FLATBAND SOLAR CELLS: A MODEL FOR SOLID-STATE NANO-STRUCTURED SOLAR CELLS

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ABSTRACT

Nano-structured solar cells are too complex for standard modeling. Here, we decouple the effects at a nm-scale from those at a µm-scale. The 3D nano-porous geometry is simplified to a quasi-periodical nm-scale ordering of “unit cells” (a TiO$_2$ sphere and its p-semiconductor or dye/p-conductor shell). It is shown that, due to the periodical boundary conditions, such a unit cell is essentially field free; it is called here a “flatband cell”. The band-diagram, including possible discontinuities, the Fermi levels, carrier density and recombination (interface and bulk) of these flatband cells is given accurately by a back-of-the-envelope calculation, as confirmed by numerical simulation. The unit cells are connected in a 1-D electrical network, which also accounts for the transport effects in the porous TiO$_2$ network and for the contact effects at the electrodes. Results for solid-state nano-structured cells are presented.

1. INTRODUCTION

All-solid-state nano-structured solar cells [1] consist of a nano-porous network of (e.g.) TiO$_2$ spheres, each of them coated with an extremely thin $p$-type absorber (ETA), or with a molecular dye and a hole conductor. They were proposed as an alternative to the more classic Grätzel cells [2], where a dye-coated porous TiO$_2$ is immersed in a redox electrolyte. Dry, all solid-state nano-structured cells have projected advantages for cell and module manufacturability and stability, but presently perform less than wet cells. There are some indications in literature to explain this [3], but nevertheless there is common agreement that presently there is still a lack of basic understanding, which is hindering further development of these cells. The complicated 3-D geometry of nano-structured cells is unmanageable with standard modeling. Here, we decouple the effects at microscopic (nm) and macroscopic (µm) scale. To do so, the complicated 3-D nano-structured geometry is simplified to a quasi-periodical nano-scale ordering of an $n$- and a $p$-type (semi)conductor, forming a “unit cell”. These unit cells are connected in a 1-D electrical network, which also accounts for the transport effects in the porous TiO$_2$ network and for possible contact effects at the electrodes. The aim is to gain insight in the working mechanisms of these cells, specifically the built-up and limitations of the open-circuit voltage, and the influence of internal microscopic phenomena like recombination (bulk and interface) and band alignment.

2. MODELING THE MICROSCOPIC UNIT CELL

2.1 Periodic boundary conditions

We propose to simplify the geometry of a nano-structured cell as sketched in Fig. 1. In a Grätzel type cell, a well conducting electrolyte is almost perfectly contacting all individual TiO$_2$/dye grains. When the geometric ordering of the TiO$_2$ particulates is somewhat simplified [4], the structure of Fig. 1(a) is obtained. For a solid-state CdTe

![Figure 2: A periodic ordering of n-type TiO$_2$ and a p-type absorber (here CdTe). The charge density $\rho$, the electrical potential $\phi$ and the band diagram are sketched. A unit cell with periodic boundary conditions is indicated.](image-url)

Figure 1: Simplification of the geometry of a nano-structured solar cell into columns of grains. (a) each column is contacted: appropriate for a wet cell; (b) structure of a solid-state cell: at the dashed line there is a periodic ordering of TiO$_2$ / absorber.
Figure 3: SCAPS simulation of the electrostatic potential of a thin CdTe/TiO₂ nanolayered unit cell. Solid curve: \( V = 0 \); dashed curve: \( V = 0.4 \) V. To mimic the Neumann boundary condition \( \partial \phi / \partial x = 0 \) at the boundaries, specific values for the "contact work function" were used: \( \phi(TiO₂) = 4.6796 \) V and \( \phi(CdTe) = 4.6616 \) V (zero bias) or 5.0816 V (0.4 V bias) (see text).

cell, arrangement (b) is more appropriate, as the contact does not penetrate in the structure. Both the TiO₂ grains and the extremely thin absorber are forming an interconnected network; both networks are supposed to interpenetrate perfectly. The geometry is then simplified in the same way as in case (a). Along the dashed line, there is (in this simplification) a periodic, nm-scale ordering of n-type TiO₂ grains and their p-type absorber shell.

