Out-door testing and long-term stability of plastic solar cells[⋆]

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Abstract. In spite of the high potential of polymer photovoltaic (PV) cells, considerable improvement of their stability under operational conditions needs to be achieved. The few published data on the stability of such cells are devoted to accelerated indoor testing at elevated temperatures. The acceleration factor is undoubtedly dependent on the PV materials, the cell architecture and may vary with the degradation. We report preliminary results of long-term evaluation of PV performance of polymer cells under real sun operational conditions. The studied devices include three types of encapsulated polymer/fullerene cells which differed by the configuration and content of the photoactive layer: (1) bulk heterojunction of MEH-PPV:PCBM; (2) bulk heterojunction of P3HT:PCBM; (3) bilayer heterojunction P3CT-C_{60}. The MEHPPV-PCBM cell exhibited the fastest degradation. The degradation of PV performance of the P3HT-PCBM cell was much slower while the P3CT-C_{60} device was found to be the most stable. Effect of restoration of I_{sc} and V_{oc} was found when the P3HT-PCBM and P3CT-C_{60} cells were kept in the dark overnight. The first I_{sc} and V_{oc} measurements every morning yielded the highest values compared to those during the rest of a day. While I_{sc} recovered only partly and exhibited significant degradation during a month, V_{oc} values recovered completely every night and showed almost no reduction on a long-term time scale.

PACS. 84.60.Jt Photoelectric conversion: solar cells and arrays – 82.50.Hp Processes caused by visible and UV light – 82.35.Cd Conducting polymers – 72.80.Rj Fullerenes and related materials

1 Introduction

Over the last decade organic photovoltaics, based on soluble conjugated polymers, has been suggested as a low-cost alternative, combining key features of inorganic semiconductors with the advantages of low-cost plastic-based technologies. One example would be plastic solar cells based on a bulk heterojunction (BHJ) between donor-type conjugated polymers and acceptor-type fullerenes (or fullerene derivatives) [1]. Although the achieved power conversion efficiencies of up to 5% [2] clearly demonstrate the high potential of polymer photovoltaics, considerable improvement of the cell stability under operational conditions needs to be achieved. It has been demonstrated already [3–5] that the degradation behavior of polymer cells involves a number of photochemical mechanisms including direct photooxidation of conjugated polymers, a photochemical reduction of the organic constituents by aluminium (from a back contact of the cells) and sub-

sequent chemical reaction between the organo-aluminium species and molecular oxygen, etc. However, the data on the stability of PV parameters of BHJ cells have been obtained by an accelerated indoor testing at elevated temperatures [4–8]. The acceleration factor is undoubtedly dependent on the PV materials, the cell architecture and may vary with the degradation. The published data on PV behavior of plastic cells under real sun out-door operational conditions are very limited [9] and to the best of our knowledge there is no report on long-term recording of evaluation of the PV performance under such conditions.

This paper reports preliminary results of long-term recording of PV performance of encapsulated plastic solar cells under real sun out-door operational conditions at Sede Boqer using the documented closeness of the noontime clear sky spectrum at that site to the standard AM1.5G spectrum [10].

2 Experiment

Three encapsulated polymer-fullerene solar cells with photoactive area of 10 cm^2 were produced in RISØ
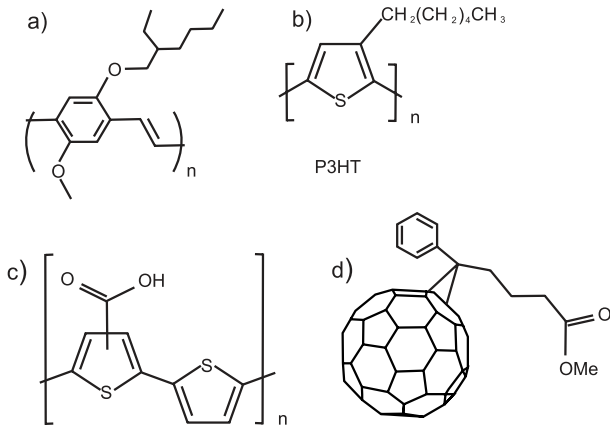

