

Reply to Comments on “Electronic Transport in Dye-Sensitized Nanoporous TiO₂ Solar Cells—Comparison of Electrolyte and Solid-State Devices”. On the Photovoltaic Action in pn-Junction and Dye-Sensitized Solar Cells

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The dye-sensitized solar cell (DSSC) is an important and promising member of the family of photovoltaic devices. In addition, this type of solar cell has turned into an interesting proving ground for our overall understanding of the photovoltaic action in solar cells. The recent interpretation^{1,2} of the exponential increase of the device capacitance with increasing negative voltage bias in terms of a diffusion capacitance like that encountered in pn-junction diodes³ has led to vivid reactions in terms of three comments by Gregg (comment 1), Bisquert (comment 2), and Augustynski (comment 3).

As will become clear in the following, the arguments given in all three comments are not wrong in themselves, but it is hard to understand how these arguments can oppose the conclusions drawn in refs 1 and 2. We rather believe that a great deal of the ongoing debate on what is called “the origin of the photovoltaic action in DSSC” originates from the lack of proper common terminology, i.e., we are experiencing a debate on words rather than on facts. We also believe that important progress in the ongoing debate could be made if all opponents would share a common understanding of the classical solid-state pn-junction solar cell.

Therefore, this reply recalls some basic knowledge about the most important example of such devices, i.e., the high-efficiency silicon solar cell.⁴ These devices consist of a p-type base with a typical thickness $d \approx 200\text{--}250\ \mu\text{m}$. The n-type $0.3\ \mu\text{m}$ thick emitter is obtained by in-diffusion of phosphorous. The width of the space charge region is several hundred nm, leaving more than 99% of the device thickness to the neutral base. Thus, the main part of the photovoltaic action takes place far away from the pn-junction or any electrical field. To obtain record-efficiency devices, much effort has been given to diminish the recombination velocity S at the surfaces of the base and the emitter by passivating these surfaces by a thermal oxide or by deposition of Si₃N₄.⁵ Electrical contacts are made only to small parts of those surfaces and recombination of minority carriers at those contacts is further minimized by applying an extra p⁺-doping to the point contacts at the rear surfaces and an extra n⁺-doping underneath the contact fingers at the front. Only these features assisted by advanced light-trapping schemes have enabled one to push the efficiency of silicon solar cells close to the theoretical limits of that material.

One consequence of surface passivation on silicon pn-junction solar cells is that the diffusion admittance Y of the base of such a device is given by³

$$Y = \frac{qn_i^2 D}{N_D L^* kT/q} \frac{SL^* \cosh(d/L^*) + D \sinh(d/L^*)}{SL^* \sinh(d/L^*) + D \cosh(d/L^*)} \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] \quad (1)$$

where q is the elementary charge, n_i is the intrinsic carrier density, D is the diffusion constant, N_D is the base doping density, kT/q is the thermal voltage, and V is applied voltage. The quantity L^* is the complex, frequency dependent diffusion length $L^* = D^{1/2}(1/\tau + i\omega)^{-1/2}$. Equation 1 has been extensively used to investigate the recombination in pn-junction solar cells.⁶ Upon transforming the complex admittance Y from eq 1 into an impedance $Z = Y^{-1}$, one might notice that in the limit $S \rightarrow 0$ we approach eq 2 from comment 2 and in the limit $S \rightarrow \infty$ eq 5. Thus, these expressions and those from ref 7 are just limiting cases of the well-established diffusion admittance³ expressed by eq 1.⁸ In view of the geometry of the DSSC, the assumption $S \rightarrow 0$ is as appropriate as it is for high-efficiency Si solar cells. We note further that we have used the same limit as ref 7 in our work under discussion¹ as well as in an earlier publication.⁹

