

# Reciprocity and Open-Circuit Voltage in Solar Cells

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**Abstract**—The equation for open-circuit voltage of a solar cell based on optoelectronic reciprocity is combined with the standard textbook formula to obtain a general result that includes photon recycling as well as losses by carrier transport. It is shown that, in indirect-gap semiconductors, the general expression reduces to the “conventional” and “optoelectronic” expressions in the limits of low and high radiative efficiency.

**Index Terms**—Light emitting diodes, photovoltaic conversion, solar cells.

Statistical and thermodynamic techniques are providing new tools to underpin as well as probe the fundamentals of photovoltaic conversion. These include, for example, the reciprocity of carrier transport in solar cells [1], [2] (which augments an earlier version by Shockley [3]), the principle of optoelectronic reciprocity [4] (discussed also in [5] for a monochromatic converter), and the generation of optical entropy in the conversion of nonconcentrated sunlight [6]. These techniques generally focus on the voltage generated by the solar cell rather than on kinetic properties such as current.

## OPTOELECTRONICS V. SOLAR CELL THEORY

By using optoelectronic reciprocity, Rau [4] obtained an expression for the open-circuit voltage  $V_{OC}$  of a solar cell based on the quantum efficiency of the cell  $Q_{LED}$  when operated as a light-emitting diode (see also [7]):

$$qV_{OC} = qV_{OC}^{rad} + k_B T_o \ln Q_{LED} \quad (1)$$

where  $V_{OC}^{rad}$  is the open-circuit voltage in the radiative limit (in the absence of nonradiative recombination),  $k_B$  is the Boltzmann constant,  $q$  is the electron charge, and  $T_o$  is the cell temperature. Since the quantum efficiency  $Q_{LED}$  is given by the balance between the quantum yield of luminescence and the probability of photon reabsorption (recycling), (1) has been used in application to materials with high radiative efficiency, usually direct-bandgap semiconductors. Equation (1), however, does not capture characteristics determined by charge carrier transport in the solar cell.

Equation (1) can be contrasted with the expression

$$qV_{OC} = k_B T_o \ln \left( \frac{I_{ph}}{I_o} + 1 \right) \quad (2)$$

obtained in standard texts on solar cell theory [8]–[10], where  $I_{ph}$  and  $I_o$  are the photogenerated and dark saturation currents, respectively, determined by solving the carrier transport equations. Unlike the parameters that enter (1), the currents  $I_{ph}$  and  $I_o$  depend on the minority carrier diffusion lengths and possibly also on other minority carrier

transport parameters, as discussed in detail in most textbooks {see, for example, [8]–[10] and (20) and (21)}. The natural question then arises about the relationship between (1) and (2).

By taking into account both carrier transport and features associated with photon emission/reabsorption and nonradiative recombination, in this note we obtain an expression for the open-circuit voltage that combines (1) and (2) and extends the applicability of the optoelectronic expression (1) to materials with low radiative efficiency such as silicon.

To begin with, we define the relevant quantities. The photon flux of black-body radiation at temperature  $T$  passing through a unit perpendicular area per unit solid angle per unit frequency ( $\nu$ ) per unit time is given by (see, e.g., [11])

$$\phi_{bb}(\nu, T) = \frac{2(\nu/c)^2}{e^{h\nu/k_B T} - 1} \quad (3)$$

where  $h$  is the Planck constant,  $k_B$  is the Boltzmann constant, and  $c$  is the speed of light. Perceiving solar radiation as due to a black body at temperature  $T_S \approx 5800$  K, the total photon flux  $\Phi_S$  incident on the cell and the total black-body photon flux  $\Phi_o^{bb}$  at temperature  $T_o$  are given by

$$\Phi_S = \omega_S A \int_{E_g/h}^{\infty} \phi_{bb}(\nu, T_S) d\nu \quad (4)$$

$$\Phi_o^{bb} = \pi A \int_{E_g/h}^{\infty} \phi_{bb}(\nu, T_o) d\nu \quad (5)$$

where  $A$  is the area of the cell and  $\omega_S$  is the solid angle subtended by the Sun ( $6.85 \times 10^{-5}$  sterad). We also define the average integrated quantum efficiencies  $EQE_S$  and  $EQE_o$  for the incident and emitted radiation:

$$EQE_{o,S} = \frac{\int_{E_g/h}^{\infty} EQE(\nu) \phi_{bb}(\nu, T_{o,S}) d\nu}{\int_{E_g/h}^{\infty} \phi_{bb}(\nu, T_{o,S}) d\nu} \quad (6)$$

where  $EQE(\nu)$  is the external quantum efficiency of the cell at frequency  $\nu$ .