Fig. 1. Molecular structures of donor (a, b, c) and acceptor (d) materials of photoactive layers of plastic solar cells studied: (a) poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV); (b) poly-alkyl-thiophene (P3HT); (c) poly(3-carboxythiophene-co-thiophene) (P3CT); (d) [6,6]-phenyl-C61 butyric acid methyl ester (PCBM).
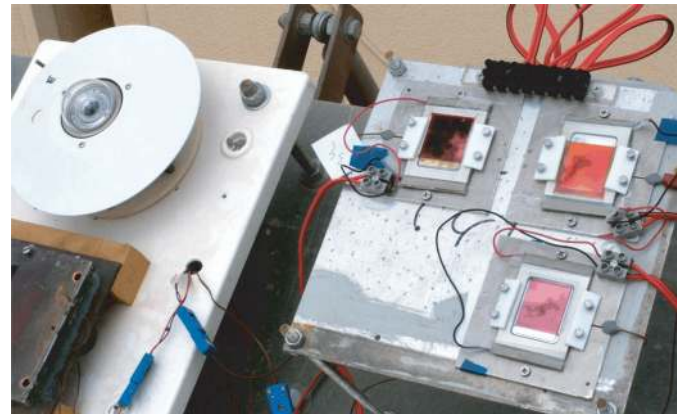

Fig. 2. Studied cells and Eppley PSP pyranometer mounted on a solar tracker.

Fig. 3. Examples of current-voltage curves of the MEH-PPV/PCBM cell at different stages of degradation. Current values were normalized to the standard irradiance value of 1000 W/m^2.

National Laboratory. Details of the cell production and encapsulation are described elsewhere [11]. Al and ITO/PEDOT:PSS layers were used as back and front electrodes, respectively. The cells differed by the configuration and content (Fig. 1) of photoactive layer: (1) BHJ of poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV):[6,6]-phenyl-C$_{61}$ butyric acid methyl ester (PCBM) (1:4); (2) BHJ of poly-alkyl-thiophene (P3HT):PCBM (1:1); (3) heterojunction formed by poly(3-carboxythiophene-co-thiophene) (P3CT) and sublimed C$_{60}$ alternating layers. The latter device does not include PEDOT:PSS sublayer.

In Sede Boqer, the outdoor current-voltage (I–V) measurements were performed on cloudless days at normal incidence to the incoming solar beam radiation, which level was measured with a calibrated thermopile pyranometer (Eppley PSP). For this purpose all of the studied cells and the pyranometer were mounted on a solar tracker (Fig. 2). During the measurements the cells had ambient temperatures varying from 25 to 45 °C as measured by a T-type thermocouple.

The measurements were carried out for a period of 32 subsequent days during daylight hours (from ∼9 AM to ∼5 PM) started from 15.03.2006. At night, the cells were kept in the dark in a glove box with a nitrogen atmosphere.

Because the outdoor solar irradiance, P_{in}, varies throughout the day, in order to record stability of the PV parameters, the measured values of short-circuit current, I_{sc}, current at the maximum power point, I_{mpp}, and maximum output electrical power, P_{out}, were adjusted to the standard irradiance value of 1000 W/m^2 assuming linear dependence of the photocurrent on P_{in}.

The power conversion efficiency η of solar cells under illumination was calculated by

$$\eta = \frac{P_{out}}{P_{in}} = FF \frac{V_{OC} I_{SC}}{P_{in}} \qquad (1)$$

where V_{oc} is the open-circuit voltage, FF, the fill factor is given by

$$FF = \frac{V_{mpp} I_{mpp}}{V_{OC} I_{SC}} \qquad (2)$$

where V_{mpp} is the voltage at the maximum power point.

3 Results and discussion

The MEHPPV:PCBM cell exhibited the fastest degradation (Figs. 3, 4). One can see that after a few hours of exposure to sunlight the efficiency of the cell decreased to 50% of its initial level. On the other hand, even initial levels of the I_{sc}, V_{oc}, FF and η were very low. We ascribe this in part to the large area of the cell and in part to degradation of the device during transport from Denmark to Israel since the PPV-based devices are subject to dark instability. It should be noted here that data on the PV performance of organic solar cells are commonly based on very small devices with active areas of only a few mm^2. Large area organic photovoltaics is a field of research that is still relatively unexplored [12].

