

# Hot carrier solar cells by adiabatic cooling

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## ABSTRACT

Hot carrier solar cell is proposed where charge carriers are cooled adiabatically in the charge transport layers adjoining the absorber. The device resembles an ideal thermoelectric converter where thermopower and therefore also carrier entropy are maintained constant during cooling from the temperature attained in the absorber to the temperature at contacts.

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Hot carrier solar cells represent an attractive opportunity for increasing the cell efficiency above the Shockley–Queisser limit.<sup>1</sup> Proposed originally by Ross and Nozik<sup>2</sup> in 1982, the area has become an active area of research to the present day.<sup>3–5</sup> Most progress has been made trying to maintain the injected carriers at an elevated temperature for extended periods of time.<sup>6–8</sup> Attempts to implement these materials into a device proved more challenging. Indeed, Ross and Nozik's idea to cool carriers in energy selective contacts has not been subjected to serious theoretical examination (see, however, Ref. 9) and few experimental studies confirm the efficacy of this approach. A similar approach was suggested by Humphrey and Linke<sup>10</sup> by means of carrier exchange at a single energy. Hot carrier solar cells enhanced by the extraction of hot holes via Ross and Nozik mechanism was reported in Ref. 11. Esmailpour *et al.*<sup>12</sup> put forward a hot carrier solar cell achieved by exploiting intervalley scattering. This paper suggests an alternative method of hot carrier extraction by adiabatic cooling, based on thermodynamics.

The proposed hot carrier solar cell is shown schematically in Fig. 1(a). The device bears a close resemblance to a standard thin-film or perovskite solar cell (see, for example, Refs. 13 and 14) with the additional feature of a controlled doping profile in the charge transport layers, to be discussed below. Photons are absorbed in the absorber, sandwiched between n and p charge transport layers, with minimum absorption in the wide-bandgap front charge transport layer.

As in a standard solar cell, the absorbed carriers are separated by the built-in electric field (see, for example, Ref. 15). In the proposed hot carrier cell, the absorber (as well the charge transport layers) is made from “hot carrier material” where thermalization has been reduced or eliminated. The carriers separated to the edges of the

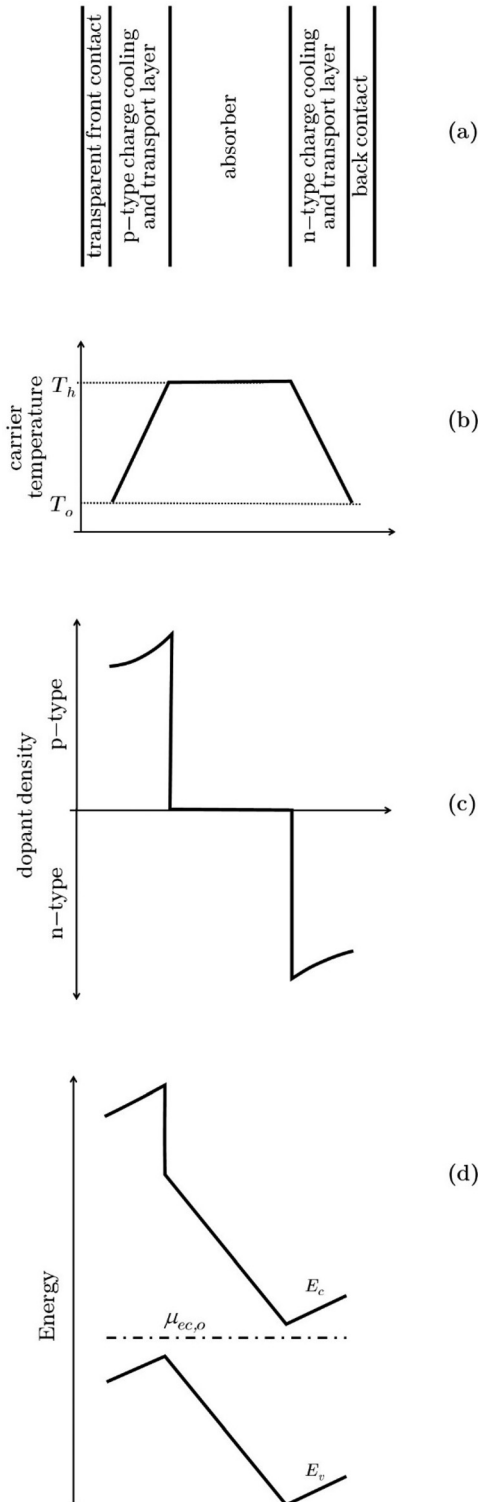
absorber will then retain an elevated temperature  $T_h$ . Carrier equilibrium at this temperature is reached after elastic scattering between carriers which is much faster than scattering from photons, which would lead to thermalization.<sup>16</sup> From a thermodynamic perspective, the absorption and charge separation represent an isothermal step (explicit in thermoelectric converters) that combines with adiabatic cooling to complete a parallel with the Carnot cycle in heat engines.