Thus equipped, we can use the optoelectronic reciprocity [4] to write the photon flux emitted by an LED or solar cell on application of voltage  $V$  in the form

$$\begin{aligned} \Phi_o^{cell} &= \pi A \\ &\left( e^{qV/k_B T_o} - 1 \right) \int_{E_g/h}^{\infty} EQE(\nu) \phi_{bb}(\nu, T_o) d\nu \\ &= EQE_o \Phi_o^{bb} \left( e^{qV/k_B T_o} - 1 \right). \end{aligned} \quad (7)$$

At the same time, the solar cell/LED produces current given by the usual ideal diode equation [8]

$$I = I_o \left( e^{qV/k_B T_o} - 1 \right). \quad (8)$$

Since the quantum efficiency of the LED is defined by

$$Q_{LED} = \frac{q\Phi_o^{cell}}{I} \quad (9)$$

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the dark saturation current  $I_o$  can be determined in terms of a ratio of the two quantum efficiencies, of the solar cell and LED:

$$I_o = q \frac{EQE_o}{Q_{LED}} \Phi_o^{bb}. \quad (10)$$

In a similar fashion, we can write, for the photogenerated current  $I_{ph}$

$$I_{ph} = qEQE_S \Phi_S. \quad (11)$$

Inserting (10) and (11) into (2) and neglecting the unity in the argument of the logarithm, we obtain

$$qV_{OC} = k_B T_o \ln \left( \frac{\Phi_S}{\Phi_o^{bb}} \right) + k_B T_o \ln \left( \frac{EQE_S}{EQE_o} \right) + k_B T_o \ln Q_{LED}. \quad (12)$$

The first term in (12) is just the open-circuit voltage of an ideal solar cell, as given by the Shockley–Queisser detailed balance [12] and the last term corresponds to a similar term in (1). The second term extends expression (1) to include carrier transport features contained in the photovoltaic EQEs. When there are no carrier transport losses,  $EQE_S$  reduces to the absorptivity of the cell for incident radiation, and  $EQE_o$  to the emissivity (and by Kirchhoff's law, to the absorptivity) of the emitted radiation at the temperature of the solar cell. The sum of the first two terms then becomes the open-circuit voltage in the radiative limit and (12) reduces to (1).

An equation equivalent to (12) also follows from [13, eq. (10)] by introducing the quantum efficiencies but is given here with a different emphasis and interpretation. As will be shown further below, the meaning of the second and third terms in (12) can be understood best in the limits of low and near-unit internal quantum efficiency  $Q$ . The second term then represents the “round-trip” losses in the carrier transport in the “traditional” picture of solar cell operation under open-circuit voltage, from carrier generation  $\rightarrow$  transport to junction  $\rightarrow$  transport to the recombination site. The third term, on the other hand, describes photon emission and “outcoupling” of light from the solar cell. The key concept in this term is photon recycling (elucidated with particular clarity by Martí *et al.* [14] and discussed in the context of the present paper by Rau *et al.* [15]). It is worth noting that, in the presence of nonradiative recombination, photon recycling hinders the escape of photons from the structure and enhances nonradiative losses (see also [15]).

### THE DARK SATURATION CURRENT

It is of interest to see how (12) and, in particular, the expression (10) for the dark saturation current  $I_o$  compare with the result given in standard texts on solid-state diodes and solar cells (see, for example, [8]):

$$I_o = qR_o \quad (13)$$

where  $R_o$ , if multiplied by the voltage factor in (8), is the total recombination rate integrated over the volume. To bring (10) and (13) into closer correspondence, we write the reciprocity theorem for charge carrier transport in terms of the radiative component of  $R_o$  as

$$R_{o,rad} = \int \frac{p_o}{\tau_{rad}} \eta_{col} dV \quad (14)$$

where  $p_o$  is the equilibrium minority-carrier density. With the use of (14), the dark saturation current (13) becomes

$$I_o = q \frac{R_{o,rad}}{Q} \quad (15)$$

where  $Q$  is the quantum yield for photon emission

$$Q = \frac{R_{o,rad}}{R_o}. \quad (16)$$

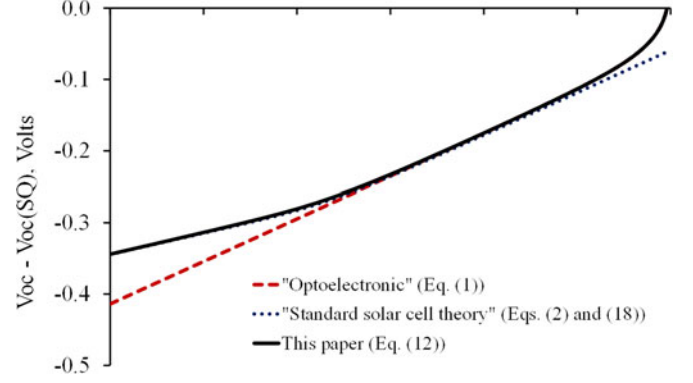


Fig. 1. Open-circuit voltage as given by the three different theories considered in this paper.  $V_{oc}(SQ)$  denotes the ideal open-circuit voltage under one-sun illumination, as given by the Shockley–Queisser theory.