Fig. 4. I_{sc} and η as a function of additive time of the sunlight exposure for the MEHPPV-PCBM cell. Vertical lines separate various days of measurements (from 15.03.2006 to 26.03.2006). I_{sc} was normalized to the standard irradiance value of 1000 W/m^2.
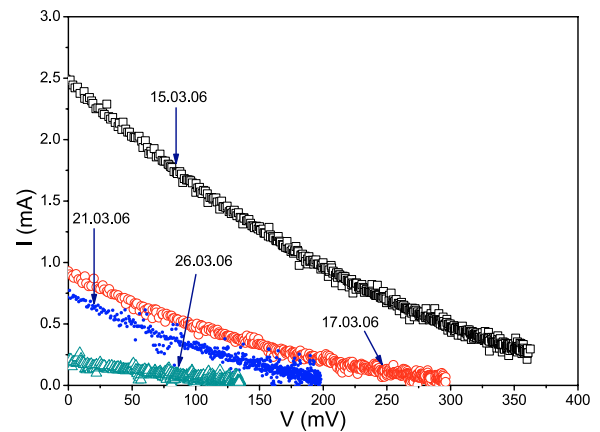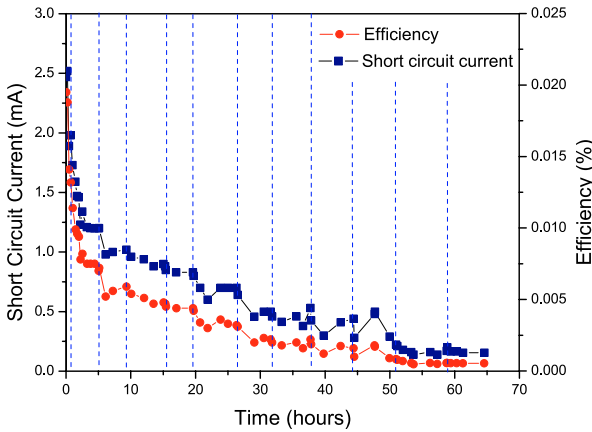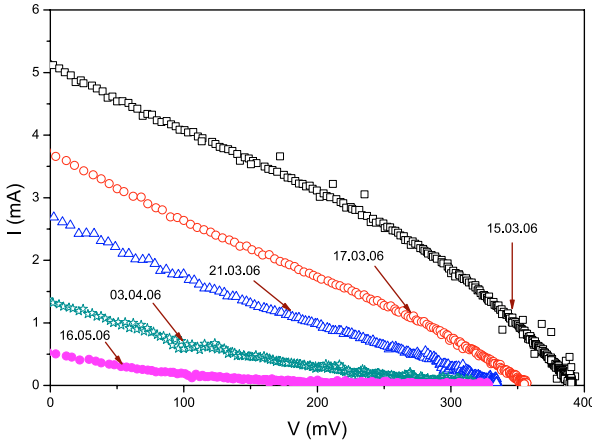

Fig. 5. Examples of current-voltage curves of the P3HT/PCBM cell at different stages of degradation. Current values were normalized to the standard irradiance value of 1000 W/m^2.

(a)

(b)

Fig. 6. Principle PV parameters as a function of additive time of the sunlight exposure for the P3HT/PCBM cell. Solid circles indicate the very first measurements every day (from 15.03.2006 to 16.05.2006). I_{sc} was normalized to the standard irradiance value of 1000 W/m^2.

Fig. 7. Examples of current-voltage curves of the P3CT/C$_{60}$ cell at different stages of degradation. Current values were normalized to the standard irradiance value of 1000 W/m^2.

