

Realization of Large Area Flexible Fullerene - Conjugated Polymer Photocells: A Route to Plastic Solar Cells

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Abstract. Bulk donor – acceptor heterojunctions between conjugated polymers and fullerenes have been utilized for photovoltaic devices with quantum efficiencies of around 1%. These devices are based on the photoinduced, ultrafast electron transfer between non degenerate ground state conjugated polymers and fullerenes. In this work we present efficiency data of solar cells based on a soluble alkoxy poly(*para* phenylenevinylene) (MDMO-PPV) and a highly soluble fullerene derivative (PCBM). Small area (mm²) photovoltaic devices show energy conversion efficiencies $\eta_e > 1\%$ and charge carrier collection efficiencies $\eta_c \sim 20\%$. We present efficiency and stability studies on large area (6 cm x 6 cm) flexible solar cells and compare them with small area devices. The process of large scale coating using printing techniques demands excellent rheological properties of the solution and the compound. We studied the influence of conventional polymers as additives for the photoactive compounds in order to improve homogenous film formation. Addition of small amounts (11 wt%) of conventional polymers does not alter the device characteristics. At higher concentrations of additives conversion efficiency drop down quickly.

Keywords: Solar Cells, Poly (phenylene vinylene) and Derivatives, Fullerenes and Derivatives, Photoconductivity, Metal / Semiconductor Interfaces

1. Introduction

The utilization of organic materials for photovoltaic devices has been investigated during the last couple of decades (for a summary of the early reports see for example [1,2]). Bilayer photovoltaic cells based on small organic electron donor and acceptor molecules [3] show a promising energy conversion efficiency, typically around 1%. Different classes of organic materials, including merocyanine, doped metallo-phtalocyanine or charge transfer systems have been studied as promising materials. The rather low efficiency of all-organic photovoltaic compounds compared to silicon photovoltaic cells or to hybrid photovoltaic cells using organic dye sensitized TiO₂ has been the major obstacle for their technological utilization. Small molecular photovoltaic device production demands the subsequent vacuum evaporation of usually two organic components from different sources at high vacuum and was therefore limited to small area applications. The advantages of polymeric photovoltaic cells, like large scale roll to roll production on flexible substrates, attracted technological interest in this sideline of organic photovoltaic devices. First conjugated polymeric photovoltaic devices showed

efficiencies below 0.1 % [4]. After the discovery of the ultrafast photoinduced electron transfer from a wide class of conjugated polymers onto fullerenes [5], photovoltaic elements based on blends between soluble derivatives of PPVs and substituted fullerenes have been realized with energy conversion efficiencies of 2.9% under monochromatic low intensity light [6]. Up to now, these polymeric solar cells based on blends of conjugated polymers with fullerenes (or acceptor type conjugated polymers) showed enhanced efficiencies compared to photovoltaic cells made of the components alone [7].

The ultrafast photoinduced electron transfer with long lived charge separation [8] in the conjugated polymer/ fullerene system offers a photoinduced charge generation efficiency near unity. Conjugated polymer devices show attractive combination of properties of semiconductors and metals with the processability and flexibility of plastic materials. This might be important for (i) large scale production with technologies known from polymer processing, (ii) reducing production costs, (iii) the possibility to optimize the properties of conjugated polymers by blending them

with proper additives or host materials to improve transport properties, stability parameters or processing conditions.

2. Experimental

For the solar cells reported here we used poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV) as electron donor, while the electron acceptor is 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{60} (denoted as PCBM) both of which show satisfactory solubility in a large number of organic solvents [9]. The enhanced solubility of PCBM compared to C_{60} allows a high fullerene to conjugated polymer ratio. Optical quality films with weight ratios of PCBM : MDMO-PPV of 3:1 are possible [6]. In order to study the influence of additives we produced a series of devices which contained various amounts of polystyrene (PS). For the blends we have used a Hoechst PS N 168, which has a rather low molar weight [$M_p \sim 187000$ g/mol] and a polydispersity M_w/M_n around 2.2. Other concentrations and conventional polymeric host materials have been investigated on their photovoltaic as well as spectroscopic properties and reported elsewhere [10, 11].