This is further simplified as in Fig. 2 (which is presented here for CdTe, but all concepts developed below are valid for any other ETA-absorber). Due to the periodicity of the structure, a unit cell can be defined between the dashed lines in Fig. 2. At these lines, Neumann-type boundary conditions apply for the electrostatic potential \( \phi \), i.e. \( \partial \phi / \partial x = 0 \). To our knowledge, all solar cell simulation tools available can only handle Dirichlet-type boundary conditions, where the electrostatic potential \( \phi \) and hence the conduction band edge \( E_C \) are imposed at the boundary, e.g. by specifying a contact work function. Simulation can be done with our software SCAPS [5] when appropriate fictitious values for both contact work functions \( \phi_{nm} \) and \( \phi_{nn} \) are introduced, which are chosen such that \( \partial \phi / \partial x = 0 \) at the boundaries. These \( \phi_{nm} \) and \( \phi_{nn} \) values have to be adapted manually at each bias voltage \( V \), which makes the numerical calculation quite laborious. In Fig. 3, a periodic unit cell consisting of 25 nm p-type CdTe and 25 nm intrinsic TiO₂ is simulated. The kink at \( x = 25 \) nm is caused by the large difference in dielectric constant between TiO₂ (\( \varepsilon = 40 \)) and CdTe (\( \varepsilon = 10 \)). The total band bending is seen to be only 2 mV, which can be totally neglected: a nano-scale periodic unit cell effectively behaves as a flat-band-cell. We note that the band bending is substantially lower with periodic boundary conditions than with contact-controlled boundary conditions used hitherto in the literature.

2.2 The flat-band solar cell

The fact that a periodic unit cell is essentially a flat-band cell, allows for a back-of-the-envelope model which is surprisingly accurate as confirmed by the much more cumbersome numerical simulation.

The recipe is outlined in Fig. 4. Conduction and valence band are flat, as well as both Fermi levels \( E_{Fp} \) and \( E_{Fp} \). A possible discontinuity in electron affinity \( \Delta \chi \) imposes the conduction band cliff. Here, we take \( \Delta \chi = \chi(TiO₂) - \chi(CdTe) = 0.4 \) eV. In the literature, values of \( \Delta \chi \) up to 0.7 eV were reported [6]. The separation between the Fermi levels equals the "applied voltage" over the cell. Now, only the position of one of the Fermi level remains to be determined, and this is done by expressing the charge neutrality condition for a unit cell in a periodic structure.

We will illustrate this in the most simple case that both layers are equally thick (\( d_p = d_n \)), and that the effective density of states is the same for both materials and for both carriers (thus, \( N_f(TiO₂) = N_f(CdTe) = N_f(TiO₂) = N_f(CdTe) \)). A more general formulation is not a problem, but it hardly doesn’t bring anything new.

In a pⁿ⁻ cell (Fig 4a, with \( N_f \gg N_A \)), holes in TiO₂ can be neglected, as well as electrons and holes in CdTe. The neutrality condition is then:

\[
N_A + n = N_D - n + p
\]

\[
N_A = N_D - p
\]

\[
E_C - E_{Fp\,TiO₂} = kT \ln \left( \frac{N_C}{N_D - N_A} \right)
\]

Finally, \( E_{Fp} \) is placed \( qV \) below \( E_{Fp} \). The CdTe grain is depleted, and the TiO₂ grain is neutralized by almost equal densities of donors and electrons. The charge is defined by the lowest of the two doping densities (thus here by \( N_A \)). At high forward bias \( V \), \( E_{Fp} \) approaches the valence band in CdTe, and holes can become important.

In a pⁿ cell (with \( N_f \gg N_A \); Fig. 4b is presented for almost intrinsic TiO₂), electrons in CdTe can be neglected, as well as electrons and holes in TiO₂. The neutrality condition now is leading to:

\[
N_A + n - p = N_D - n + p
\]

\[
N_A - p = 0
\]

\[
E_{Fp} - E_V = kT \ln \left( \frac{N_f}{N_A} \right)
\]

and \( E_{Fp} \) is placed \( qV \) above \( E_{Fp} \). Again the charge is related to the lowest of the two doping densities. At high
forward bias $V$, $E_{Fp}$ approaches the conduction band in TiO$_2$ (when $\Delta \xi > 0$), and electrons can become important. Since the periodic boundary conditions, together with the small thickness impose charge neutrality, the charge in both particles, and hence the potential drop over them is very small. A net charge of 2 $10^{15}$ cm$^{-2}$ over two 25 nm thick grains indeed results in an electrical potential drop $\Delta V < 2$ mV over one unit cell. This $\Delta V$ however has to be compared with the built-in voltage $V_{bi}$ (or diffusion voltage) in a thick planar diode. It should not be confused with a voltage drop $V$ which could be measured at the external contacts, which is related to the splitting of the quasi-Fermi levels: $qV = E_{Fp} - E_{Fp'}$.

Simulation shows that the rule of a thumb expressed in Eq. (1) and (2) also holds under illumination, but only for $E_{Fp}$ at the p-side and for $E_{Fn}$ at the n-side. The “minority carrier” Fermi levels ($E_{Fp}$ at the p-side and $E_{Fn}$ at the n-side) are determined by the illumination intensity.

