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Kyohei Nakano,¹∗† Yujiao Chen, and Keisuke Tajima¹∗†

AFFILIATIONS
RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

¹Electronic addresses: kyohei.nakano@riken.jp and keisuke.tajima@riken.jp

ABSTRACT

Accurate determination of charge carrier density in organic solar cells under light irradiation is essential because charge carrier density is directly related to the bimolecular recombination rate and open-circuit voltage of the cells. We investigate the robustness of transient photovoltage/current (TPV/C) and impedance spectroscopy (IS) to interference from the geometric capacitance of the cells. TPV/C quantifies the charge carrier density of bulk heterojunction cells with small geometric capacitance, while IS fails to separate the charge carriers in the organic layer from those in the electrodes. In contrast, TPV/C eliminates the effect of geometric capacitance and gives a reasonable estimation of the charge carrier density in the organic layer with the planar heterojunction, demonstrating that TPV/C is more robust than IS to interference from geometric capacitance of the cells.

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Power conversion efficiency of organic solar cells (OSCs) has been improved up to 16%, mainly driven by the development of new organic semiconductor materials. Although the short-circuit current density ($J_{SC}$) and fill factor (FF) of OSCs are now comparable with those of inorganic and perovskite solar cells, the open-circuit voltage ($V_{OC}$) of OSCs could be improved. The electronic energy levels of the materials should be tuned appropriately to increase $V_{OC}$ while maintaining a sufficient energy difference for efficient charge generation. Alternatively, suppressing bimolecular recombination produces a higher charge carrier density under light irradiation, increasing $V_{OC}$. The bimolecular recombination depends on the square of the charge carrier density; however, in contrast to inorganic solar cells, the recombination rates in OSCs are much lower than those expected from the Langevin recombination model. This discrepancy has been explained by the involvement of the interfacial charge transfer state, but the details of the recombination mechanism in OSCs are still unclear. Therefore, to relate the interfacial structures to the recombination kinetics of the charge carriers in OSCs, it is vital to obtain accurate information about the charge carrier density in the organic layers.

Charge extraction (CEX) is widely used to evaluate the charge carrier density. In this technique, OSCs are initially kept under open-circuit conditions with steady light irradiation, and then, short-circuit conditions are rapidly applied (within ~100 ns) while simultaneously turning off the light. The integration of the transient current over time gives the electric charges stored in both the organic layer and the electrodes. In OSCs, there is a thin (approximately 100 nm) organic layer between two electrodes, resulting in a large geometric capacitance ($C_{geo}$). Consequently, many charge carriers are stored in the electrodes, which makes quantifying the charge carriers in the organic layer by CEX difficult in some cases. Instead of counting all the charge carriers by CEX, differential charging techniques, such as transient photovoltage/current (TPV/C) and impedance spectroscopy (IS), can quantify the charge carrier density indirectly by using the differential capacitance ($C_{diff}$). $C_{diff}$ is the voltage-dependent capacitance, defined as the ratio between small changes in the charge and voltage ($\Delta Q/\Delta V$), and it is measured by applying a small charge density perturbation to the cell. The integration of $C_{diff}$ from 0 V to $V_{OC}$ gives the number of total charge carriers in OSCs under irradiation. Differential charging methods have the advantage that they can evaluate the number of charge carriers in the organic layer separately from those stored in the electrodes. OSCs have been analyzed by TPV/C and IS; however, the accuracy and the robustness to the cell geometric capacitance of these methods for determining the charge carrier density in OSCs need careful assessment.
In this study, we examine the suitability of TPV/C and IS techniques for evaluating the charge carrier density in OSCs with bulk heterojunction (BHJ) and planar heterojunction (PHJ) structures. The major differences between BHJs and PHJs are the donor/acceptor (D/A) interface area and the film thickness. BHJs have a larger D/A interface area and larger film thickness and thus have a small \( C_{\text{geo}} \) contribution to the apparent charge, whereas PHJs have a larger \( C_{\text{geo}} \) contribution. We discuss separate evaluations of the charge carriers stored in the organic layer and the electrodes, and the reliability of the experimentally obtained charge carrier density.