A quick estimate is useful to illustrate the feasibility of this process. The carriers are separated in time  $\tau_{sep} = d/v$ , where  $d$  is the absorber thickness,  $v = \mu E$  is the carrier velocity,  $\mu$  is the mobility, and  $E$  is the electric field. If the absorber is made from material that maintains carriers hot over time  $t > \tau_{sep}$ , carriers separated to the edges of the absorber will retain an elevated temperature  $T_h$ . A typical absorber thickness is of the order of micrometers. Taking a typical carrier velocity  $v \sim 10^7$  cm/s,<sup>17</sup> we arrive at a time  $\tau_{sep}$  of the order of 10 ps, already achieved in some research materials,<sup>18</sup> putting separation of hot carriers in a junction/absorber within reach.

The challenge is to cool down these carriers in the charge transport layers to ambient temperature  $T_o$  at contacts without losing energy by thermalization. In thermodynamic terms, this means that the cooling has to take place adiabatically, by keeping the carrier entropy  $s$  constant. A standard result, using the Sackur–Tetrode equation,<sup>18</sup> gives

$$s = k_B \ln \left( \frac{T^{3/2}}{n} \right) + \text{constant}, \quad (1)$$

where  $n$  is the carrier density, and the constant is independent of temperature or doping but depends on the bandgap. An alternative argument based on carrier thermopower (Seebeck coefficient)  $S = \pm s/q$ ,



**FIG. 1.** (a) A schematic diagram of the hot carrier solar cell with adiabatic cooling in the charge transport layers. (b) The carrier temperature profile in operation. (c) The doping profile. (d) The band diagram at equilibrium.

where  $q$  is the elementary charge, leads to the same result. With temperature profile such as in Fig. 1(b), a doping profile with

$$n = \text{constant} \times T^{3/2} \quad (2)$$

in the charge transport layer [Fig. 1(c)] will keep the carrier entropy constant, achieving adiabatic cooling. In particular, the required doping at the absorber and contact edges of the cooling/charge transport layers satisfies

$$\frac{n(\text{absorber})}{n(\text{contact})} = \left(\frac{T_h}{T_o}\right)^{3/2}. \quad (3)$$

The corresponding band diagram of such a hot carrier solar cell at equilibrium is shown in Fig. 1(d).

During adiabatic cooling in the charge transport layer, the thermal energy of carriers at the absorber edge is transformed into electrostatic energy (equivalent to work in standard thermodynamics), thereby increasing the voltage. Mahan<sup>19</sup> found theoretically that variable doping can improve the efficiency of thermoelectric generators, but without a thermodynamic interpretation nor optimum doping profile required for adiabatic cooling.

The temperature profile in the charge transfer layers which determines the doping according to Eq. (2) is determined by heat transport in the layer. In the case of an ideal hot carrier material, this temperature dependence will be linear, as shown in Fig. 1(b). For materials with a degree of thermalization, the temperature profile can be determined experimentally (see, for example, Ref. 20) or by modeling. The temperature will depend on the illumination intensity and, to some degree, also on the operating point on the I-V characteristic. The optimum doping profile therefore has to be designed bearing a specific application in mind and, most likely, operation at the maximum power point.

