What is the highest voltage that can be generated by a solar cell ?

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The ultimate photovoltaic efficiencies are usually determined with the use of the Shockley-Queisser detail balance theory. Discussed many times and generally accepted as the theoretical efficiency limit for single junction solar cells, the "detailed balance" in question indicates that the electron (particle) current produced by the solar cell can be equated to the difference between the absorbed and emitted photon fluxes. In the original SQ paper [1], the emitted photon flux was equated to the equilibrium photon flux scaled by the factor (np/n_i^2) where n,p and n_i are the electron, hole and intrinsic carrier concentrations in the semiconductor converter (the solar cell), respectively. In a later modification, the theory was formulated in terms of the "generalised Planck distribution" for photons with non-zero chemical potential.

Unlike the theoretical treatment of chemical conversion devices such as fuel cell or battery, the voltage generated by the solar cell is almost incidental to this argument. We shall find it useful to obtain it directly, from an argument based on thermodynamics. Suppose that the solar cell is considered as a cavity or "box" filled with photons which are to be converted into electricity. The box (of volume V, say) is maintained at temperature T_o, assumed to be equal to the temperature of the surroundings. If multiplied by the electron charge, the voltage generated by the cell is equivalent to the useful work (to be denoted by w) that can be produced for one photon of this radiation. As the process takes place at constant volume, this is equal to the Helmholtz free energy F per photon – in other words, the chemical potential:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_V = \left(\frac{\partial U}{\partial N}\right)_V - T_o\left(\frac{\partial S}{\partial N}\right)_V = u - T_o s \tag{1}$$

where U, S and N are the internal energy, entropy and number of photons in volume V, and u and s the energy and entropy per photon. Key to this approach is the assumption that the "working medium" (electron-hole pairs in the semiconductor) and the emitted photons are in thermal equilibrium. The emitted photons are then characterised by the same of temperature T_o and chemical potential μ. If desired, the quantities in (1) can be referred to the thermodynamic functions of the emitted beam rather than of photons in the cavity [2-4]

A more general view can be obtained if we use an argument based on exergy or availability (see, e.g., [5,6]). Denoting by p_o the equilibrium pressure and v the volume per photon V/N, we can define the availability per photon of radiation in the box as

$$a = u - T_o s + p_o v \tag{2}$$

The maximum work w per photon is then equal to the difference of availability Δa between a photon in the box and a photon in thermal equilibrium at temperature T_o:

$$w = \Delta a = \Delta u - T_o \Delta s + p_o \Delta v \tag{3}$$

The conversion process takes place at constant volume so that $\Delta v = 0$. Noting that the equilibrium state corresponds to black body radiation with zero chemical potential, we then have

$$w = (u - T_o s) - (u_o - T_o s_o) = u - T_o s \tag{4}$$

where u_o and s_o refer to the equilibrium radiation. Since u and s are evaluated at temperature T_o, equation (4) just confirms the previous result (1).

Let us now consider the complete picture where photons in the box (solar cell) are produced by the absorption of high temperature radiation from the Sun, with $T = T_s \cong 6000K$. In a standard solar cell, photon absorption creates electron-hole pairs which are rapidly cooled to room temperature by interaction with phonons, and subsequently converted into electricity. It is not unusual for the separate steps of the conversion process to take part in different parts of the solar cell [7]. Solar radiation is then absorbed by an absorber/emitter of radiation which interacts with the photon field; the generated electron-hole pairs are cooled and transported to a converter which separates the charges and delivers electrical energy into the external circuit.

There appears to be no fundamental reason why photon cooling in the absorber cannot be impeded or even completely prevented. The photon gas in the absorber would then exist at a temperature T_a such that $T_S \geq T_a \geq T_o$, and the maximum work that each photon can carry out is equal to

$$w = \Delta a = u(T_a) - T_o s(T_a) \tag{5}$$

where the energy $u(T_a)$ and entropy $s(T_a)$ per photon correspond to the detailed balance between absorption of the solar beam and photon emission at temperature T_a. It can be shown [2,3] that the difference between (5) and (1) is simply $T_o \sigma_c$, where σ_c is the entropy gain due to irreversible cooling of the photon gas from T_a to T_o.

Therefore, the maximum work (voltage multiplied by the electron charge) that can be generated by such a "hot carrier" solar cell is equal to the availability (or exergy) of a photon in the emitted beam. This generalises the standard result (1) where this work is equal to the chemical potential of the emitted photons. The voltage values given by Eq. (5) are shown as a function of the bandgap of the semiconductor in Fig. 1a. Figure 1b shows the resulting photovoltaic efficiencies. We shall discuss further constraints which are imposed by the thermodynamics of the process, and possible structures for practical realisation.

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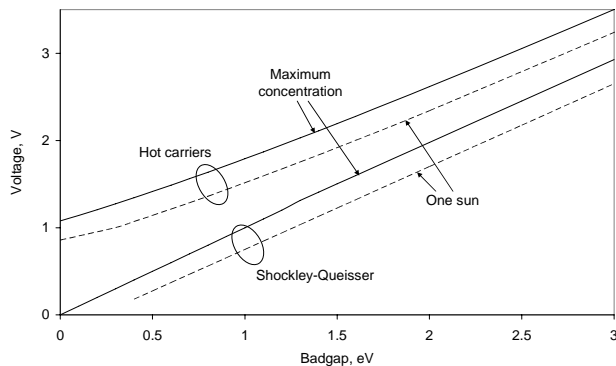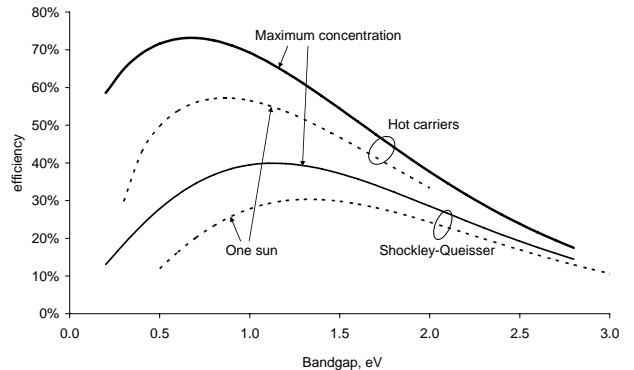
(a)   (b)

Figure 1. The voltages (a) and solar cell efficiencies (b) of hot carrier cells as functions of the bandgap, compared with results which follow from the Shockley-Queisser detailed balance.