To progress, we need to examine more closely equation (14) for the radiative recombination rate. To this end, we note that  $\mathcal{V}p_o/\tau_{rad}$  is the total rate of radiative recombination events in thermal equilibrium. The resulting thermal photon flux emitted by the cell can be equated to  $\varepsilon\Phi_o^{bb}$ , where  $\varepsilon$  is the emissivity, which, by Kirchhoff's law, is equal to the absorptivity  $a$ . Since internally emitted photons will be emitted to the exterior of the structure unless reabsorbed (with average probability  $r$ , say), we can write

$$(1 - r) \mathcal{V}p_o/\tau_{rad} = a\Phi_o^{bb} \quad (17)$$

which transforms, with the use of (14) and (15), into

$$I_o = \frac{q}{Q(1 - r)} a \langle \eta_{col} \rangle \Phi_o^{bb} \quad (18)$$

where

$$\langle \eta_{col} \rangle = \frac{1}{\mathcal{V}} \int \eta_{col} dV \quad (19)$$

is the average collection probability.

Equation (18) provides a clear link between the more general equation (10) for  $I_o$  and the standard textbook expression (13): (18) represents an approximation valid in the limit of low radiative efficiency when reabsorption of radiation outside the “escape cone” (and not trapped by total internal reflection) can be neglected. Indeed, the factor  $Q(1 - r)$  is an approximation for  $Q_{LED}$  in the limit of small  $Q$  [16], [17], and it can readily be shown from the definition that  $EQE(\alpha)$  becomes  $a\langle \eta_{col} \rangle$  in the limit of small absorption coefficient  $\alpha$ . The reabsorption probability  $r$  then includes only contributions from radiation trapped by total internal reflection.

Fig. 1 illustrates the results considered in this paper for the open-circuit voltage in silicon as a function of the quantum yield  $Q$  [see (1) and (13)], and  $V_{oc}$  obtained by substituting (18) into (2); we assumed, for simplicity, that  $EQE_S$  for the incident light is equal to unity). Neglecting surface recombination, the standard results for  $I_o$  and  $EQE(\alpha)$  are [10]

$$I_o = Aqp_o \frac{D}{L} \tanh \left( \frac{W}{L} \right) \quad (20)$$

$$EQE(\alpha) = \frac{\alpha L}{1 - \alpha^2 L^2} \left\{ \tanh \left( \frac{W}{L} \right) - \alpha L \left( 1 - \frac{e^{-\alpha W}}{\cosh \left( \frac{W}{L} \right)} \right) \right\} \xrightarrow{\alpha \rightarrow 0} \alpha L \tanh \left( \frac{W}{L} \right) \quad (21)$$

where  $L$  and  $D$  are the minority-carrier diffusion length and diffusion constant, and  $W$  is the thickness of the quasi-neutral region. In this case, typical for indirect-gap semiconductors, the two formulas (1) and (2) combined with (18) provide an accurate description of the open-circuit voltage in the two overlapping regions of small and near-unit values of  $Q$ , with the more general formula (12) providing a more complete overarching picture. The situation becomes more complicated for direct-gap semiconductors where photons may contribute toward carrier/energy transport to the junction, and there is no clear separation between the two approximate limiting formulas.

#### ACKNOWLEDGMENT

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# Correction

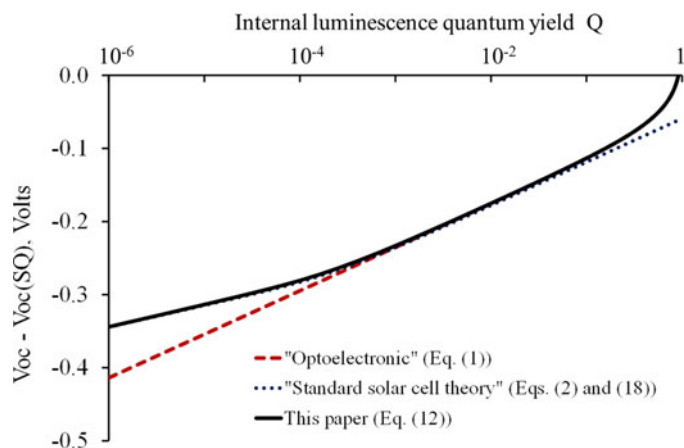
## Correction to “Reciprocity and Open Circuit Voltage in Solar Cells”

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Fig. 1 in [1] was inadvertently submitted and published without labels to the horizontal axis. The corrected version of this figure is shown below.

### REFERENCE

- [1] T. Markvart, “Reciprocity and open circuit voltage in solar cells,” *IEEE J. Photovolt.*, vol. 8, no. 1, pp. 67–69, Jan. 2018.



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