for solar cell degradation without encapsulation the complete degradation is observed for 3 days, whereas for the encapsulated solar cells their efficiency loss during 6 weeks was from 3 to 15 %. Overall the curve of efficiency change versus time is presented in figure 3.

Tendencies *I-V* output parameters have clear order in decreasing of *I-V* filling area – preliminary power loosing (firstly from 0,72 to 0,54 during during first 36 hours). Then perovskite cells lost their quantum efficiency, that's causes J_{sc} decreasing (after 72 hours of operatin) and finally perovskite molecules lost their stability – decreasing of V_{oc}. This affecting is proportional to decreasing of R_{sh} and increasing R_s respectively to degradation of PCBM – Al interface, in its turn it

Table 1 – Initial I-V parameters measurement of 4 perovskite cells at 1.5 AM

№	U_{oc} (V)	J_{sc} (mA/cm²)	FF	Efficiency (%)	R_{sh} Ohm·cm²	R_s Ohm·cm²
1	0.90	12.69	0.71	8.04	2.94 106	15.42
2	0.90	12.76	0.72	8.19	1.96 106	15.13
3	0.90	12.69	0.72	8.23	2.56 106	14.10
4	0.90	12.54	0.72	8.13	1.10 106	13.62

Table 2 – 36 hours № 3 perovskite cell I-V parameters measurement

Time, h	U_{oc} (V)	J_{sc} (mA/cm²)	FF	Efficiency (%)	R_{sh} Ohm·cm²	R_s Ohm·cm²
as produced	0.90	12.69	0.72	8.23	2.56 106	9.10
12	0.88	12.95	0.66	7.48	2.87 106	10.40
24	0.90	12.85	0.55	6.34	2.92 106	12.09
36	0.90	12.38	0.54	6.01	1.96 105	12.37

Table 3 – 72 hours № 3 perovskite cell I-V parameters measurement

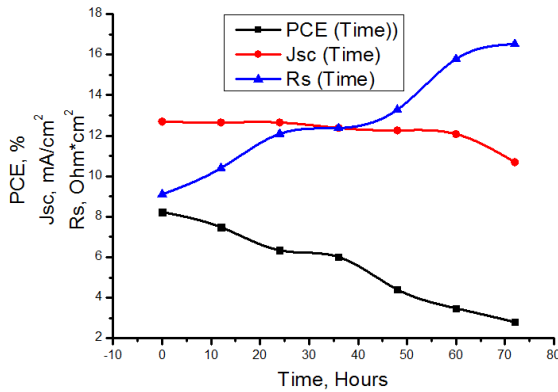| Time, h	U_{oc} (V)	J_{sc} (mA/cm²)	FF	Efficiency (%)	R_{sh} Ohm·cm²	R_s Ohm·cm²
48	0.76	12.46	0.46	4.41	13.28	1.86 104
60	0.69	12.08	0.42	3.48	15.78	1.41 104
72	0.67	10.69	0.39	2.80	6.52	1.00 103

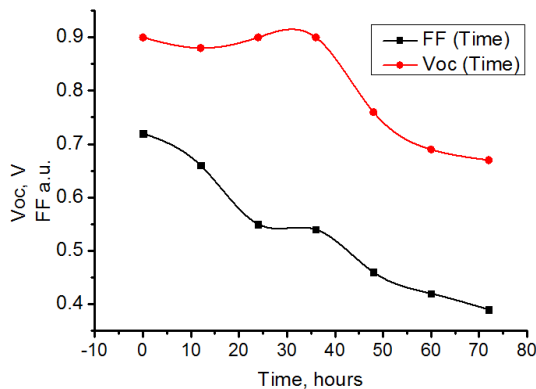**Fig. 3** – PCE, J_{sc} and R_s versus time dependence

Fig. 4 – FF and V_{oc} versus time dependence

was obtained in higher value of leaks in dark measurements and degradation of al cathode- acceptor PCBM interface – bigger slope of UI curve in I quadrant in linear region.

Sufficiently high open circuit voltage for the solar cells on an organic basis - more than 0.6 V is due to the low position of the HOMO level donor relatively to the PEDOT: PSS hole-transport layer. This is due to its lower position levels HOMO / LUMO = – 5.4 eV / – 3.6 eV, and the width of the band gap 1.8 eV. This is value of PCBM increases the open circuit voltage of solar cells based on perovskite to 0.8 V. When working in air the moisture saturation and donor and acceptor oxidation occur, result increased and their specific surface resistance increases. The contacts of the junction metal-semiconductor and semiconductor – a hole-transport PEDOT : PPS layer become high-resistance, and in the heterojunction dark current leakage increases. The effect of forming a solar cell structure under such conditions is clearly seen on the *I-V* curve. By the type of graph it can be determined the noticed degradation points: Large slope of the curve in the current-voltage characteristics in the first quarter is characterized by high series resistance R_s, which reached 100 Ohm·cm²; Large slope of the curve in the third *I-V* quarter is characterized by the dark current leakage and the decreasing in shunt resistance R_{sh} 1000 Ohm·cm²;- The general graph is characterized by insufficient slope of exponential growth, reduced the corresponding values of R_s and R_{sh}. The value of leakage is inversely proportional to the shunt resistance R_{sh}, which, in turn, should be as large as possible. In the real structures, R_{sh} is characterized by the quality of p-n junction and its isolation from the electrodes to prevent punctures. However, at the same time there was a voltage drop to a value ~ 0,4 B, followed by a decrease in the filling factor. This effect should be related to the deterioration of the contact phases of the donor and acceptor. The process described above gave the expected results, the growth of the main values of output parameters. The output characteristics of the sample № 3 showed the highest efficiency 8.23 %. Besides the standard I – V removal from the solar cell pixel, it was also carried measurements out through the optical aperture calibrated mask with a diameter of 1000 microns. This type *I-V* measurement on the area equal to 0.0075 cm² (equivalent circle area with a diameter of 1 mm) allows fixing inhomogenity in the element microstructure of the on the pixel area thus it becomes possible to determine higher or lower performance results which solar cell is able to produce.

4. SUMMARY

The *I-V* investigation show that output parameters trend have clear order in decreasing of *I-V* filling area due to preliminary power loss. Then perovskite cells lost their quantum efficiency, that's causes J_{sc} decreasing and finally perovskite molecules lost their stability – decreasing of V_{oc}. This influence is proportional to R_{sh} decreasing and R_s rising, respectively, in its turn it was obtained in higher value of leaks in dark measurements and degradation of Al cathode- acceptor PCBM interface – larger slope of *I-V* curve in first quadrant in linear

region. Degradation occur a lot of goals for scientists, firstly of course it's molecule stability – doping of perovskite is main trend with two direction – dopants to methyl amin, such as form amide, introducing of small molecule cations – Cs, Ga, Cu an others. This improvements should lift up tolerance factor and finally stabilize operation of devices, that can be checked with transient measurements at power point and optical studies – internal quantum efficiency stable as absorbance level.

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