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Dependence of the characteristics of organic solar cells on cathode polymer interface

Ourida Ourahmoun* and Mohammed Said Belkaïd

Laboratory of Advanced Technologies of Genie Electrics,
Electronic Department, University of Mouloud Mammeri, 'UMMTO'
B.P. N°17, Tizi-Ouzou, Algeria

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Abstract - *Increasing energy assumption and rising energy prices in the world forces to look for energy alternatives, one of the most promising is the photovoltaic energy. Solar cells made from organic materials are particularly attractive because they are relatively easy to produce, structurally flexible, and can be applied to large areas at low cost. Fill Factor is a more sensitive parameter compared to open-circuit voltage (V_{oc}) and short-circuits current density (J_{sc}). This FF depends also on the thickness of the active-polymer layer, on the morphology of the cathode-polymer interface and on temperature. In this article, we study the dependence of fill factor (FF) on different parameters in organic bulk heterojunction solar cells.*

Résumé – *L'augmentation de la consommation d'énergie et la hausse des prix de l'énergie dans le monde, font que pour ces énergies alternatives, la plus prometteuse est l'énergie photovoltaïque. Les cellules solaires à base de matériaux organiques sont particulièrement intéressantes, car elles sont relativement faciles à produire, structurellement flexibles, et peuvent être appliqués à faible coût sur de grandes surfaces. Le facteur de remplissage est aussi un paramètre très sensible par rapport à la tension en circuit ouvert (V_{co}) et à la densité de courant de court-circuit (J_{cc}). Ce facteur de remplissage dépend aussi de l'épaisseur de la couche active-polymère, sur la morphologie de l'interface cathode-polymère et de la température. Dans cet article, nous étudions la dépendance du facteur de remplissage (FF) sur les différents paramètres des cellules solaires organiques à hétérojonction.*

Keywords: Photovoltaic energy conversion - Organic semiconductors - Efficiency - Fill factor.

1. INTRODUCTION

Organic photovoltaic devices offer great technological potential to make renewable source of electrical energy. The potential of organic photovoltaic resides in their low cost, not because of the low price of the materials applied, but due to the printing techniques applied for their fabrication. Among the challenges to overcome for this technology are the improvement of solar cell efficiency and lifetime.

Lifetime limitation resides in the degradation of the organic semiconductors due to presence of oxygen or moisture from the atmosphere, thus encapsulation of these devices is requirement.

Several attempts have been made in order to find new electron transport materials with better transport properties and higher stability towards oxygen.

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* ourahmourida@yahoo.fr

Semiconductor oxides emerged as attracting alternative to replace PCBM in organic photovoltaic cells due to their appealing properties. Besides lower cost these oxides are wide bandgap materials.

Electron injection is also difficult when using Al as a cathode and hence low function metals such as LiF/Al and CsF/Al have been used to improve electron – injection properties.

Modification of the cathode interface by incorporation of acac (acac = acetyle acetonate) between Ca and the polymer layer has been shown to improve the performance of organic devices [2].

Our study reports on the dependence of fill factor on electrodes polymer interface and the influence of temperature in performances of organic bulk hetero junction solar cells.

2. PHOTOVOLTAIC EFFECT

The production of electric energy from sunlight is the result of chain process. Sunlight photons are absorbed inside the device, carriers are then generated from exciton dissociation, and carriers are collected by the electrodes and driven into the external circuit.

The different effects of the photovoltaic process are presented in figure 1.

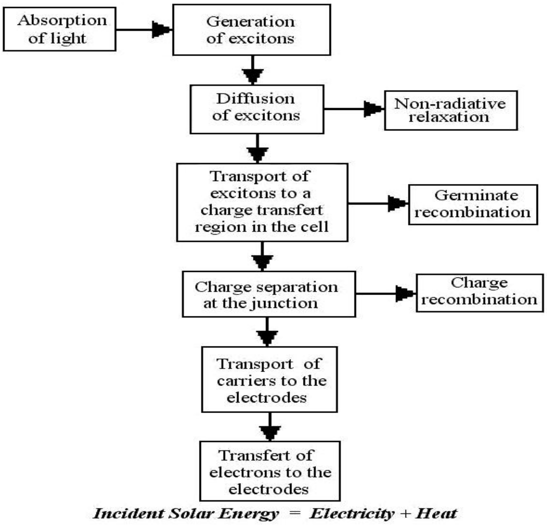

Fig. 1: Conversion steps and loss mechanism of light power into electric power

3. CHEMICAL STRUCTURE OF ORGANIC SOLAR CELLS

The prerequisite for a safe fabrication of polymer solar cell device is that the materials should be stable in air. As far as a certain donor polymer is concerned, the polymer whose HOMO–highest unoccupied molecular orbital; level is close to 5.2 eV or lower can maintain its electrochemical stability in air.

