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# Theory of analyzing free energy losses in solar cells

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We make up the free energy balance for thermalized electrons and holes in a solar cell. Equations for the loss rates of free energy due to recombination and transport of carriers are derived. The well known expression for Joule heat dissipation also holds for the free energy loss by diffusive transport. All loss rates have units of mW/cm$^2$. Thus transport losses become directly comparable in magnitude to recombination losses. The latter are usually quantified in mA/cm$^2$ rather than mW/cm$^2$. The impact of various loss mechanisms on the power output of the cell, also in mW/cm$^2$, becomes directly apparent. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3006053]

Solar cells absorb solar radiation and produce electrical power. Electrical power is free of entropy and may therefore be considered as a rate of free energy $\dot{F}$ being provided by the solar cell. Numerical solutions of the semiconductor equations[1] are commonly used to optimize a cell design for maximum electrical power output $\dot{F}=J_Q U$, where $U$ is the terminal voltage and $J_Q$ is the terminal charge current, e.g., both taken at the maximum power point. In the analysis of these solutions, two often considered loss channels are carrier recombination and resistive losses. Recombination losses are commonly quantified as charge current densities $j_Q$ per cell area (mA/cm$^2$) while resistive losses are usually determined as dissipated resistive heat $\dot{f}_{\text{heat}}$ per cell area (mW/cm$^2$).[2,3] The relative impact of the two losses on cell efficiency is difficult to judge due to the different units.

Recombination currents that occur at positions in the cell where the splitting of the quasi-Fermi level is large dissipate more free energy than recombination currents of identical magnitude occurring at positions with little quasi-Fermi level splitting. Thus, simply multiplying the recombination currents by the terminal voltage $U$ is not appropriate. Instead, weighting the recombination current losses with the local quasi-Fermi level splitting transforms current losses into loss rates of free energy and makes transport losses and recombination losses directly comparable (both in mW/cm$^2$). In this paper we therefore introduce a free energy loss analysis (FELA), which makes the potential gain in output power by avoiding losses immediately apparent.

Textbook knowledge[4] of solar cells is the starting point for deriving our free-energy analysis. The free energy (or electrochemical potential) of electrons is identical to the quasi-Fermi level of electrons in the conduction band $E_{\text{FC}}$, while the free energy of holes (electrochemical potential of holes) equals the negative quasi-Fermi level of holes in the valance band $-E_{\text{FV}}$. The charge current density of electrons

$$\vec{j}_{Q,e} = q^{-1}\sigma_e \vec{\nabla} E_{\text{FC}} \tag{1}$$

and the charge current density of holes

$$\vec{j}_{Q,h} = q^{-1}\sigma_h \vec{\nabla} E_{\text{FV}} \tag{2}$$

both depend on the respective conductivities $\sigma_e$ and $\sigma_h$ with $q$ being the elementary charge. The current density of the free energy $F$ carried by negatively charged electrons through the electron contact is

$$\vec{j}_{F,e} = E_{\text{FC}}[\vec{j}_{Q,e}/(-q) - \vec{j}_{Q,h}/(+q)] = -E_{\text{FC}}(\vec{j}_{Q,e}+\vec{j}_{Q,h})/q, \tag{3}$$

and the current density of the free energy carried by positively charged holes through the hole contact is

$$\vec{j}_{F,h} = -E_{\text{FV}}[\vec{j}_{Q,h}/(+q) - \vec{j}_{Q,e}/(-q)] = -E_{\text{FV}}[\vec{j}_{Q,h}+\vec{j}_{Q,e}]/q. \tag{4}$$

The division by the elementary charge with the appropriate sign converts charge currents to particle currents. Nonzero minority carrier current densities in Eqs. (3) and (4) account for possible surface recombination at the contacts.

Figure 1 sketches the solar cell volume $V$ that has the boundary surface $\delta V$. The surface of volume $V$ consists of the electron contact $\delta V_e$ to an $n$-type semiconductor, the hole contact $\delta V_h$ to a $p$-type semiconductor, and the noncontacted surface $\delta V_{\text{nc}}$. The free energy extracted per time

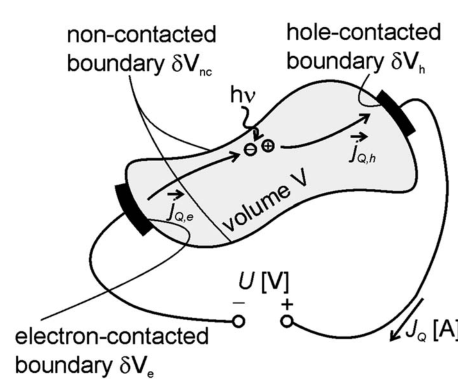


FIG. 1. A photon generates an electron-hole pair in a solar cell of volume $V$. Electrons and holes contribute to the electron and hole currents $\vec{j}_{Q,e}$ and $\vec{j}_{Q,h}$, respectively. Some of the generated charge carriers are extracted through the respective contacts. The boundary $\delta V$ of the cell volume $V$ consists of contacted and noncontacted regions.