The degradation of PV performance of the P3HT:PCBM cell was much slower (Figs. 5, 6) while the P3CT-C$_{60}$ cell was found to be the most stable (Figs. 7, 8). A totally different time-dependence of FF is evident for these two devices. FF of the P3HT:PCBM cell degraded from 0.26 to 0.21 quickly (during the first few hours of the exposure) and then started to exhibit a slow linear degradation (Fig. 6b). FF of the P3CT-C$_{60}$ cell was almost constant along the entire test process (Fig. 8b).

We also observed an unusual behavior of I_{sc} and V_{oc} for both the P3HT:PCBM and P3CT-C$_{60}$ cells (Figs. 6a, 8b). A restoration, or recovery, effect was observed for I_{sc} and V_{oc} during each night (when the cells were kept in the dark). The first I_{sc} and V_{oc} measurements every morning (indicated by solid circles) yielded the highest values compared to those during the rest of a day. While I_{sc} recovered at nights only partly and exhibit significant degradation
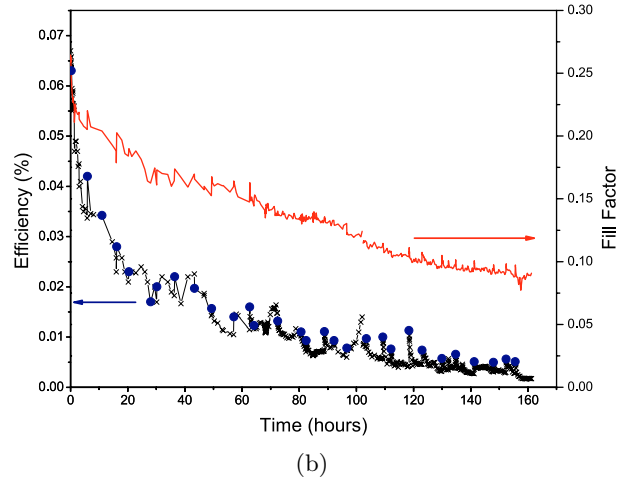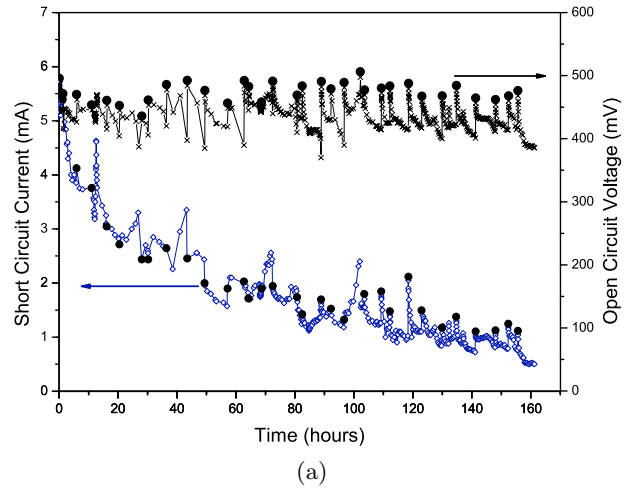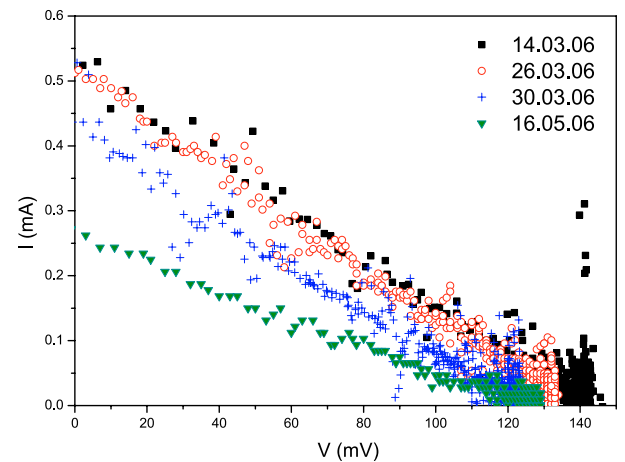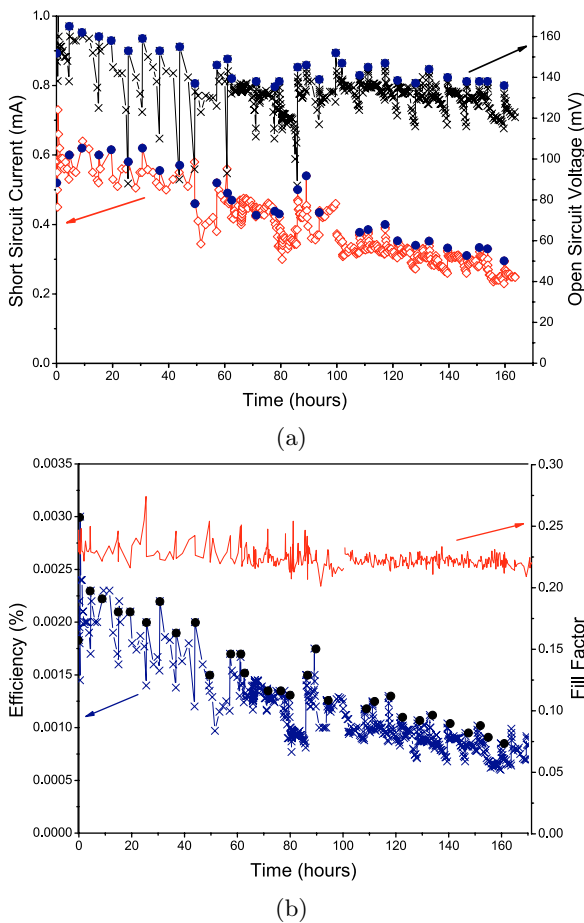
(a)