The donor materials widely used in the present polymer solar cell are the conjugated polymers MEH-PPV – poly[(2-methoxy5-((2-ethylhexyl)oxy)-1,phenylene)vinylene];

P3HT-poly (3-hexylthiophene), and (MDMO-PPV)- poly-2-methoxy-5-(3', 7'-dimethyloctyloxy)-1, 4-phenylene vinylene: whose HOMO levels are 5.4, 5.2, and 5.1 eV, respectively. Based on this result, we could assume that they are all chemically stable in air.

Single Organic solar cells are formed by an organic semiconductor layer (active layer) sandwiched between two electrodes. The anode is a transparent oxide (TCO) and the cathode is formed by Al or Ca. the structure of the device is represented in figure 2.

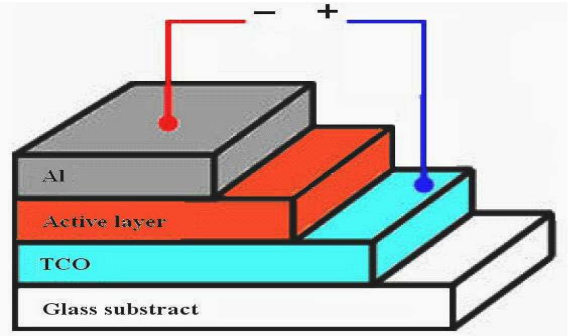

Fig. 2: Structure of the hybrid solar cell

4. PARAMETERS OF ORGANIC SOLAR CELLS

4.1 Short-circuit current (J_{sc})

The current that flows in a PN junction under illumination is given by:

$$J = J_0 \left[\exp\left(\frac{qV}{kT} \right) - 1 \right] - J_{ph} \tag{1}$$

where: J_{ph} is the density of photo generated current, k is the Boltzman constant and J_0 is the current density at saturation given by:

$$J_0 = N_v N_c kT \times \exp\left(\frac{-E_g}{kT} \right) \cdot \left(\frac{L_n}{n\tau_n} + \frac{L_p}{p\tau_p} \right) \tag{2}$$

N_c and N_v are the density of states in the conduction and valence band respectively, p and n are the density of the electrons and holes, L_n and L_p are the diffusion length, τ_v and τ_p are the lifetimes of electrons and holes respectively.

At $V = 0$ volts (the short-circuited cell), the current J_{sc} generated by the cell is: $J_{sc} = J_{ph}$.

4.2 Open circuit voltage (V_{co})

The open circuit voltage of a solar cell is achieved when the current flowing through the cell is zero. For photovoltaic cells based on organic materials, this origin is controversial. It depends directly on the band gap E_g.

The open circuit voltage of a solar cell based PN junction is given by:

$$V_{co} = \frac{n\,k\,T}{q}\ln\left(\frac{I_{sc}}{I_s}+1\right) \tag{3}$$

Where: I_{sc} is the short-current circuit density, I_s is the saturation current and V_{oc} as function of E_g, is given by the following equation:

$$V_{co} = \frac{n\,E_g}{q} - \frac{n\,k\,T}{q}\ln\left[\left(\frac{q\,N_c\,N_v}{I_{cc}}\right).\left(\frac{L_n}{n\,\tau_n}+\frac{L_p}{p\,\tau_p}\right)\right] \tag{4}$$

4.3 Fill factor

In order of improving the efficiency of organic solar cells, the most critical factor for a large impact on the different strategies depends on better fill factor FF which is given by the following relation:

$$FF = \frac{V_{max}}{V_{oc}}\frac{I_{max}}{I_{sc}} \tag{5}$$

Where: V_{max} and I_{max} are the voltage and at maximum awarded by the cell extract of the characteristic $I(V)$ of the cells.

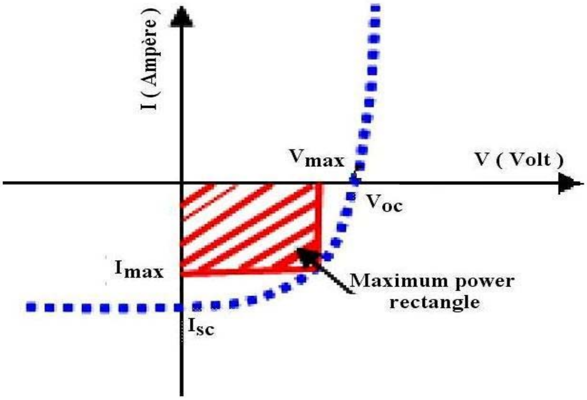

Fig. 3: $I(V)$ characteristic of a solar cell

4.4 Efficiency

The efficiency of organic solar cells is one of the factors limiting there commercialization. It is given by:

$$\eta = \frac{I_{sc}\,.\,V_{oc}\,.\,FF}{P_{in}} \tag{6}$$

Where: P_{in} is power of the incident light. It is directly related at the open circuit voltage, and the short current circuit.