Comment 3 also starts with a series of correct arguments, that are, however, not in contradiction to our results and interpretation. There is little doubt that current continuity as expressed in eqs 1–5 of comment 3 is valid under steady state conditions of the DSSC. However, current continuity is also valid in a pn-junction solar cell, and eqs 1–5 of comment 3 may equally apply to the current densities carried by electrons and holes in the base region of such a device. We just would need to replace the subscripts “sol” by “p” and “TiO₂” by “e” to obtain

$$-\frac{d}{dx}J_n = \frac{d}{dx}J_p = q(g - r) \quad (2)$$

where the difference between the generation rate g and the recombination rate r multiplied with the elementary charge corresponds to the transfer current I^* . It is, however, a property of the diffusion equation that the direction of the diffusion current

$$J_n = qD \frac{dn}{dx} \quad (3)$$

and hence of the gradient of the excess electron density n , likewise in the TiO₂ of the DSSC or the conduction band of the base of a pn-junction solar cell, *exclusively* depends on the boundary conditions. For example, the boundary condition under short circuit is $n = 0$ at the collecting junction (SnO₂:F/TiO₂ interface for the DSSC, edge of the space charge region of the pn-junction solar cell). This implies $J_n > 0$ and $dn/dx > 0$, in contrast to what is concluded in comment 3. For further reading on current continuity in the DSSC, we refer to different analytical^{10–12} and numerical^{13,14} models that are available in the literature.

Let us now come to the discussion of “the origin of the photovoltaic action in pn-junction solar cells”. Because of the thickness of the base region, the major part of the photocurrent in silicon solar cells is driven by diffusion, i.e., by a gradient $\nabla\mu$ of the chemical potential just as described in comment 1. As mentioned above, the direction of the net particle flow depends on the boundary conditions. This is why passivation of the surfaces plays such an important role in providing

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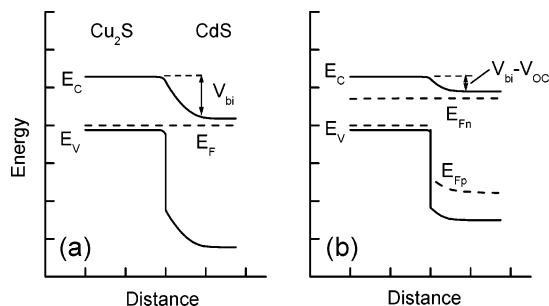


Figure 1. Schematic drawing of the band diagram of a CdS/Cu₂S heterojunction solar cell under equilibrium (a) and under open circuit conditions (b). The photovoltaic active part of the device is the Cu₂S absorber, whereas the built-in voltage V_{bi} is carried by the CdS window material. Charge separation occurs at the metallurgical interface between the two heterojunction partners, whereas the open circuit voltage V_{oc} is built up in the CdS window layer by diminishing V_{bi} (b).

nonrecombining boundary conditions, whereas the pn-junction should provide *perfectly collecting boundary conditions*. This brings us directly to the role of the pn-junction silicon and other solid-state solar cells. This role is quite different under different operating conditions of the solar cell:

(i) *Under short circuit conditions*, the junction serves for charge separation, i.e., provides the “collecting” boundary condition for the diffusion of the respective minority carriers from either side, i.e., the junction cares for the short circuit current J_{SC} . In terms of eq 1 in comment 1, an ideally *collecting* junction under short circuit conditions warrants that the chemical potential of minority carriers at the location $\mathbf{r} = \mathbf{r}_{jct}$ equals that in equilibrium, i.e., $\mu_{SC}(\mathbf{r}_{jct}) = \mu_{eq}(\mathbf{r}_{jct})$. We note that a junction built-in field is *not* mandatory to achieve charge separation under short circuit conditions. The physical property that is sufficient for charge separation might be denoted as the *selectivity*¹⁵ of the contacts; that is, the perfect “junction” contact is transparent for minority carriers and reflects majority carriers, whereas the “ohmic” contact is transparent for majority carriers and reflects minority carriers.

(ii) *Under open circuit conditions*, the junction (at least that of a pn-junction solar cell) is the place where the externally measured voltage, i.e., the open circuit voltage V_{OC} , is created. In terms of eq 1 in comment 1, an ideally *rectifying* junction warrants that the electrostatic potential ψ is given by $\psi = \psi_{eq}$ on one side and $\psi = \psi_{eq} - V_{OC}$ on the other side of the junction. Basically, the role of the junction as the “capacitive element”¹⁶ of the junction, i.e., as the location for building up the photovoltage in accordance with Maxwell’s equations, is *not identical* to the role as one of the selective contacts under short circuit conditions.