(b)

Fig. 8. Principle PV parameters as a function of additive time of the sunlight exposure for the P3CT/C$_{60}$ cell. Solid circles indicate the very first measurements every day (from 15.03.2006 to 17.05.2006). I_{sc} was normalized to the standard irradiance value of 1000 W/m^2.

during a month, V_{oc} values recovered completely every night and show almost no reduction on a long-term time scale.

As we already mentioned, at night the cells were usually kept in the dark in a glove box with a nitrogen atmosphere. In order to check the role of the atmosphere on the recovery effect we kept the cells in the dark but in air, for several nights, and observed the same recovery behavior of I_{sc} and V_{oc}. Furthermore, we observed almost complete restoration of both I_{sc} and V_{oc} parameters after shadowing the P3CT-C$_{60}$ cell for 30 minutes, at daytime (afternoon) (Fig. 9). Simultaneous recording of the cell temperature and the input light intensity variations during this experiment (not shown) indicated that they are not responsible for the recovery effect. Shadowing the cell for 10 minutes resulted only in the partial recovery of I_{sc} and V_{oc} (Fig. 9). A time threshold appears to exist for the recovery effect. For this particular cell this threshold is between 10 and 30 minutes.

A similar effect of partial recovery of I_{sc} was observed after keeping quasi-solid-state dye sensitized solar cells in
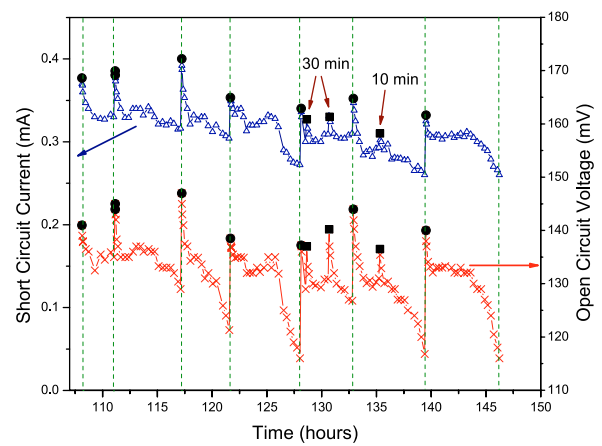

Fig. 9. I_{sc} and V_{oc} behavior of the P3CT/C$_{60}$ cell during last days of measurements. Vertical lines separate various days of measurements. Solid circles indicate the very first measurements every day while arrows and solid squares indicate the first measurements after the cell was shadowed for 10 or 30 minutes. I_{sc} was normalized to the standard irradiance value of 1000 W/m^2.

