

The challenge of kinetic charge separation in nano solar cells

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In the long term nano-crystalline solar cells promise significant advantages with respect to cost efficient mass production. A clear advantage is that they are not based on imprinted chemical potential gradients for charge separation (e.g. electrical fields generated by p, n doping). In order to sustain such a potential gradient without simultaneously favouring a destructive chemical transport, the device structure has to provide a very stable and homogeneous crystal structures. This is an essential cost factor.

The most basic function of a solar cell is simply that of a membrane, which, during solar illumination, generates a directional electronic current. Such a device is subject to linear irreversible thermodynamic laws and will, in a stationary state, adjust to minimal entropy production, within the given system parameters. This law of minimal entropy production corresponds to the general principle of least action. It, for example, also adjusts energy distribution and energy losses to parallel and series connected resistors within Ohm's law. System parameters are size and position of resistances. Being an open system, a solar cell maintains, due to the absorption of solar energy and the generation of electric power and waste heat, entropy fluxes with the outside environment¹. What are the internal system parameters of solar cells?

The mechanism of entropy production provides clues for the optimisation of the power output from a basic point of view. The entropy production σ is the sum of products of thermodynamic forces and currents involved, both from transport (S_d) and from chemical reactions (S_{ch}):

$$\sigma = \sum_i I_i F_i = S_d + S_{ch} \quad (1)$$

I_i = thermodynamic flux, F_i = thermodynamic force, with

$$S_d = - \sum_i j_i \nabla \frac{\mu_i}{T} \quad (2)$$

j_i = current flux, $-\nabla \mu_i$ = thermodynamic potential gradient (e.g. voltage, concentration gradient) and

$$S_{ch} = \sum_i w_i \frac{A_i}{T} \quad (3)$$

w_i = reaction rate, A_i = chemical affinity = deviation from equilibrium

In order to modify minimum entropy losses so that a gain in useful energy output is achievable, thermodynamic forces or fluxes acting within the solar cell device have to be optimized for electric power which can be extracted from the system. This occurs either via chemical or electrical potential gradients, and additionally by favourable transport conditions in classical solar cells (via (2)). Where inbuilt thermodynamic forces ($\nabla \mu_i$) can not be sustained, such as in nano-structures, the chemical entropy production term (3) can be used to optimise the cell for electric power production. Mechanisms have to be implemented which allow the excited electron to run only into one preferred direction. Nano solar cells have mainly been developed by trial and error and rely on a kinetically determined directional separation of photo-induced

electronic charges (a role played by the I^-/I_3^- redox system in the dye solar cell, and by the fullerene in the polymer cell). For a simple charge separation reaction within a nano solar cell:



the chemical activity A in (3) yields

$$A = k_B T \log \frac{k_1 [R]}{k_2 [P^-]} \quad (5)$$

and the reaction rate w in (3)

$$w = k_1 [R] - k_2 [P^-] \quad (6)$$

By providing a reaction mechanisms, in which k_1 of the photoreaction is much larger than k_2 of the reverse reaction (such as with the fullerene in polymer solar cells) one increases both, w and A in (5) and (6), and thus the chemical entropy production term S_{ch} . By properly organizing molecules one can create directed currents. Within the total equation of entropy production for a solar cell one can thus manipulate the molecular and structural cell properties to obtain larger contributions of useful extractable power.

A basic theoretical understanding and knowledge for identifying suitable mechanisms for kinetic charge separation ($k_1 \gg k_2$ in (4)) is critical for the development of efficient and stable nano solar cells². At present the current rectifying elements in nano solar cells are also partially responsible for insufficient stability. New current rectifying elements have to be identified and understood. This is not easily achievable on the basis of the established Marcus theory of electron transfer. It is only applicable to weak interactions and completely neglects the effect of polarization of the molecular environment during electron transfer. But polarization and feedback on electron transfer within a non-linear electron transfer theory is a necessary precondition for generating directional electron transfer³.

The efficiency and stability problems of electrochemical and solid state dye solar cells are discussed. Also the lipid solar cell is addressed which pointed attention to the feasibility of a nano- surface conductivity solar cell.

Experimental progress is presented on the basis of two approaches:

- dye solar cells which just use a quasi-stable, atmosphere dependent surface electrolyte film on nano-particles for hole transport. It allows to maintain the chemical flexibility of wet solar cells (for charge rectification) while providing solid-state like properties and improved conditions for long term stability⁴
- photocurrent generation based on WS_2 nano-sheets in TiO_2 structures assisted by rectifying molecules. Cysteine and other Thiols are shown to be useful surface active molecules with appropriate rectifying electron transfer properties .

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