Theoretical study of the open circuit voltage decay on Organic Photovoltaic (OPV) solar cells based on space radiation ionizing damage

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Abstract. Organic photovoltaic (OPV) solar cells have progressed quite significantly as an affordable energy technology, with high-throughput roll-to-roll solution processing driving down costs to the point of competitiveness with current technologies. They potentially offer significant advantages over classical inorganic semiconductor cells; specifically, down costs, lightness, flexibility and controlled donor-acceptor film composition. Our specific interest is based on the applicability of organic photovoltaics cells for use in space based solar panels. The present work is a theoretical study of ionizing radiation effects in the organic photovoltaic structure P3HT: PCBM for total accumulated doses up to 1kGy (SiO2). We find that the open circuit voltage (Voc) varies with the accumulation of irradiation; however, other parameters such as relaxation time, short circuit current, and charge carrier density remain to first order constant. At the interface, the energetic mismatch of the molecular orbitals provides enough driving force to split the exciton in order to create free charge carriers (an electron (e-) and the corresponding hole (h+)). This is consistent with observations on preirradiation cases that depend directly on the Voc, due to carriers and quasi states; this leads to a linear recombination according to the Dose Damage Displacement (Dd) and Non-Ionizing Energy Loss (NIEL). Finally, we conclude that the organic photovoltaics will survive in a space environment up to 1 kGy (SiO2), contrary to popular belief that organics would be radiation “soft.”

1. Introduction
Organic based solar cells (OPVs) involved in space exploration devices are primarily exposed to energetic electrons and protons (even at low orbits), which lose their energy as ionization during the interaction with the blend film of the heterojunction [1]. Therefore, is mandatory to study the consequences of this interaction in order to evaluate the possibilities and scopes for further optimization of solar cells’ performance in space.

Insights on this interaction are decisive because space exploration devices depend on solar arrays to generate electrical power to operate the spacecraft and payloads. Emerging technologies involving organic materials as donor/acceptor heterojunctions are being researched because they offer solutions to...
several of the challenges posed today [2]. Also, this kind of research programs are crucial in the fabrication of OPVs, because they are fabricated and characterized as a function of the solar intensity, temperature and aging at vacuum conditions under extreme conditions of illumination [3].

On the other hand, it’s well known that $V_{oc}$ is one of the key parameters of photovoltaic devices, which defines the voltage for which the current in the external circuit equals zero. In polymer:fullerene solar cells, limitations of the $V_{oc}$ have been attributed to Fermi level pinning and to bond bending contact [4]. Consequently, our main interest consists in the simulation of the behaviour of potential $V_{oc}$ when a polymer:fullerene film blend is exposed to ionizing radiation of high energies.

The latter in order to describe the defects generated by the ionizing radiation at the HOMO/LUMO orbitals, to include NIEL, to apply an alternative methodology without loses and high fidelity as $D_d$, to find a model that can describe the possible relationships between the potential $V_{oc}$ and the ionizing radiation, and to relate the latter challenges with the End-of-Life Prediction (EOL). It is important to mention that most of our work is based on the results of Kouhestani [1], Messenger [5,7] and Koster [4,6].

Messenger’s proposal consists in two parts, namely, the determination of the irradiation spectrum and the calculation of the net loss of energy due to the cell’s architecture, for later, in a second part, calculate the net value of $D_d$ and the degradation of the cell via some suitable parameter [5,7]. This can be achieved via the product between the particle flux as a function of the ionizing energy, namely $\Phi(E)$, and the appropriate value of NIEL (which is the product of the particle fluence and the displacement mass-stopping power), as presented in the following equation:

$$D_d(E) = \Phi(E) \cdot NIEL(E) \left[ \frac{NIEL(E)}{NIEL(E_{ref})} \right]^{n-1}$$

where NIEL describes the rate of energetic interchange between the irradiated particle and the surface via non ionizing events, $n$ is an experimentally determined parameter ($n = 1.7$ according to Messenger et al.) and $E_{ref}$ is an arbitrary reference electron energy (typically set to 1 MeV) [5]. It’s important to mention that NIEL is the parameter that most affects the properties of solar cells in space environments [8].