2.3 Current in a flat-band solar cell

In dark, all carrier densities are easily obtained from the simple model. The dark current $J_0$ in our flat band solar cells is determined by recombination. Under low injection, all possible recombination mechanisms are proportional to the minority carrier density. Contact recombination is excluded, since in the periodic structure, there are no contacts to the unit cells. Bulk recombination can only be important in the lower $E_x$ material CdTe. The minority concentration in CdTe depends on the doping ratio of CdTe to TiO$_2$ in a p/n cell (Fig. 4a), $n_{minor} = \frac{n}{1 + n_{CdTe}}$, and in a p/n cell (Fig. 4b), $n_{minor} = \frac{n}{n_{CdTe}}$, at moderate bias voltage $V$. The dominant path for interface recombination is between the conduction band of TiO$_2$ and the valence band of CdTe, when $\Delta \xi > 0$ (the case shown in Fig. 4). In a p/n cell (Fig. 4a) the minority concentration at the interface is $n_{minor} = \frac{n}{n_{CdTe}}$, and in a p/n cell (Fig. 4b), $n_{minor} = \frac{n}{n_{TiO2}}$. In all cases, $n_{minor}$ varies exponentially with applied voltage $V$, and can easily be calculated from either (1) or (2). Hence recombination current follows from:

$$J_x = q \tau p n_{minor} \quad \text{or} \quad J_x = qS \tau S n_{minor}$$

where $\tau$ describes bulk recombination, and $S$ interface recombination.

It is not possible to verify this result (3) with a one dimensional device simulator, as in the real 1-D periodic structure of Fig. 2 there can be no current $J_x$ in the x-direction. In the simulation of one unit cell, a $J_x$ is possible when a hole selective contact to CdTe, and an electron selective contact to TiO$_2$ are applied; the minority recombination at both “contacts” is assumed to be zero. One-D SCAPS simulations were carried out, adapting manually $\phi_{n1}$ and $\phi_{p2}$ for each bias voltage and for each illumination in order to obtain $\phi_{p2} - \phi_{n1} = 0$ at the boundaries (see Section 2.1). They confirm (not shown) the gross features of the simple model described above: the dark characteristics have an exponential form, and the light I-V curve is a shift down of the dark curve. We realize however that a unit cell in our periodic structure cannot be purely one-dimensional, as the current has to be drawn away as a lateral current $J_y$.

We stress that the absence of an electrical field $E$ in a flatband unit cell does not render collection of light generated carriers impossible. It is well accepted and illustrated in literature that there are other driving forces (besides $E$) for the separation of generated e-h-pairs: the band edge discontinuities at the conduction band $\Delta E_c = \Delta \xi$ (favorable when it is positive, as in Fig. 4), and at the valence band $\Delta E_v = \Delta E_c + \Delta E_v$ (always favorable since TiO$_2$ is a wide band gap material), and the selectivity of the contacts [7,8,9]. In the remaining treatment, we will consider that all absorbed photons are collected as electrical current $J_x$ in our unit cells. Ideally (i.e. at $T = 0$) they should have a $V_{oc}$ corresponding to the CdTe bandgap $E_g$, or to the “interface bandgap” $E_{ci}$, $\Delta \xi > 0$, but that $T > 0$, the dark recombination current lowers $V_{oc}$ by an amount of $(kTq) \ln(\alpha/\xi_d)$ or $(kTq) \ln(Sa/\tau)$), obtained by inserting (3) in the equation for $V_{oc}$, $a$ being an appropriate constant. We will treat $V_{oc}$ as a parameter.

3. MODELING THE MACROSCOPIC SOLAR CELL

3.1 One-dimensional approach

In a real solid-state nano-structured solar cell, a 3-D network connects all TiO$_2$ spheres and makes electrical contact with one electrode. The p-absorber (or the dye/p-conductor) forms a complementary network which makes contact to the opposite electrode. To keep the model manageable, both networks are simplified to one dimension, see Fig. 5. Each diode in the row stands for a periodic unit cell as just described, the resistors for the percolation in the p-network (top), and in the TiO$_2$ network (bottom). Two contact diodes describe possible Schottky barriers at the electrodes. The cells are illuminated from one side, which implies that the unit cells generate less current and voltage as the light penetrates in the cell. Ideally, all generated currents are added to the total light current. The open circuit voltages however are not summed, they are rather averaged. This is an essential difference with classical solar cells. Constant resistors stand for transport by drift. Transport by space-charge limited currents needs appropriate I-V laws for the resistors (namely $I = V/d^2$ where $d$ is the length of a resistor). A resistor network is not appropriate to describe transport by diffusion.

