



Reply to 'Ideal solar cell efficiencies'

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Reply to 'Ideal solar cell efficiencies'

Guillemoles et al. reply — We wrote our Comment¹ as a brief and concise guide to the Shockley–Queisser (SQ) model², chiefly aiming to explain how real-world solar cells (non-concentrating, single-junction) must be related to the efficiency limits that result from the SQ model. There is a need for such a Comment, especially in the context of a widened portfolio of new very efficient solar cell materials and a rapidly growing community. As obvious from the title¹, we target non-specialist readers. Such approach³ has the risk that the resulting text is unsatisfactory for specialist readers. The author of the Correspondence on our Comment⁴ is certainly such specialist reader. Thus, to reply to the Correspondence we need to leave the level at which we presented the topic in our Comment, to make clear that while there can be differences of opinion as how to explain the issue to the 'perplexed', what is written in our comment is a valid description of the SQ model.

The most important issue brought up in the Correspondence, and the one we concentrate on in our reply, is the role of étendue expansion as a main loss, especially in the case where all recombination is radiative. In ref. ¹, we introduced the term 'isothermal losses' for the actual heat generation (loss of total, that is, internal, energy per incoming photon) that occurs in the device in addition to the initial non-absorption and thermalization losses. Étendue losses, in contrast, refer specifically to the entropy increase associated with photon exchange between the sun, the device and the environment. Étendue expansion refers to the fact that the étendue ε_{in} of the incoming solar radiation differs by a factor of ~46,000 from that of the outgoing radiation (emitted by the solar cell), ε_{out} , if no additional measures are in place to either concentrate the light or limit the solid angle of the emitted radiation.

To put our explanation of the SQ model into its thermodynamic context requires splitting the total energy into the Helmholtz free energy and an entropic term resulting in a simple refinement to Fig. 2c of ref. ¹, as shown in Fig. 1. To focus the discussion, we consider the available power after thermalization losses and non-absorption losses have been discounted in the solar cell. This can be represented as the area of a rectangle (Fig. 1) where one side is the photogenerated current J_{SC} and the other is the maximum open circuit voltage $V_{\text{OC}}^{\text{max}}$, obtained with full concentration of

the sunlight (or matching étendues, that is, $\varepsilon_{\text{in}} = \varepsilon_{\text{out}}$). Note that $J_{\text{SC}} = q\dot{v}_{\text{in}}$ is defined by the total incoming photon flux \dot{v}_{in} and the elementary charge q . Also included in Fig. 1 is the current versus voltage characteristics of the solar cell as calculated from the balance of incoming and outgoing radiation (see Supplementary Information). Each working point (the maximum power point is used in the figure) defines a horizontal line that separates the emitted photon flux \dot{v}_{out} from the collected electron current $J = q(\dot{v}_{\text{in}} - \dot{v}_{\text{out}})$ and a vertical line at the voltage V_{mpp} that separates the free energy (work) carried by each particle on the left from the dissipative processes (heat) incurred by each particle on the right.

These two lines separate the initial rectangle $J_{\text{SC}} \times V_{\text{OC}}^{\text{max}}$ into four subareas, each representing a power with a tangible physical meaning. The light red area is the chemical potential F_{eh} (per particle) of the electron–hole pairs multiplied by the collected electrical current J , divided by q (that is, the net electron flux) and corresponds to the electrical output power. The dark-red area then stands for the entropy production in the electronic system (referred to as isothermal losses in ref. ¹). The light-blue area corresponds to the power radiated by the cell at the chemical potential F_{ph} of photons emitted from the solar cell multiplied by the number of emitted photons per unit time \dot{v}_{out} . Finally, the dark-blue area represents the entropy flow in the photonic system and includes the étendue change. As pointed out by the Correspondence author^{5,6}, the entropy production per incident photon is the sum $\sigma = \sigma_{\text{et}} + \sigma_{\text{kin}}$ of a contribution of étendue expansion (controlled by the way photons enter and leave the cell) and a 'kinetic' term associated with charge-carrier collection (controlled by the amount of particles leaving the cell in the form of electron–hole pairs; see also Supplementary Information). This entropy term defines the shift between the maximum open circuit voltage and the voltage of the actual working point at maximum power according to $V_{\text{mpp}} = V_{\text{OC}}^{\text{max}} - T(\sigma_{\text{et}} + \sigma_{\text{kin}})/q$, with the absolute cell temperature T , and defines the width of both the dark-red and the dark-blue area, as well as by default the width of the light areas as well.

The entropy generation per particle, measured in the photon system (by σ_{et} and σ_{kin}), defines simultaneously the entropy generation per particle in the

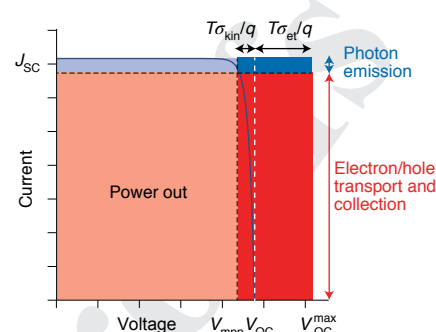


Fig. 1 | Power losses in the SQ model including the effect of étendue expansion. Current–voltage curve of a solar cell in the SQ model without concentration (that is, with étendue expansion). The maximum open circuit voltage is reduced by two entropy terms towards the actual open circuit voltage V_{OC} and by towards the voltage V_{mpp} at the maximum power point. The power losses due to photon emission are indicated as blue rectangles (dark blue losses associated with entropy generation, light-blue losses at the free energy of the emitted photons). The electrical output power is defined by the number of extracted hole pairs multiplied by their free energy (light-red area). The largest loss channel (dark-red) is that of the entropy losses in the electron–hole system. On the energy axis this loss equals the entropic losses in the photonic system. However, the height on the current axis is much larger than the contribution from the emitted photons because the number of collected electron–hole pairs at the maximum power point, fortunately, exceeds the number of emitted photons by far. With suitable units, the vertical axis represents a particle flux and the horizontal axis an energy per particle, so that the product is still a power.

electronic system. This follows from an important implication of the SQ model, namely that both systems mirror each other exactly: the free energy F_{eh} of the electron–hole pairs equals F_{ph} and the free energy of the emitted photons⁷, and both equal qV_{mpp} . All three quantities are defined by the same vertical line shown in Fig. 1. In turn, the horizontal line reflects the conservation of particles across both systems, namely that the incoming photons must leave the cell either in the form of an emitted photon or as electron–hole pairs at the cell's terminals. Considering the power loss, that is, energy multiplied with particle flow, we see that although the largest power loss, the isothermal loss (dark-red area) carries the same dissipation per particle as

correspondence

the power loss in the photon system, the dissipation actually occurs within the solar cell.

Thus, while the undisputed elegance of the SQ model results from describing the solar cell only via its input and output balance, the model contains strong implications on what happens inside the cell as discussed above and in ref. ¹. Furthermore, a closer look into the solar cell becomes mandatory as soon as further loss channels that actually happen inside the cell, like non-radiative recombination or resistive ones, are added. To relate these additional losses to the losses and the assumptions implied by the SQ model was one aim of ref. ¹.

The second criticism in the Correspondence concerns the way we treat the departure of the photovoltaic quantum efficiency of a real-world solar cell from an ideal step-function. There is admittedly

not a unique solution for this problem and any proposition has pros and cons. In ref.

¹ we use a specific approach⁸ that has been successfully used to analyse and compare solar cells across all technologies^{9,10}.

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Competing interests

The authors declare no competing interests.

Additional information

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