Figure 1(a) shows the molecular structures of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PC_{61}BM) used as the donor and the acceptor, respectively. We prepared the PHJ by transferring a P3HT film onto a PC_{61}BM film by using the contact film transfer method.\(^{20,21}\) The BHJ was prepared as a randomly mixed thin film by spin-coating a mixed solution of P3HT and PC_{61}BM (1:1 by weight). The electrodes were polyethyleneimine ethoxylated (PEIE)-modified ITO and MoO_{3}/Ag. The film thicknesses of the BHJ and PHJ were 183 and 45 nm, respectively.

The average photovoltaic performances under AM1.5 100 mW/cm\(^2\) simulated sunlight irradiation were \( J_{\text{SC}}, V_{\text{OC}}, \text{FF}, \text{and } PCE \) of 1.0 mA/cm\(^2\), 0.50 V, 0.56, and 0.28%, respectively, for the PHJ and 0.61 mA/cm\(^2\), 0.61 V, 0.72, and 4.2%, respectively, for the BHJ. The limited D/A interface area of PHJs resulted in a \( J_{\text{SC}} \) one order of magnitude lower than that of BHJs. Figure S1 shows the current density-voltage characteristics.

TPV/C measurements were performed under steady light irradiation with a white light-emitting diode (LED) and neutral-density filters to tune the light intensity. Irradiation with a 0.4 ns pulsed laser shot in the TPV/C measurement, evaluated by the integral of the transient photocurrent signal over time.\(^{14,15}\) \( V_{\text{OC}} \) is the maximum perturbation of \( V_{\text{OC}} \) by the single pulsed laser shot, which was below 10 mV. \( C_{\text{diff}} \) of TPV/C should include both chemical capacitance \( C_{\text{ch}} \) and geometric capacitance \( C_{\text{geo}} \). IS can evaluate these capacitances separately if their time constants are different enough. \( C_{\text{diff}} \) in TPV/C and \( C_{\text{geo}} \) in IS depend exponentially on \( V_{\text{OC}} \), whereas \( C_{\text{geo}} \) is almost constant (solid lines in Fig. 2(a)). As expected for BHJs, \( C_{\text{geo}} \) was smaller than \( C_{\text{ch}} \) due to the large D/A interface area and thick film thickness.

We calculated charge carrier density \( n \) by integrating the capacitance over voltage from 0 V to \( V_{\text{OC}} \),

\[
n(V_{\text{OC}}) = \frac{1}{qAd} \int_{0}^{V_{\text{OC}}} C(V) dV,\tag{2}
\]

where \( q \) is the elemental charge, \( A \) is the electrode area, and \( d \) is the film thickness. The integration of \( C_{\text{geo}} \) over \( V_{\text{OC}} \) is the charge carrier density in the device. For TPV/C, the number of charges stored in the electrodes was subtracted,

\[
n_{\text{TPV}}(V_{\text{OC}}) = \frac{1}{qAd} \left\{ \int_{0}^{V_{\text{OC}}} C_{\text{diff}}(V) dV - C_{\text{diff}}(0) V_{\text{OC}} \right\}.\tag{3}
\]

where \( C_{\text{diff}}(0) \) is the differential capacitance at 0 V, which represents the geometrical capacitance.\(^{7} \) Thus, \( C_{\text{diff}}(0) \times V_{\text{OC}} \) is the amount of charge stored in the electrodes. Figure 2(b) shows the
FIG. 2. (a) Capacitance measured by transient photovoltage/current and impedance spectroscopy for the P3HT:PC$_{61}$BM BHJ. The solid lines are the exponential fitting. (b) Charge density in the organic layers calculated by the integral of the capacitance over the voltage. (c) Small perturbation lifetime $\tau_{\Delta n}$. All the data were plotted against $V_{OC}$ under steady light irradiation of different intensities.

calculated charge carrier densities. TPV/C and IS gave similar charge densities, in agreement with previously reported values.$^{8,28}$ The difference in charge carrier density measured by two these methods was less than 20% within the experimental range of the irradiation intensity.

We also evaluated the small-perturbation lifetime ($\tau_{\Delta n}$) of charge carriers at the D/A interface by using TPV/C$^{11,19}$ and IS$^{29}$ [Fig. 2(c)]. The TPV/C measurement provides $\tau_{\Delta n}$ as the single-exponential decay rate of small perturbed $V_{OC}$.

$$\Delta V_{OC}(t) = \Delta V_{OC} \times \exp \left( -\frac{t}{\tau_{\Delta n}} \right).$$  (4)

In the IS measurements, the time constant of the D/A interfacial component, $C_{\mu} \times R_{\text{rec}}$, is defined as $\tau_{\Delta n}$. This is because the single exponential decay in the time domain in TPV/C is equivalent in Fourier transformation to the impedance response of the RC parallel circuit in the frequency domain in IS. $\tau_{\Delta n}$ of BHJ cells evaluated by TPV/C and IS matched well as previously reported,$^{30,31}$ indicating the high reliability of these measurements [Fig. 2(c)]. The difference in $\tau_{\Delta n}$ determined by TPV/C and IS was about 20%.