An instructive look at the historical example of CdS/CuS heterojunction solar cells¹⁷ tells us that both purposes (i) and (ii) of the junction can be fulfilled even by different parts of the junction. As is schematically shown in Figure 1a, the Cu₂S part with the lower band gap energy is the photovoltaic absorber material, the metallurgical interface between the two heterojunction partners provides the collecting boundary condition for the photogenerated charge carriers. However, as sketched in Figure 1b, the photovoltage is built up in the CdS part of the junctions space charge region because, in these solar cells, the doping of the Cu₂S absorber is much higher than that of the CdS window layer. Thus, the collecting and the electrostatic action of this heterojunction takes place at two well distinguishable locations.

Another interesting and, possibly, the most instructive example for the nontrivial interaction between charge carrier

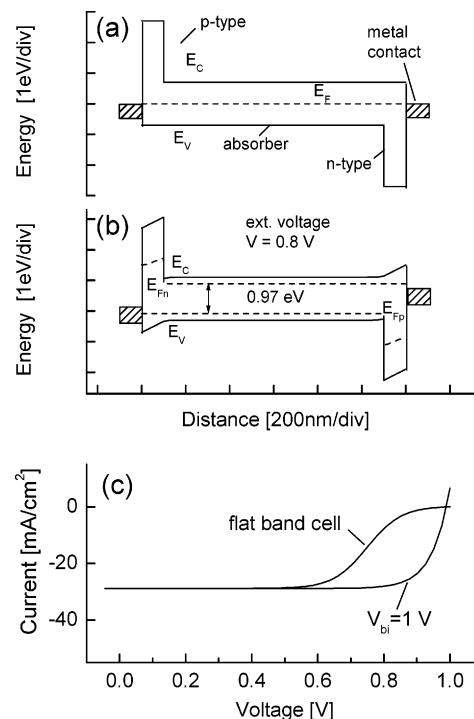


Figure 2. Band diagram of Wurfel’s flat band solar cell¹⁵ under equilibrium (a) and under illumination at bias voltage $V = 0.8$ V (b). The split of the Fermi levels E_{Fn} , E_{Fp} in the bulk of small gap absorber material is 0.97 eV, i.e., larger than the voltage $V = 0.8$ V available at the metallic contacts. The corresponding voltage loss is reflected in the poor fill factor $FF = 0.58$ of the current-voltage characteristics (c). A solar cell that has a built-in voltage of $V_{bi} = 1$ V but otherwise identical parameters achieves $FF = 0.80$.

kinetics (that is influenced by the selectivity of the contacts) and the electrostatic properties of the solar cell (that depends on the capacitive properties of the device) is given by Wurfel’s flat band solar cell.¹⁵ Figure 2a shows the equilibrium band diagram of such a solar cell that is built up by an undoped semiconductor layer that acts as the photovoltaic absorber. Selective contacts to the left and to the right are achieved by two thin layers of higher band gap semiconductors. The electron contact at the left possesses a high valence band offset ΔE_V^{left} and a zero conduction band offset ΔE_C^{left} , whereas the hole contact at the right has a nonzero conduction band offset ΔE_C^{right} and a zero valence band offset ΔE_V^{right} . To achieve a perfect flat-band situation under thermodynamic equilibrium, i.e., equal work functions for all materials, the hole and the electron contact material have to be slightly p-type and n-type, respectively.¹⁵ The device is completed with two metal contacts having work functions equal to those of the semiconductors. The band diagram in Figure 2, parts a and b, is obtained by implementing the structure into a numerical device simulator.^{18,19}

Figure 2b yields the band diagram of the flat band solar cell that results from illuminating the solar cell and, simultaneously, applying a bias voltage of 0.8 V. Two features are important in the band diagram of Figure 2b. First, we see that the applied voltage drops to about equal shares across the two high band gap semiconductors that were initially thought only to provide the selectivity for charge separation. Thus, even without predefinition by a built-in voltage of a junction, there is at least one, in the present case yet two, capacitive elements in any solar cell. Second, we see that the split of the quasi Fermi levels E_{Fn} and E_{Fp} in the low gap absorber of the device is about 0.97 eV, i.e., much higher than the voltage $V = 0.8$ V available at the metal contacts. Because we have chosen a high mobility μ

of $\mu = 5 \times 10^3 \text{ cm}^2/\text{Vs}$ for electrons and holes in all semiconductors, the quasi-Fermi levels are flat through all semiconductor layers. Thus, transport forth and back in the system of the three semiconductors is not a problem. However, a loss occurs between the electrochemical potentials E_{Fn} and E_{Fp} in the semiconductor and the electrostatic potential of the respective metal contact. The sum of the losses across both metal/semiconductor contacts, summing up to about 0.17 eV, is due to the difficulty to extract charge carriers over the two metal–semiconductor interfaces, where thermionic emission provides a fundamental bottleneck.¹⁹