5. THE EFFICIENCY AND THE STABILITY OF ORGANIC SOLAR CELLS

A photovoltaic device should be exposed to sunlight for a period large than 10 years in order to become competitive alternative to silicon. That is more than 10 000 hours of sun; this is not an easy assignment. The causes of degradation have different origins [4]:

- Photochemicaly: it can be intrinsic property of the molecules or an extrinsic one (photooxidation with oxygen for instance);
- Electrochemically: ionic impurities or water may promote redox reactions at the electrodes;
- Structurally: low transition temperature (T_g) may reorganise, recrystalyse, or diffuse one into another owing to repeated heating and cooling in out door conditions;
- Electrodes: they can react with molecules, metal diffusion from ITO into polymers for instance.

Improvement of the stability of organic photovoltaic cells requires the choice of intrinsically stable materials (stable under storage, under sunlight and under reduction or oxidation conditions), the use of efficient purification methods and the structure of the device.

6. STUDY OF THE INTERFACE ELECTRODES POLYMER

Most of the organic semiconductors, especially polymers, are amorphous in nature and have very low charge carrier motilities. The charge carriers injected from the metal electrode into the organic semiconductors form a space charge, which limits the current through the semiconductors.

This current is known as SCLC (space charge limited current). Hence, the study of the electrode polymer interface is required.

6.1 Improving the anode contact

Organic semiconductors are increasing interest as new materials for electronic devices, due to their easy processing and potential for low cost fabrication.

One of the fundamental requirements for efficient operation of all- organic electronic devices is the process of carrier injection / extraction from the electrodes into the active region. A poor carrier extraction property limits the organic solar cell’s power conversion efficiency.

The energy barrier for carrier injection / extraction is determined by the energy difference between the metal work function and the ionization potential / electron affinity of the organic material.

Indium tin oxide (ITO) has been the preferred anode for all organic optoelectronic devices owing to its optical transparency. However, the work function of ITO is quit low.

One method of increasing the work function of ITO / organic interface is the use of high – work - function metal oxides or self assembled monolayer between the ITO and organic material to increase the hole injection efficiencies.

The most common way to improve hole - injection / extraction is to incorporate a hole transporting layer (buffer layer) such as poly (3,4- ethylene dioxythiophenene): poly(styrene sulfonat) (PEDOT: PSS) on top of the ITO surface.

One of the main features of the (buffer layer) is that it increases the hole injection from the ITO to the organic layer by increasing the work function of the anode.

6.2 Comparison of SnO_2 with TiO_2, Nb_2O_5 and ZnO thin films

The voltage of the organic solar cells is dependent on the type of semiconductor oxide applied [3]. The highest Voc and Jsc have been observed for hybrid solar cells (HSC) applying TiO_2 and Nb_2O_5 (about -0.74 V) followed by SnO_2 with -0.50 V, ZnO with V_{oc} of about -0.38 V, and on the positive side CeO_2 with a value of +0.42 V and CeO_2-TiO_2 with a value of +0.42 V as shown in **Table 1**.

The hybrid solar cells are characterized by low fill factors (never higher than 44 %). This could be an indication of high internal resistances and leakage currents present in these systems, usually observed in devices with high recombination problems. Current leakages could come from the in homogeneity of the oxide thin film or due to their thickness that are not more than a couple of tenths of nanometres (between 15 and 30 nm thick).

The degradation of the polymer with time and the decrease of photovoltaic properties have been inevitable in the HSC. The time it takes to degrade the polymer depends on the semiconductor oxide applied as follows (from the oxide showing the fastest degradation to the slowest): ZnO > SnO_2 > Nb_2O_5 > TiO_2 > CeO_2 > CeO_2 – TiO_2.

The performance of HSCs applying thin film semiconductor oxides and the MEH-PPV polymer are presented in **Table 1** [3].

Table 1: Performances of ITO / semiconductor oxide / MEH-PPV/ Al

TCO	E_g (eV)	J_{sc} $(mA/cm^2)^c$	V_{oc} $(V)^d$	FF (%)
TiO_2	3.0	0.42	-0.74	0.30
$Nb_2O_5^a$	2.3	0.28	-0.64	0.40
$Nb_2O_5^b$	2.3	0.34	-0.40	0.36
SnO_2	3.1	0.20	-0.50	0.33
ZnO	3.2	0.30	-0.38	0.35
CeO_2	3.0	0.004	+0.12	0.25
CeO_2-TiO_2	3.2	0.007	+0.42	0.32

[a] *ITO substrates on aluminosilicate glass*

[b] *ITO substrates on sodalime glass.* [c] *At maximum* J_{sc}

[d] V_{oc} *at the beginning, before stabilisation. Active area is 3.3* cm^2

6.3 Improving the cathode contact

Electron injection is also difficult when using Al as a cathode and hence low function metals such as LiF/Al and CsF/Al have been used to improve electron – injection properties.