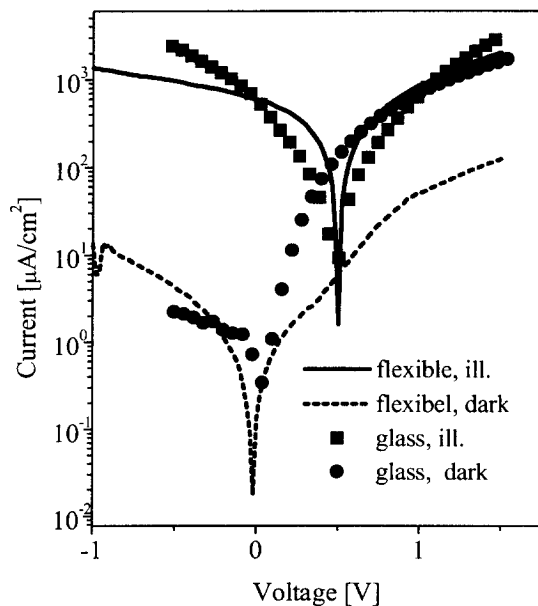


Figure 1: I/V characteristics of small area glass cell (● dark - ■ illuminated with 488 nm, 10 mW/cm²) and a flexible large area polyester cell (- - dark; — illuminated with 488 nm, 10 mW/cm²).

Weight ratio of the fullerene to the conjugated polymer was kept for all composites at 3 : 1. The weight concentration of the PS in the final device composites was varied from 0%, 11%, 20%, 33%, 50%, 66% and 80%. Current-voltage characteristics are measured with a Keithley 2400 sourcemeter and action spectra are taken by spectrally resolved light from Xe lamp source. Samples are evacuated to 10⁻⁵ mbar during measurements.

We studied the photovoltaic characteristics of the fullerene/conjugated polymer thin films on two different substrates with different active areas: (i) devices on ITO glass

substrates with active areas around 15 mm², and (ii) flexible devices on ITO polyester substrates with typical areas of 6 cm by 6 cm and active areas of 4 times 360 mm².

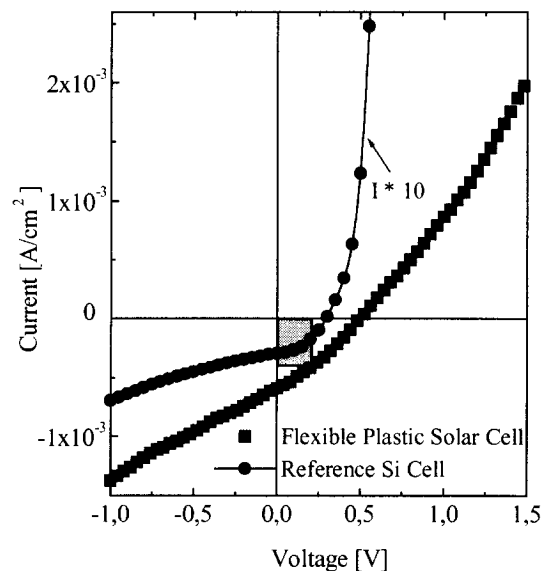


Figure 2: I/V characteristics of a large area plastic solar cell (■ illuminated with 488 nm, 10 mW/cm²). FF for the ITO plastic cell is 0.35. As reference a photocurrent of polycrystalline Si cell is plotted (●), 10 times reduced.

3. Results and Discussion

Figure 1 shows a comparison between the two photovoltaic cells: the small area on glass and large area on plastic substrates, respectively. Both cells show comparable open circuit potential, V_{oc} (~ 0.53 V) and short circuit current, I_{sc} . The ohmic contribution to the photocurrent is larger for the glass cell. The overall conversion efficiency, η_e , of the flexible plastic solar cell presented here is calculated with app. 1,2 % under monochromatic illumination (488 nm) with 10 mW/cm² and a filling factor FF ~ 0.35 . Typical values for η_e are between 1% and 1,5%. These data show clearly, that upscaling to flexible substrates does not influence the efficiency of the cells based on conjugated polymer/fullerene composites. Figure 2 shows the characteristics of the flexible cell in comparison to a polycrystalline Si cell in a linear plot, where the I/V characteristics in the 4th quadrant can be seen more precisely for the determination of the FF.