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$$UJ_Q = \int_{\delta V_e} d\vec{A}\vec{j}_{F,e} + \int_{\delta V_h} d\vec{A}\vec{j}_{F,h} \tag{5}$$

is the free energy flux carried by electrons through the electron contact plus the one carried by holes through the hole contact. Here, $d\vec{A}$ is the differential area vector normal to a surface element of $\delta V$ and pointing outward. Inserting Eqs. (3) and (4) we find

$$UJ_Q = -q^{-1}\left[\int_{\delta V_e} d\vec{A}E_{\mathrm{FC}}\vec{j}_{Q,e} + \int_{\delta V_h} d\vec{A}E_{\mathrm{FV}}\vec{j}_{Q,h} + \int_{\delta V_e} d\vec{A}E_{\mathrm{FC}}\vec{j}_{Q,h} + \int_{\delta V_h} d\vec{A}E_{\mathrm{FV}}\vec{j}_{Q,e}\right]. \tag{6}$$

Extending the first two surface integrals to the full surface $\delta V$ gives the relation

$$\begin{aligned}UJ_Q = -q^{-1}\Bigg[&\int_{\delta V} d\vec{A}E_{\mathrm{FC}}\vec{j}_{Q,e} - \int_{\delta V_{\mathrm{nc}}} d\vec{A}E_{\mathrm{FC}}\vec{j}_{Q,e} \\ &- \int_{\delta V_h} d\vec{A}E_{\mathrm{FC}}\vec{j}_{Q,e} + \int_{\delta V} d\vec{A}E_{\mathrm{FV}}\vec{j}_{Q,h} \\ &- \int_{\delta V_{\mathrm{nc}}} d\vec{A}E_{\mathrm{FV}}\vec{j}_{Q,h} - \int_{\delta V_e} d\vec{A}E_{\mathrm{FV}}\vec{j}_{Q,h} \\ &+ \int_{\delta V_e} d\vec{A}E_{\mathrm{FC}}\vec{j}_{Q,h} + \int_{\delta V_h} d\vec{A}E_{\mathrm{FV}}\vec{j}_{Q,e}\Bigg].\end{aligned} \tag{7}$$

At the noncontacted surface the total current vanishes. Thus $\vec{j}_{Q,e}+\vec{j}_{Q,h}=0$. Using this relation and sorting the terms in Eq. (7) we find

$$UJ_Q + \dot{F}_s = -q^{-1}\int_{\delta V} d\vec{A}(E_{\mathrm{FC}}\vec{j}_{Q,e} + E_{\mathrm{FV}}\vec{j}_{Q,h}), \tag{8}$$

where

$$\dot{F}_s = \int_{\delta V_{\mathrm{nc}}} d\vec{A}(E_{\mathrm{FC}} - E_{\mathrm{FV}})\vec{j}_{Q,h}/(+q) + \int_{\delta V_e} d\vec{A}(E_{\mathrm{FC}} - E_{\mathrm{FV}})\vec{j}_{Q,h}/(+q) + \int_{\delta V_h} d\vec{A}(E_{\mathrm{FC}} - E_{\mathrm{FV}})\vec{j}_{Q,e}/(-q) \tag{9}$$

has the meaning of the free energy loss rate due to recombination (i) at the surface of the noncontacted regions, (ii) at the electron contact, and (iii) at the hole contact, respectively. Using Eq. (8) and Gauss theorem we convert

$$UJ_Q + \dot{F}_s = -q^{-1}\int_V dV\vec{\nabla}(E_{\mathrm{FC}}\vec{j}_{Q,e} + E_{\mathrm{FV}}\vec{j}_{Q,h}) \tag{10}$$

to a volume integral. Application of the product rule yields

$$UJ_Q + \dot{F}_s = -q^{-1}\int_V dV(\vec{\nabla}E_{\mathrm{FC}}\vec{j}_{Q,e} + E_{\mathrm{FC}}\vec{\nabla}\vec{j}_{Q,e} + \vec{\nabla}E_{\mathrm{FV}}\vec{j}_{Q,h} + E_{\mathrm{FV}}\vec{\nabla}\vec{j}_{Q,h}), \tag{11}$$

where the divergence of the charge current densities

$$\vec{\nabla}\vec{j}_{Q,e} = -q(g-r), \tag{12}$$

$$\vec{\nabla}\vec{j}_{Q,h} = +q(g-r) \tag{13}$$

are given by the local carrier generation rate $g$ and the local carrier recombination rate $r$.[4] We thus find

$$UJ_Q + \dot{F}_s = \int_V dV[(E_{\mathrm{FC}} - E_{\mathrm{FV}})(g-r) - q^{-1}\vec{\nabla}E_{\mathrm{FC}}\vec{j}_{Q,e} - q^{-1}\vec{\nabla}E_{\mathrm{FV}}\vec{j}_{Q,h}]. \tag{14}$$