For the P3HT:PC$_{61}$BM BHJ solar cell, TPV/C and IS provided similar charge carrier densities and lifetimes. The small differences may originate from the error in the equivalent circuit fitting of IS, which is improved as difference increases between the time constants of the components from the bulk and the D/A interface in the frequency domain. Because the charge carrier density and lifetime are typically measured over several orders of magnitude and plotted on a logarithmic scale, the difference of about 20% is acceptable for discussing the recombination.

The same experimental and analytical procedures were applied to the P3HT/PC$_{61}$BM PHJ, and the results are shown in Fig. 3. The differential capacitance of the PHJ depended weakly on voltage.

FIG. 3. (a) Capacitance measured by TPV/C and IS for the P3HT/PC$_{61}$BM PHJ. The solid lines are exponential fitting. (b) Charge density in the organic layers calculated by the integral of the capacitance over the voltage. (c) Small perturbation lifetime $\tau_{\Delta n}$. All the data were plotted against $V_{OC}$ under steady light irradiation of different intensities.
[Fig. 3(a)]. For the TPV/C data, however, $C_{\text{diff}}$ was fitted with an exponential curve, as for the BHJ, and the contribution of chemical capacitance in the cell was derived from the differential capacitance. In contrast, $C_0$ in IS did not show the expected exponential dependence on voltage. The unexpected behavior of $C_0$ in IS may arise from the comparable $C_0$ and $C_{\text{geo}}$ in the PHJ, which makes the separation of these components in the frequency domain difficult owing to the similar time constants. We observed only one semicircle in the Cole-Cole plot, indicating that the impedance response was dominated by one RC component (Fig. S3). $C_{\text{geo}}$ calculated by IS was similar to $C_{\text{diff}}(0)$ of TPV/C, indicating that the dominant impedance response was from the geometric capacitance. Therefore, we did not obtain an accurate value for the charge carrier density in the organic layer by IS. Consequently, the calculated charge carrier density [Fig. 3(b)] and small-perturbation lifetime [Fig. 3(c)] evaluated by TPV/C and IS did not match.

We also evaluated the charge carrier density by CEX, in which all the charge carriers stored at the electrodes and D/A interface were directly counted via the integral of the transient current over time. The amount of collected charge in the CEX measurements depended linearly on the voltage for the PHJ [Fig. S4(a)], whereas it depended exponentially on the voltage for the BHJ [Fig. S4(b)]. The linear voltage dependence in the PHJ implies that most of the collected charge came from the electrodes (geometric capacitance contribution), not from the D/A interface.

The dependence of the small-perturbation lifetime on charge carrier density differed between the BHJ and the PHJ (Fig. S5). The reaction order of the recombination in the BHJ was estimated as 2.8 using the slope parameter of the $V_{\text{OC}}$–$n$ plot [Fig. S5(a)], whereas the PHJ showed a steeper slope with a reaction order of 6.5. The slope parameter of the PHJ in the $n$–$V_{\text{OC}}$ plot was bigger than that of the BHJ, meaning that in the PHJ, a smaller change in the charge carrier density caused a larger change in $V_{\text{OC}}$ [Fig. S5(b)]. This is because of the inhomogeneous charge carrier distribution in PHJs: in IS may be an excellent tool for obtaining information about the charge carrier distribution in devices.

In summary, when the geometric capacitance contribution was large, only TPV/C was able to estimate the charge carrier density in the cell, implying that the differential charging used in TPV/C is more robust than IS for quantifying the charge carrier density. The accurate estimation of the charge carrier density, lifetime, and distribution in PHJ structures with well-defined interfaces will contribute to revealing the link between the D/A interfacial structure and charge carrier recombination kinetics. Once guidelines are established for an ideal D/A structure that suppresses the recombination without decreasing charge carrier generation, the structure will improve the performance of OSCs.

See the supplementary material for the experimental setup procedure and supplementary material figures.

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