This drawback of a flat band solar cell becomes evident when comparing the calculated current/voltage characteristics of the flat band solar cell shown in Figure 2c with the one of a solar cell that has a built-in voltage V_{bi} of $V_{\text{bi}} = 1 \text{ V}$. The latter cell is derived from the flat band cell simply by decreasing the work function of the lhs metal contact by 0.5 eV and increasing that of the rhs contact by another 0.5 eV. With respect to the short circuit current density J_{SC} and open circuit voltage V_{OC} both cells behave in the same way. However, the fill factor of the flat band solar cell is degraded because of the restricted carrier collection under working conditions, whereas the solar cell with $V_{\text{bi}} = 1 \text{ V}$ has a fill factor $\text{FF} = 0.80$. The fill factor degradation of the flat band solar cell might be looked at as resulting from the conflict between the two tasks (i) carrier collection and (ii) building the photovoltage. These tasks are managed simultaneously in any bias condition by a pn-junction but apparently not by the flat band contacts. We note that similar fill factor degradations are found in ref 20 when simulating different types of flat band solar cells. Reference 20 distinguishes here between “organic” and “inorganic” solar cells dependent whether the primary photovoltaic action is the generation of excitons (“organic”) or pairs of free electrons and holes. However, both types of those simulated solar cells exhibit fill factors that are lower than the ideal ones.

Turning now back to the photovoltaic action in the DSSC, we see from the above discussion that, with the notable exception of pin-junctions, in all other solar cells, including silicon pn-junction cells and DSSCs, the generation of a nonequilibrium distribution of charge carriers occurs well outside of any field region, leaving diffusion as the only transport mechanism for carrier collection. The photogeneration of an electron in the TiO_2 with the help of the dye and the subsequent reduction of the dye by the electrolyte is, in fact, the primary photovoltaic action of the DSSC,²¹ i.e., the *engine* of the device.

In how far complete charge separation of electrons and I_3^- ions in a DSSC after electron injection into the TiO_2 and dye regeneration by the electrolyte is really accomplished is a gradual question. Certainly, a free electron and hole in a solid-state solar cell are already more “charge separated” than the electron and hole that are bound in an exciton.²⁰ However, free electrons and holes in a solid-state device, as well as electrons and ions in the DSSC, have still a finite recombination probability unless the corresponding charges are not fed into the external circuit. Note that the effective minority carrier lifetime τ_{eff} , a measure for that recombination probability, can amount up to 30 ms in properly passivated crystalline silicon.²² This lifetime is about 3 orders of magnitude larger than the “collection” time constant τ_{c} that is the average time that a minority carrier (with diffusion constant $D = 30 \text{ cm}^2/\text{s}$) needs to diffuse through the base region of thickness $d = 300 \mu\text{m}$ of such a solar cell. The effective lifetime τ_{eff} of an electron in the TiO_2 of the DSSC is between 10 ms and 1 s, dependent on

light and bias conditions²³ where this long lifetime is due to trapping processes in the TiO_2 ²⁴ that in turn also increase the collection time τ_{c} .²⁵ Because, the quantity that is important is *the ratio* $\tau_{\text{eff}}/\tau_{\text{c}}$, we see no fundamental difference between the photogenerated electron in the base of a pn-solar cell and that of an electron in the TiO_2 of a DSSC. There is no fundamental difference because two duties are not yet fulfilled at the stage of an electron/hole pair in the base region of a pn-junction solar cell nor at the stage of the electron being “charge separated” into the TiO_2 of the DSSC: (i) The charge carriers are not yet *definitely* separated and (ii) they not yet deliver any electrical power because the nonequilibrium electrochemical potentials are not yet translated into an electrical potential. Therefore, the $\text{SnO}_2/\text{F}/\text{TiO}_2$ interface of the DSSC plays a similar role in fulfilling these two tasks as does the junction region of a pn-junction solar cell, i.e., providing the *gear* and the *wheels* to the otherwise useless *engine*.