Figure 3 shows the total efficiencies of an ITO- glass cells under 10 mW/cm² illumination. Calculation of η_e has been performed after $\eta_e = (V_{oc} [V] * I_{sc} [A/cm^2] * FF) / (P_{inc} [W/cm^2])$ and demands the knowledge of the fill factor FF of the device. As the complete I/V curve for each wavelength is not known, we estimated the FF to be 0.25 at all wavelengths. Calculation of η_e was performed by $I_{sc} = 1240/\lambda * I_{sc} [\mu A/cm^2] / I_{inc} [W/m^2]$, where I_{inc} is the intensity of the incident light, which has not been corrected for absorption – reflection processes at the ITO side. For better comparison the optical density of this device is plotted

at the right-hand axis. One can see very clearly, that all three curves have the same onset as well as the same spectrally resolved maximum. This behavior is typical for low optical density cells, where (i) the amount of absorbed light within the cell is small and when (ii) separated charges can travel to both electrodes. Although light absorption is very low, the electron to photon conversion efficiency is surprisingly high. The maximum value is found to be $\sim 18\%$ at 505 nm.

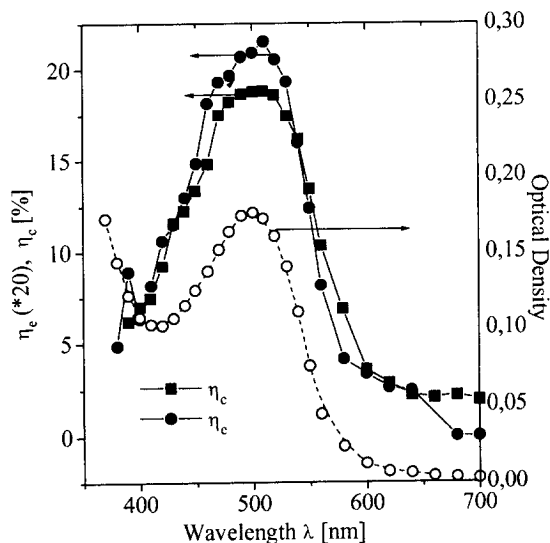


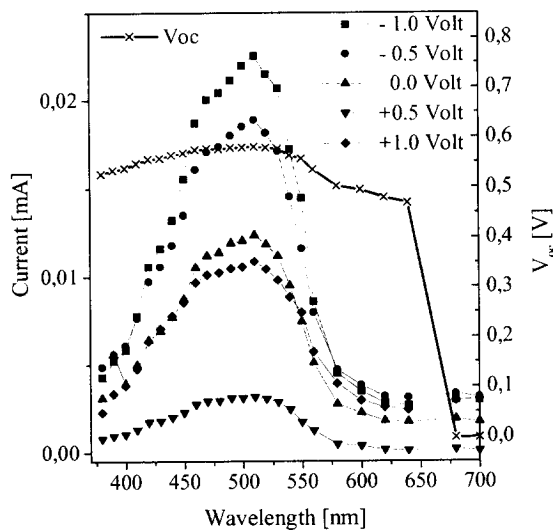
Figure 3: Energy (\bullet η_c) and charge carrier collection (\blacksquare η_c) efficiency of ITO glass cells (left axis). η_c is multiplied by a factor 20 for better comparison. Optical absorption (\circ) is plotted for better comparison (right axis).

From the comparison of the relatively high carrier collection efficiency with the power efficiency, which is approximately fifteen times lower, we conclude, that the limiting factor for the thin film interpenetrating network cells is the charge transport across the cell. When the electrons and holes travel across the device they have numerous possibilities to meet each other and undergo a non-radiative recombination. The bimolecular scaling behavior of the photocurrent with the excitation intensity is in accordance with that finding.

Figure 4 shows the spectral I_{sc} response of the pure device at 4 different voltages and at zero bias. One can see that the spectral response of the device is similar under forward as well as reverse bias. Applying a voltage sufficiently larger than V_{oc} reverses the polarity of the internal field and electrons and holes are attracted to the opposite electrodes (i. e. holes to the Al and electrons to the ITO side). However, the spectral response of the photocurrent is not influenced by that, indicating very clearly, that the thin film interpenetrating network cells have a homogenous charge generation and distribution all over the cell.

In order to investigate the influence of polymeric additives on the characteristics of conjugated polymer – fullerene solar cells we studied a series of PS blended photocells. The form of the I/V curve, the FF and the V_{oc} of the PS blended cells did not show remarkable differences compared to the pure cells. We calculated the efficiencies η_c of these cells and plotted them in Figure 5 in dependence on the PS concentration and on the light intensity.

Addition of up to 11 wt% PS does not influence the efficiency of the device. At higher PS concentrations efficiency decreases steadily and makes a sharp drop for the device with 80 % PS, 15



% PCBM and 5 % alkoxy PPV.