the dark for 9 hours [13]. Probably some restoration of I_{sc} was observed in the accelerated lifetime measurements of non-encapsulated BHJ solar cells after changes of solar simulator light bulbs [7] in spite of the fact that the authors attributed the effect only to the variation in the emission of the lamp. One should further check if the recovery effect is reproducibly observed for other plastic cells (encapsulated and non-encapsulated). If so it would point to the fact that in addition to the nonreversible photochemical degradation of the plastic cell some reversible mechanisms could be in play. The latter may include photoinduced generation of charge traps that then slowly disappear in the dark.

4 Conclusions and directions for future studies

We report preliminary results of long-term recording of PV performance of polymer cells under real sun operational conditions. The studied devices include three types of encapsulated polymer/fullerene cells which differed by the content of photoactive layer: (1) MEH-PPV:PCBM; (2) P3HT:PCBM; (3) P3CT- C60. The MEH-PPV:PCBM cell exhibited the fastest degradation. The degradation of PV performance of the P3HT:PCBM cell was much slower while the P3CT-C$_{60}$ device was found to be the most stable. Effect of restoration of I_{sc} and V_{oc} was found when the P3HT-PCBM and P3CT-C$_{60}$ cells were kept in the dark for nighttime. The first I_{sc} and V_{oc} measurements every morning yielded the highest values compared to those during the rest of a day. While I_{sc} recovered only partly and exhibit significant degradation during a month, V_{oc} values recovered completely every night and show almost no reduction on a long-term time scale.

In general, variation in PV performance across a day reflects simultaneous effects of changes in sunlight intensity and spectrum and ambient temperature. In order to properly interpret experimental data on such variation for encapsulated plastic solar cell we are initiating the detailed experimental program that includes measurements of temperature dependence of PV parameters and spectral response of the cells at various stages of degradation together with a recording of the variation in sunlight spectrum across a day. Further steps in such a program will involve comparison of the results of parallel studies of plastic cell degradation under real sun outdoor operational conditions with those of accelerated indoor studies at various elevated temperatures.

References

1. G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science **270**, 1789 (1995)
2. M. Reyes-Reyes, K. Kim, D.L. Carroll, Appl. Phys. Lett. **87**, 083506 (2005)
3. H. Neugebauer, C.J. Brabec, J.C. Hummelen, N.S. Sariciftci, Sol. Energ. Mat. Sol. C. **61**, 35 (2000)
4. F.C. Krebs, J.E. Carlé, N. Cruys-Bagger, M. Andersen, M.R. Lilliedal, M.A. Hammond, S. Hvidt, Sol. Energ. Mat. Sol. C. **86**, 499 (2005)
5. K. Norrman, F.C. Krebs, Sol. Energ. Mat. Sol. C. **90**, 213 (2006)
6. S. Schuller, P. Schilinsky, J. Hauch, C.J. Brabec, Appl. Phys. A **79**, 37 (2004)
7. F.C. Krebs, H. Spanggaard, Chem. Mater. **17**, 5235 (2005)
8. R. De Bettignies, J. Leroy, M. Firon, C. Sentein, Synthetic Met. **156**, 510 (2006)
9. E.A. Katz, D. Faiman, S.M. Tuladhar, J.M. Kroon, M.M. Wienk, T. Fromherz, F. Padinger, C.J. Brabec, N.S. Sariciftci, J. Appl. Phys. **90**, 5343 (2001)
10. D. Berman, D. Faiman, Sol. Energ. Mat. Sol. C. **45**, 401 (1997)
11. F.C. Krebs, Sol. Energy Mater. Sol. Cells **90**, 3633 (2006)
12. F.C. Krebs, J. Alstrup, M. Biancardo, H. Spanggaard, Proc. SPIE **5938**, 593804 (2005)
13. M. Biancardo, K. West, F.C. Krebs, Sol. Energy Mater. Sol. Cells **90**, 2575 (2006)