Once the relationship between $D_d$ and NIEL is established, potential $V_{oc}$ can be related with the usual relevant parameters of the cell’s performance as the energy gap between orbitals HOMO/LUMO, the effective density of states, and the electron (hole) concentration. The theoretical mainframe of these relationships is the quiddity of Kouhestani’s [1] and Koster’s [4,6] work, and also the starting point of the present paper.

To obtain new insights about the behavior of $V_{oc}$ as a function of the ionizing radiation at high energies, both proposals were analyzed to obtain a new relationship that will include, directly or indirectly, non-ionizing effects (through NIEL), band gap between HOMO and LUMO orbitals, temperature and electron (hole) concentration, namely Equation (9). With this equation relaxation times can be calculated in order to establish an EOL prediction.

Results obtained from Equation (9) are compared and discussed versus Kouhestani’s experimental results [1], the central part of sections 3 and 4. Methodology is presented in section 2, while in section 3 development and theoretical arguments used to obtain Equation (9) are discussed. Finally, conclusions and scopes are given in section 5.

2. Simulation method and parameters

$V_{oc}$ degradation studies entail two primary parts. The first one deals with the analysis of the ground-test solar cell radiation data while the second deals with the analysis of the space radiation environment. However, both parts can be described using the Total Ionizing Dose (TID) that results from the energy deposition from ionizing radiation.

Currently, the Multi Layered Shielding Simulation Software (MULASSIS) is a very useful Monte Carlo simulation-based tool for dose and particle fluence analysis, associated with the use of radiation
shields and that results in a well-performed calculation of TID. Also, the structure of MULASSIS allows the definition of the shielding and detector geometries, the materials and density of each layer, the elemental/isotopic composition, among other characteristics that bring about several benefits. It is important to mention that this software has been incorporated into the Space Environment Information System (SPENVIS) [9], and the present study was performed using the MULASSIS via SPENVIS suite. The latter allows us the calculation of the TID and the simulation of the response of different OPV in different space radiation environments, with the consequential evaluation of the proposed degradation of $V_{oc}$, in terms of the TID, via Equation (9).

2.1 Orbit parameters

The spectral content and intensity of the radiation environment depends on the specific orbital mission. Once the orbit has been specified, the environment can be calculated using existing models like the NASA AP8 and AE8, both integrated in SPENVIS. In our case, space environment was simulated under the ISS orbit conditions (Table 1) for a one-year long mission [11].

Table 1. Orbit Parameters for ISS orbit conditions.

| Parameter                     | Value          |
|-------------------------------|----------------|
| Eccentricity                  | 0.0005480      |
| Inclination                   | 51.6399°       |
| Perigee                        | 402 km         |
| Apogee                         | 409 km         |
| Longitude of the ascending node| 142.7584°      |
| Argument of Periapsis          | 17.8906°       |
| Mean anomaly                  | 342.2439°      |

Proton and electron spectra generated by orbit parameters listed in Table 1 are shown in Figs. 1 and 2, respectively. The solar cell radiation response is different for the proton irradiation compared to the electron, due to the energy differences shown in Figs. 1 and 2, where the range of proton energy is higher compared to the energy of the electron. Evidently, the response of the cell depends on the energy of the irradiation particle.

**Figure 1.** Proton Spectra. Left axis represents the integral flux and right axis the differential flux, based on the specified ISS orbit conditions. Inset shows the world spectrum for $p^+$.  

**Figure 2.** Electron Spectra. Left axis represents the integral flux and right axis the differential flux, based on the specified ISS orbit. Inset shows the world spectrum for $e^-$.  

2.2 OPV Cell Architecture
The theoretical setup has been provided by the experimental results of Kuheshtani et al [1]. The P3HT:PCBM 1:1 cells used in this study are listed in Table 2, according to reference [1].

| Table 2. P3HT:PCBM OPV composition cell. |
|-----------------------------------------|
| Parameter       | P3HT          | PC61BM        |
| Chemical Formula| C_{10}H_{14}S | C_{61}H_{14}O_{2} |
| Density         | 1.1 g/cm³     | 1.72 g/cm³    |
| Thickness       | 110 nm        | 110 nm        |
| Cell Total Area | 1.5cm x 1.5cm |               |
| Pmax            | 0.269416884   |               |

3. Theory and calculation
The recombination rate of charge carriers is reliant on the carrier density present at the BHJ, which directly influences the values of $V_{oc}$. The recombination rate is higher when the carrier density increases which in turn is contingent on the voltage. As the forward bias voltage is applied, it counteracts the built-in photovoltage causing the carriers to stagnate within the device and leading to increase the carrier density. As is well known, $V_{oc}$ is the voltage at which the photo-generation rate and the recombination rate exactly cancels out each other. Maurano et al. [9] quantified carrier densities and recombination rates under open-circuit conditions at different light intensities.