Let $A$ be the cell area (projection of the volume $V$ in the direction of the sun) and $j_Q=J_Q/A$ and $\dot{f}_s=\dot{F}_s/A$. Using Eqs. (1) and (2) for replacing the gradients of the quasi-Fermi levels yields the extracted free energy density rate

$$Uj_Q = \dot{f}_g - \dot{f}_r - \dot{f}_{t,e} - \dot{f}_{t,h} - \dot{f}_s, \tag{15}$$

where the photogeneration rate of the free energy density is

$$\dot{f}_g = A^{-1}\int_V dV(E_{\mathrm{FC}} - E_{\mathrm{FV}})g, \tag{16}$$

the free energy density dissipation rate by recombination is

$$\dot{f}_r = A^{-1}\int_V dV(E_{\mathrm{FC}} - E_{\mathrm{FV}})r, \tag{17}$$

the free energy density dissipation rate by transporting electrons is

$$\dot{f}_{t,e} = A^{-1}\int_V dV|\vec{j}_{Q,e}|^2/\sigma_e, \tag{18}$$

and finally the free energy density dissipation rate by transporting holes is

$$\dot{f}_{t,h} = A^{-1}\int_V dV|\vec{j}_{Q,h}|^2/\sigma_h. \tag{19}$$

Equations (18) and (19) are the expressions to be expected for resistive heating. However Eqs. (18) and (19) cause a loss $\dot{f}_t>0$ even if the electric field vanishes and the current is driven by diffusion only. This is the case for minority carriers at low-level injection in a homogeneously doped semiconductor. Currents driven by a gradient of the electrostatic potential (drift), by a gradient of the chemical potential (diffusion), or by a mixture of both all cause a free energy loss expressed via the same Eqs. (18) and (19).

The physical origin for the dissipation of free energy by diffusion is less intuitive than for resistive heating. Carriers diffuse from positions of high to positions of low concentration. A high carrier concentration corresponds to a small amount of entropy per particle. When diffusing, the carriers increase their entropy and thus reduce the entropy-free part of their total energy. This explains the dissipation of free energy by diffusion.

Please note that the free energy loss rates by transport as expressed in Eqs. (18) and (19), respectively, may easily be split in losses that originate from transport into orthogonal direction by using $|\vec{j}_{Q,h}|^2=|\vec{j}_{Q,h,\perp}|^2+|\vec{j}_{Q,h,\parallel}|^2$. A directional decomposition enables quantifying the relative significance of current sinks at different positions.

We now briefly sketch a first application of the FELA. Here, the purpose is to understand fill factor (FF) losses in emitter wrap through (EWT) cells. FF reductions can occur if the electrical resistance $R_{via}$ of the vias that connect the front side emitter and the rear side emitter is large. We simulate an EWT cell in two dimensions (base is $p$-type and of resistivity 0.77 $\Omega$ cm, contact periodicity 1600 $\mu$m, thickness 200 $\mu$m, lifetime 20 $\mu$s, emitter saturation current density 400 fA/cm$^2$, emitter sheet resistance 40 $\Omega/\square$, 50% emitter coverage on the rear side, no surface recombination, photogeneration 41.5 mA/cm$^2$) at various values for sheet resistance $R_{via}$. The simulated FF is 82% at $R_{via}=0$, drops to a minimum value of FF=55% at $R_{via}=10^4$ $\Omega/\square$, and increases again to FF$>$80% for $R_{via}>10^6$ $\Omega/\square$. For $R_{via}=10^4$ $\Omega/\square$ the FELA determines an enhancement of the sum of all free energy transport losses by 1 mW/cm$^2$, while the sum of all free energy losses by recombination increases by 8 mW/cm$^2$ when both are compared with the case of $R_{via}=0$ and when both are taken at the respective maximum power points. This proves what has been argued before:[5] the power loss that accompanies the FF reduction is not dominated by Joule heat dissipation in the resistive vias but is dominated by recombination losses. The high resistance of the vias forces the carriers to take an alternative route to the contacted rear side emitter: diffusion through the base. The carrier concentration gradient that drives this diffusion implies a carrier concentration enhancement in the front region relative to the rear region. Thus we have a current-dependent extra recombination in the front part of the cell that causes the FF loss.

In conclusion, equations for analyzing free energy losses in solar cells were derived. By integrating separately over various device regions, contributions of these regions to the total losses in the cell can be analyzed. In particular, transport losses due to Joule heating, due to diffusion, or a combination of both become directly comparable in magnitude to recombination losses. We also show that the well known expression for Joule heat dissipation also accounts for free energy losses of diffusive transport. We expect that the FELA introduced here will open new strategies for device optimization by numerical modeling.

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