Modification of the cathode interface by incorporation of (acac) (acac=acetyle acetonate) between Ca and the active layer has been shown to improve the performance of organic devices [2].

The reduction of FF can also arise due to the chemical degradation of the metal–polymer interface.

A thin layer of aluminium oxide present in the cathode–polymer interface has also been shown to facilitate the injection of electrons from the cathode when significant amount of holes accumulated in the Al_2O_3 – polymer interface, in an OLED geometry.

Figure 4 shows the current - voltage characteristic of Al/ PCBM:P3HT/ ITO structure, the characteristic shows that J_{SC} = 3.08 mA/cm^2, V_{OC} = 0.59 V and FF = 62.6 % under white light illumination with power density 80 mW/cm^2.

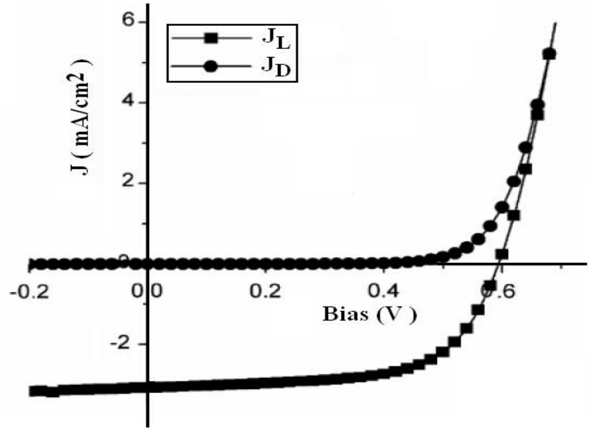

Fig. 4: J (V) characteristics of a P3HT:PCBM solar cell with active area 25 mm^2 [6]

7. INFLUENCE OF THE DEPOSITION METHOD IN FILL FACTOR

The fast evaporation process of Al gives rise to concavity in the fourth quadrant of the J (V) characteristic and consequently a low FF of 12.5 %, with V_{CO} = 0.52 V and J_{SC} = 1.47 mA/cm^2 , (P_{in} = 20 mW/cm^2).

The slow evaporation rate improves the FF to 45 %, with V_{CO} = 0.4 V and J_{SC} = 4.3 mA/cm^2 (P_{in} = 80 mW/cm^2).

8. CONCLUSION

The research of organic solar cells is interesting due to novel photo physical phenomena, where as technologically low fabrication costs due to roll-to roll printing possibilities drive the economic point of view. Efficiencies, routinely exceeding 4–5 % have been reached in thin-film organic solar cells today.

There are four main important processes which might limit the power conversion efficiency of photovoltaic devices.

- Light absorption in the film.
- Free charge carrier generation.

- Charge transport to the opposite electrodes and extraction by the electrodes.
- Carrier recombination.

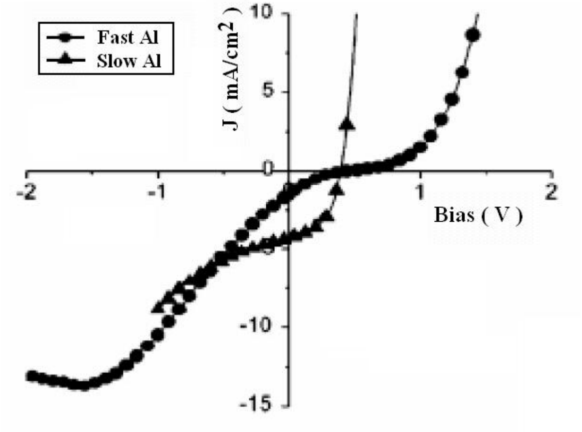

Fig. 5: Illuminated $J(V)$ characteristics of a P3HT–PCBM solar cell with Al deposited at an extremely fast evaporation rate (200 nm/5 s) and at a slow evaporation rate (200 nm/100 s) [6]

This study shows that the characteristics $J(V)$ strongly depend on the quality of polymer cathode. A chemically modified layer can reduce the fill factor drastically in other wise efficient solar cell device.

Physico-chemical defects in the polymer-metal interface gives rise to the charge carrier accumulation (due to inefficient collection). For better FF, a conformal coating of metal which is follows the polymer surface undulations is always preferable.

To reach better performance and polymer stability the modification of the device configuration is required, by using the adequate organic material and TCO like SnO_2, ZnO for example.

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