Figure 4: Spectral dependency of the photocurrent at different applied voltages and of the open circuit voltage V_{oc} . Illumination with monochromatized light from Xe lamp with 1 mW/cm^2 .

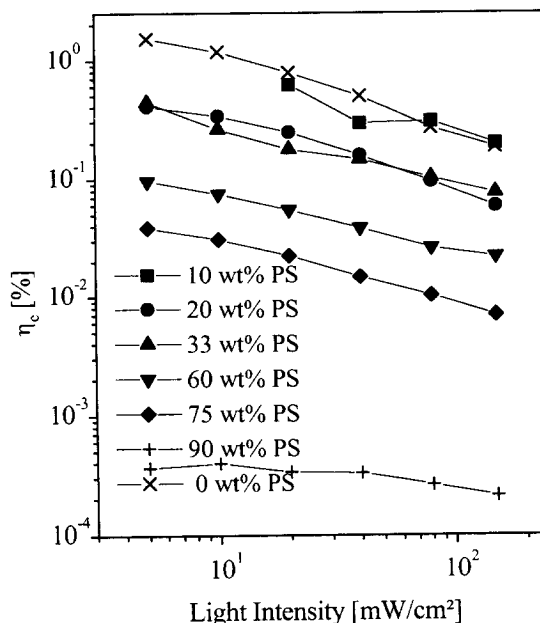


Figure 5: η_c for different wt. concentrations of PS and different light intensities. For comparison data of a pure cell are shown.

Obviously one of the electroactive components in this device is below the percolation threshold. We presume the fullerene

percolation to be responsible for this, because the conjugated polymers have a very low percolation thresholds and because of the 3:1 ratio of fullerene : conjugated polymer weight ratio in these blends.

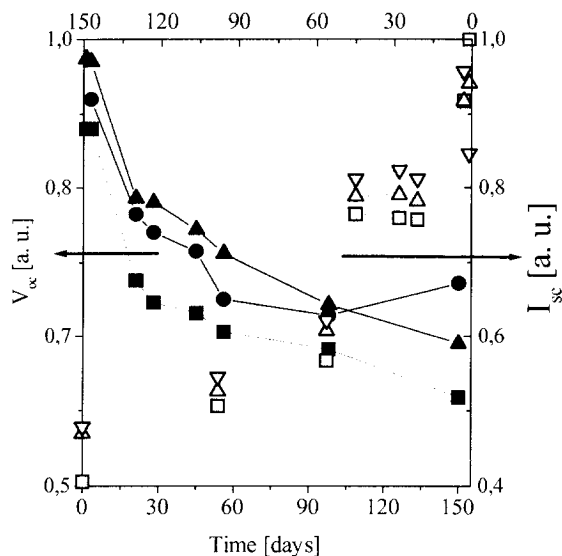


Figure 6: V_{oc} (lower x axis) and I_{sc} (upper x axis) vs. shelf life time [days] of protected plastic solar cells.

In general, conjugated polymers exhibit sensitivity to photodegradation in ambient environments. We studied the degradation behavior of the plastic solar cell and of a 1 : 1 composite by *in situ* FTIR measurements in ATR geometry (attenuated total reflection) [12]. The combination of light and oxygen led to a very fast degradation of the polymer. Effects on fullerenes are found to be much slower, and the same seems to be true for the mixtures of conjugated polymers and fullerenes. Exclusion of oxygen slows down the degradation process remarkably, and no degradation is found to occur within the measurements time (8 hours).

In Figure 6 the V_{oc} and I_{sc} of protected plastic solar cells is monitored. Cells have been produced under ambient room conditions and sealed after application of the top electrode. No actions were taken to remove residual oxygen from the cells, which may be adsorbed by the surface during production and can diffuse into the film. One can see, that the shelf life time of this devices is more than 150 days.

4. Conclusion

The power efficiency of plastic solar cells based on conjugated polymer – fullerene bulk heterojunctions is limited by charge transport. Recombination processes between electrons and holes allow only the charges close to electrodes to contribute to the photocurrent. It is possible to produce these cells on flexible substrates without loosing efficiency. Addition of small amounts of conventional polymers (11 wt%) for improving film formation properties does not alter the energy and carrier conversion efficiencies. Further improvements in device efficiencies are

expected by optimizing the composite composition, the network morphology and the charge transport properties of the single components.

5. Acknowledgement

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