In their report they parameterized the recombination rates by employing an empirical power-law dependence, while the carrier density was parameterized by using an empirical exponential dependence on voltage. Combining these two factors, a logarithmic dependence of $V_{OC}$ as a function of light intensity was observed, in agreement with experimental data [10].

While this general approach can define the behavior of numerous material systems in terms of $V_{oc}$, it offers limited physical insight on the origins of the dissimilarities observed in the different values reported for $V_{oc}$. The ideal BHJ diode model postulated by Koster et al. [4], at the same time based on Shockley’s ideal–diode equation, under assumption of Langevin recombination, predicts values of $V_{oc}$ in terms of physical parameters such as the donor–acceptor energy gap and the recombination rate coefficient [4,6], as expressed in Equation (2)

$$V_{oc} = \frac{E_{gap}}{q} - \frac{kT}{q} \ln \left( \frac{(1-P)\gamma N_c^2}{PG} \right)$$

where $T$ is the temperature, $k$ the Boltzmann constant, the elementary charge is $q$, $E_{gap}$ defines the effective band gap ($E_{FullereneLUMO} - E_{PolymerHOMO}$), $N_c$ is the effective density of states (DOS), $P$ the dissociation probability of a bound electron–hole pair into free charge carriers, $G$ stands for the generation rate of bound electron–hole pairs, and $\gamma$ the Langevin recombination constant; where generation rate $G$ and Langevin constant $\gamma$ are related by the following equation:

$$G = \gamma np(1-P)/P$$

Given Equation (3), it can be said that product $PG$ represents the generation rate of free charge carriers [4]. But this model fails to envisage the exact dependence of $V_{oc}$ on the light intensity for a vast majority of real devices; this equation is equivalent, in terms of charge carrier densities of the electrons and holes in the BHJ, $n$ $y$ $p$, to [10]:

$$V_{oc} = \frac{E_{FullereneLUMO} - E_{PolymerHOMO}}{q} - kT \ln \left( \frac{(1-P)\gamma N_c^2}{PG} \right)$$
\[ V_{oc} = \frac{E_{gap}}{q} - \frac{kT}{q} \ln \left( \frac{N_c^2}{n_p} \right) \]  

(4)

Under the assumption of a specific constant \( N_c \), for a specific donor–acceptor blend, a higher steady-state charge carrier concentration leads to an increase of \( V_{oc} \).

As an initial starting point to correlate \( V_{oc} \) in terms of ionizing radiation for space applications, we assumed a first order charge generation mechanism (the first term on the right side of Equation 5 and a simple linear relaxation term). Then, the relation obtained is consistent with indirect recombination in the limit of low-level injection, namely,

\[ \frac{d\Gamma}{dt} = D\sigma_p P (\Gamma_{max} - \Gamma) - \tau \Gamma \]  

(5)

The latter yields the following solution for the evolution of the charge density as a function of time:

\[ \Gamma = \frac{D\sigma_p P \Gamma_{max}}{D\sigma_p P + \tau} \left( 1 - e^{-(D\sigma_p P + \tau)t} \right) \]  

(6)

where \( \Gamma(t) \) is the trapped charge concentration, \( D \) the dose rate, \( \sigma_p \) the charge captures cross section (neutral traps), \( P \) the dissociation probability of a bound electron–hole pair into free charge carriers, \( \Gamma_{max} \) the maximum density of traps and \( \tau \) a relaxation parameter. Equation 5 suggests that their dose-rate depends of two factors:

a) if \( \tau > D\sigma_p P \) or \( \tau \sim D\sigma_p P \) then the saturation level is less than \( \Gamma_0 \) and is reduced to \( \frac{D\sigma_p P \Gamma_{max}}{\tau} \) for those instances in which \( \tau \gg D\sigma_p P \).

b) The initial slope \( \frac{d\Gamma}{dt} \bigg|_{t \to 0} \) is equal to \( D\sigma_p P \Gamma_{max} \).