The maximum achievable open-circuit voltage can be estimated by using the relationship between thermopower and the electrochemical potential,  $\mu_{ec}$ <sup>21</sup>

$$\nabla \mu_{ec} = -qS \nabla T = \pm s \nabla T \quad (4)$$

with the  $-$  sign for holes and  $+$  sign for electrons. Integrating (4) over the cell from the n to the p contact, we obtain

$$qV_{oc} = - \int_{n \text{ contact}}^{p \text{ contact}} s \nabla T = (s_n + s_p)(T_h - T_o), \quad (5)$$

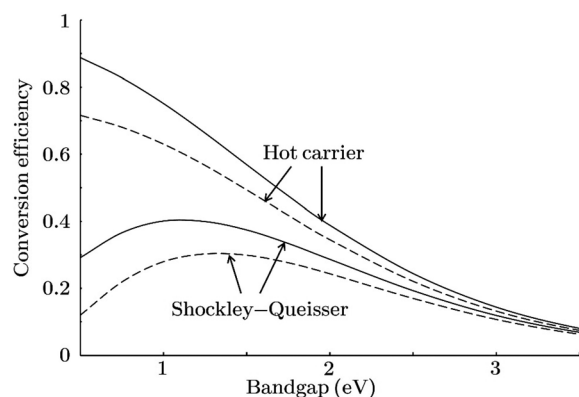
bearing in mind that the electron ( $s_n$ ) and hole ( $s_p$ ) entropies are constant. Now,  $(s_n + s_p)T_h$  is the combined heat  $Q$  per carrier that flows from the absorber into the charge transport layers which, if the absorber is made of a perfect hot carrier material, is equal to the energy absorbed. Therefore, for an ideal hot carrier cell,

$$qV_{oc} = (s_n + s_p)T_h \left(1 - \frac{T_o}{T_h}\right) = Q \left(1 - \frac{T_o}{T_h}\right). \quad (6)$$

Hence, the voltage efficiency is equal to

$$\eta_V = \frac{qV_{oc}}{Q} = \left(1 - \frac{T_o}{T_h}\right). \quad (7)$$

In other words, the hot carrier cell produces voltage with Carnot efficiency, avoiding thermalization losses. A similar idea to improve the generated voltage could be applied to thermoelectric converters.



**FIG. 2.** The efficiency of hot carrier solar cell as a function of the bandgap, at maximum concentration of sunlight (full lines) and at one sun illumination (dashed lines).

The power conversion efficiency that follows from Eq. (7) is shown in Fig. 2 as a function of the semiconductor bandgap, compared with the maximum efficiency attainable by a single-junction cell, as given by the Shockley–Queisser detailed balance.<sup>1</sup> In the absence of thermalization, the efficiency of hot carrier cells reaches a maximum 86.4% at zero bandgap, limited only by the reversible loss (6) and losses implied by finite-time thermodynamics to produce power rather than energy, and expressed by the fill factor.<sup>22</sup> Even for standard photovoltaic materials with bandgaps in the range 1–1.8 eV, the hot carrier cell efficiency exceeds the Shockley–Queisser limit by a factor of 1.4–1.9 under concentrated sunlight and by a factor of 1.5–2.2 under one sun illumination—a worthwhile goal to aim for.

This theoretical gain is mitigated by efficiency losses encountered in practice. In addition to challenges represented by the search for suitable hot carrier materials, there are standard optical and resistive losses, as well as losses by nonradiative recombination which are well researched in conventional solar cells. In addition, another loss should be taken into account: losses implied by photons transported to the solar cell by radiative transfer rather than heat transfer. As a result, near-equilibrium solar photons at temperature  $T_S \sim 6000$  K generate carriers with the same energy but away from equilibrium. An equilibrium at a different temperature  $T_h$  is reached via carrier–carrier scattering within less than some 100 fsec, faster than scattering with phonons.<sup>16</sup> This process, however, is irreversible and increases entropy, resulting in energy (and hence voltage) loss, although there is potential for reducing this loss by distributing excited carriers between several bands.<sup>12</sup>

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors has no conflicts to disclose.

## Author Contributions

**Tom Markvart:** Conceptualization (equal); Writing – original draft (equal).

## DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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