3.2 Results

In our simulation, the I-V characteristics of a unit flatband cell are assumed to be purely exponential, and are somewhat arbitrarily characterized by $J_0 = 15 \text{ mA/cm}^2$ and $V_{oc} = 0.8 \text{ V}$ if all the light were absorbed in one unit cell, which is of course not realistic. The I-V characteristics of individual unit cells are scaled to account for the actual light input on each cell, which decreases as $\exp(-\alpha y)$ where $y$ is the distance to the plane of light incidence. The value of $\alpha$ to be used is an effective value, which can
account for possible optical pathway enhancement by e.g. scattering; this was however not considered here. The resistances of the two subnetworks add up to a total distributed series resistance. For the n-part (TiO$_2$) $R_{nA} = \rho_p dp/3$, where $\rho_p$ is the specific resistivity of the porous n-layer, $p$ its porosity, and $d$ the distance between the electrodes; the factor 1/3 is because the series resistance is distributed. Likewise, the p-part is characterized by $R_{pA}$. We concentrate on the influence of the absorption $\alpha$ and of the series resistances $R_{nA}$ and $R_{pA}$. In our numerical simulation, the cell thickness was divided in a few hundred slabs, thus a few hundred diodes in the network of Fig. 5. The slabs were chosen thinner at the side of the incident light. The actual number of slabs and their thickness distribution was chosen in dependence on the absorption coefficient $\alpha$, the cell thickness $d$ and the resistivities of both subnetworks.

![I-V curve](image)

**Figure 6:** Calculated $I$-$V$ curves. The case of no series resistance is compared with the case of $R_{n,A} = (R_n + R_p)A = 10 \Omega \cdot cm^2$, where $R_{n,A}$ is completely in the n-network or completely in the p-network, or equally deviated between both. In the first case, currents for 3 values of the absorption coefficient $\alpha$ are shown.

In Fig. 6, the $I$-$V$ curves without and with series resistance are compared. Even when $R_{n,0}$ = 0, $V_{nc}$ does not reach its ideal value of 0.8 V. That is because all cells in the stack of Fig. 5 are forced to the same voltage. The unit cells at the illuminated side are then below their own local $V_{nc}$, the cells in the bulk and at the rear end of the stack are above their local $V_{nc}$: at open circuit of the whole cell, current flows from the rear cells to the front cells, and energy is internally dissipated. This is an inherent disadvantage of the geometrical ordering of the cells under discussion. We see in Fig. 6 that resistance in the n-subnetwork improves $V_{nc}$. This is because cells deep in the stack, adversely contributing to $V_{nc}$, are effectively decoupled by a larger $R_p$; however the cells at the front are able to carry their generated hole current with no losses to the rear contact, because $R_p = 0$. This is also the reason why resistance in the p-subnetwork is detrimental: it decouples the most illuminated cells at the front from the rear contact.

This could be an explanation for the substantially poorer $V_{nc}$ behavior of “dry” or all solid-state cells compared to “wet” or Grätzel cells: the ion conduction in the electrolyte is better than the hole conduction in the ETA absorber or the solid-state p-conductor, and this is crucial for the cell performance, as we showed. Resistance in the n-TiO$_2$ network is not crucial, it can even be beneficial. We note that the role of the $p$ and $n$ subnetwork will be interchanged when we would illuminate the cell from the $p$-contact side.

Further calculations (not shown) were carried out to assess the efficiency enhancement $\Delta\eta$ resulting from the beneficial effect of resistance in the n-network. For the parameters used, the optical absorption should exceed 3 $10^{19} / \text{cm}^2$ to see any positive $\Delta\eta$ at all. The effect is modest, e.g. 1.5% (absolute) for a highly unrealistic $\omega = 10^9 / \text{cm}^2$ and $R_{nA} = 1 \text{k} \Omega \cdot \text{cm}$. However, the mere fact that a moderately poor conduction in the TiO$_2$ network does not completely destroy the cell performance, is a result in itself.

4. CONCLUSIONS

Due to the periodical boundary conditions, the “unit cell” is essentially a “flatband cell”. The band-diagram, including possible discontinuities, the charge density and recombination (interface and bulk) of these flatband cells is found accurately by a back-of-the-envelope calculation, as is confirmed by numerical simulation. A 1-D electrical network accounts for the transport effects in the porous TiO$_2$ and absorber networks. The open circuit voltage obtained from such a macroscopic assembly of microscopic (nanoscopic!) elementary cells is adversely affected by the non-homogeneous illumination which is inherent to a nanostructured cell. This negative influence on $V_{nc}$ can be limited by the resistance (if moderate) in the TiO$_2$ subnetwork. Resistance in the $p$-subnetwork, however, is detrimental for the cell performance. In this regard, electrolyte cells have an advantage over poorer conducting all solid-state cells.

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