Let us consider a monochromatic cell and calculate the irreversible entropy generation rate $\dot{S}_{\mathrm{irr}}$ in the whole device. With the aid of the general equation (4.44) and equation I-4 in Table 4.1, it is given by

$$T_a \dot{S}_{\mathrm{irr}}/\Delta\varepsilon = (\mu_x \dot{n}_x + \dot{\omega}_x) - (\mu \dot{n}_r + \dot{\omega}_r) - qV(m\dot{n}_x - m\dot{n}_r) \tag{4.71}$$

where the source of photons has been substituted by its equivalent room-temperature luminescent radiation characterised by the chemical potential μ_x and the ambient temperature T_a. The open-circuit conditions are achieved when $\mu_{\mathrm{OC}} = \mu_x$. For this value the entropy rate is zero since then $\dot{n}_x = \dot{n}_r$ and $\dot{\omega}_x = \dot{\omega}_r$.

Let us calculate the derivative of the irreversible entropy generation rate (equation 4.71) with respect to μ and particularise it for the open-circuit value of μ. Considering what follows V as only an unknown function of μ and independent of the way of obtaining the excitation (which is the case for infinite mobility) and using the fundamental relationship $\partial\dot{\omega}_r/\partial\mu = -\dot{n}_r$, the result is

$$\left[\frac{\mathrm{d}(T_a \dot{S}_{\mathrm{irr}}/\Delta\varepsilon)}{\mathrm{d}\mu}\right]_{\mu_{\mathrm{OC}}} = (qmV_{\mathrm{OC}} - \mu_{\mathrm{OC}})\left[\frac{\mathrm{d}\dot{n}_r}{\mathrm{d}\mu}\right]_{\mu_{\mathrm{OC}}} \tag{4.72}$$

This derivative is only zero if $qmV_{\mathrm{OC}} = \mu_{\mathrm{OC}}$. Since $\mu_{\mathrm{OC}} = \mu_x$ can take any value by changing the source adequately, we obtain the result $qmV = \mu$. Any other value would produce a negative rate of entropy generation in the vicinity of the open circuit, against the second law of thermodynamics. This is a demonstration, based on the second law of thermodynamics, of the relationship between the chemical potential of the photons and the voltage (or electron and hole quasi-Fermi level split).

If we could choose m freely, the maximum power is achieved if we can maximise the integrand of equation (4.70) for each value of the energy [43, 44]. Once this is done, the reduction in ε_g so that it tends towards zero increases the power output. For the limit of $\varepsilon_g \to 0$, the maximum efficiency is the same as in equation (4.53), where a stack of an infinite number of cells was studied. Here $qVm(\varepsilon)$ is the variable that plays the same role as $qV(\varepsilon)$ earlier, although here V is the same for all the terms. In consequence, the upper efficiency is the same as for the tandem cell stack, 86.8%.

The higher-than-one quantum efficiency behaviour has been actually found [45, 46], although very close to one, for visible photons of high-energy and UV photons. The effect is attributed to impact ionisation, a mechanism in which the electron or the hole created by the high-energy photon, instead of thermalising by scattering with phonons, by means of impact processes transfers its high energy to a valence-band electron that gets pumped into the conduction band. This mechanism has a detailed balance counterpart that is the Auger recombination, in which the energy recovered in the recombination is transferred to an electron or a hole, which thus acquires a high kinetic energy.

4.5.5 Hot Electron Solar Cells

Wurfel [47] has studied the impact ionisation cells from another perspective and has shown that they become identical to the hot carrier solar cells proposed by Ross and Nozik [48]