The charge captures cross section \( \sigma_p \) present in Equations 5 and 6 is related to the introduction equation of NIEL, which depend on the differential cross section for elastic Coulomb scattering for electrons or protons on nuclei.

Based on the generation rate of bound electron–hole pairs \( G \), suggested by Kouhestani [1], and assuming the charge density \( \Gamma \) as function of the dose rate, equal to the proposal of charge carrier densities of electrons and holes in the BHJ, \( n \) and \( p \), by Cheyns [10], we can reorder Equation (3) to define a new function based on the time dependence of the dose rate, namely

\[ G^* = \gamma \Gamma^* (1 - P) \]  

(7)

Equation 7 considers the electron hole mobility based on Langevin recombination constant defined as \( \gamma = q(\mu_e + \mu_h)/\epsilon \). \( \mu_e \) and \( \mu_h \) are the electron and hole mobility respectively, \( \epsilon \) is the dielectric constant.

Therefore normalizing \( \Gamma \) we obtain the following expression

\[ \Gamma^* = \frac{\Gamma}{P} \]  

(8)

According to Equation 5, we can assume the product \( np \) as the charge carrier density, to get

\[ V_{oc} = V_{oc_i} - \left[ \frac{E_{gap}}{q} - \frac{kT}{q} \ln \left( \frac{N_c^2}{g^*} \right) \right] \]  

(9)
4. Results
In the present investigation we focused on several parameters providing information about the $V_{oc}$ degradation of P3HT:PC$_{61}$BM based solar cell for space application. Based on TID calculations, a systematic theoretical investigation on the influence of the proton and electron radiation spectra, based on the ISS orbit, was performed as shown in Fig. 3; moreover, calculations on the $V_{oc}$ degradation correlated in terms of TID, were also performed.

![Figure 3](image)

**Figure 3.** Visualization of one hundred particles interaction on the P3HT (cyan) and PCBM (dark yellow) layers under ISS orbit conditions: (a) proton interaction, (b) electron interaction. Inset: zoom of bilayer’s interface.

4.1 Total Ionizing Dose
The Total Ionizing Dose (TID) was determined using SPENVIS suite through $1 \times 10^7$ particles interactions according to the ISS orbit and the parameters of the OPV cell architecture. The ionizing dose generated by protons based on the energy spectrum for the P3HT was 282.63 Gy (compared to that of PCBM, an ionizing dose of 283.41 Gy is observed as shown in Fig. 4.)

![Figure 4](image)

**Figure 4.** TID on P3HT and PCBM based on electrons and protons spectrum energy.
According to the electron’s energy spectrum, the ionizing dose for the P3HT was 931.73 Gy and the PCBM had an ionizing dose of 901.49 Gy (see Fig. 4 for comparison).

Finally, the Total Ionizing Dose was the sum of the protons and electrons interactions on both layers. The P3HT had a TID of 1214.36 Gy and the PCBM TID was 1184.90 Gy; which means that the Dose rate was approximately 0.00230974 Gy/min in one year orbit.

4.2 Voc Degradation
$V_{oc}$ degradation was determined using Equation (9) and following the parameters provided by Koster et al. [4]. According to the evaluation of the damage dose rate based on parameter TID, of both layers during one year orbit, the maximum TID present on the P3HT:PCBM based cell was 1214.36 Gy as shown in Fig. 5.

![Figure 5. Open circuit voltage degradation as function of the total ionizing dose.](image)

5. Conclusions
The primary effect of irradiation on the OPV cell characteristics is to decrease the apparent open circuit voltage, $V_{oc}$. The initial objective of the work was to examine how ionizing radiation would impact the performance of organic semiconductor based photovoltaic cells, such as those based on P3HT:PCBM blends. Results of the simulation described above led to a series of conclusions important for our ultimate goal: to understand the effects of ionizing radiation. In particular, from our results we can conclude that OPVs will survive in space environments for one-year missions under ISS orbit conditions, up to the commercial test standard 100 Gy (SiO$_2$) and contrary to popular belief that organics would be radiation “soft.”

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