Note that we consider a built-in voltage as *neither* mandatory for charge separation under short circuit *nor* indispensable for producing a photovoltage under open circuit, *regardless* of whether we are dealing with inorganic or organic solid-state devices or with DSSCs. We therefore are unable to see any fundamental difference among all these devices. Nevertheless, when thinking of *any of these types of solar cells* in terms of *output power*, a nonexistent or insufficient built-in field that makes charge collection bias dependent and thereby degrades the power output of the solar cell is an unsatisfactory solution. This is the message that is mathematically expressed by our model in ref 1. We note that the features predicted by that model, namely fill factor degradation, occur in the DSSC when reducing the built-in field by choosing contact materials to the TiO_2 network with lower work functions than that of SnO_2/F ,²⁶ whereas J_{SC} and V_{OC} remain essentially unaffected by these changes.

Hence, one key question for DSSC is the location of the capacitive element that accommodates the photovoltage. As we have discussed in ref 1, there are two possibilities, the $\text{SnO}_2/\text{F}/\text{TiO}_2$ interface and the $\text{TiO}_2/\text{electrolyte}$ interface, both elements being related to a specific capacitance C_{ST} and C_{Te} , respectively. These elements are connected in series, and the smaller one of the two capacitances, i.e., C_{ST} of the $\text{SnO}_2/\text{F}/\text{TiO}_2$ interface will dominate.² However, under forward bias, the diffusion capacitance C_{d} connected in parallel to C_{ST} increases exponentially until, at a certain bias voltage, $1/(C_{\text{d}} + C_{\text{ST}}) > 1/C_{\text{Te}}$ and the device capacitance will approach C_{Te} . Thus, the observation of a diffusion capacitance^{1,2} is an important observation that definitely puts the primary capacitive element in the DSSC toward the $\text{SnO}_2/\text{F}/\text{TiO}_2$ interface.

It is interesting to notice that none of the three comments discusses our result on the solid-state device, i.e., the observation of the inductive behavior. We recall that, in pn-junctions, such a negative reactance is *always* expected under high-injection conditions, i.e., as soon as injected minority carriers modulate the number of majority carriers and therefore the series resistance of the device.²⁷ Therefore, inductive behavior, the bipolar equivalent of a diffusion admittance, is especially likely in low-doped base materials. In the DSSC, the charge concentration in the electrolyte, likewise the doping of the hole conductor in the solid-state DSSC, plays a role that is analogous to the base doping of pn-junction diodes. Hence, we would expect inductive behavior also in electrolyte based DSSCs if the concentration of ions is kept low. Figure 3 compares the low-frequency capacitance (measured at frequency $f = 50 \text{ mHz}$ and room temperature) of three DSSCs having three different

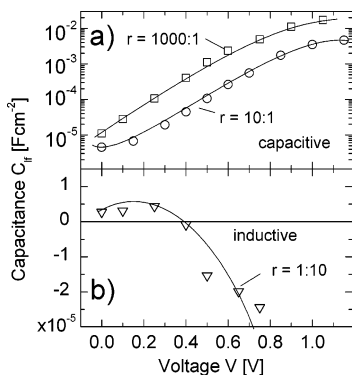


Figure 3. Measured voltage dependence of the low-frequency capacitance of DSSCs with a concentration ratio $[\text{LiI}]:[\text{I}_2]$ of $r = 1000:1$ and $10:1$ (a). In this case, application of forward bias voltage leads to an exponential increase of the capacitance until saturation is reached at a voltage of about $V = 1$ V. The device with a $\text{LiI}_2:\text{I}_2$ ratio $r = 1:10$ (b) exhibits inductive behavior at voltages $V > 0.4$ V. All capacitances are measured at a test frequency $f = 50$ mHz at room temperature.

ratios r between the LiI and the I_2 added to the electrolyte.²⁸ The capacitance/voltage curves in Figure 3a stem from DSSCs with $r = [\text{LiI}]:[\text{I}_2] = 5:0.005 \text{ M} = 1:1000$ and $r = 0.5:0.05 \text{ M} = 10:1$, respectively. Both devices exhibit an exponential increase of the capacitance with increasing forward bias with a saturation a voltage of about $V = 1$ V. In contrast, the device shown in Figure 3b has $r = [\text{LiI}]:[\text{I}_2] = 0.05:0.5 \text{ M} = 10:1$ and exhibits inductive behavior at $V > 0.4$ V, very similar to the solid-state DSSC reported in ref 1. This behavior results from the fact that in the latter device not enough Li^+ ions are present to counterbalance the charge of the injected electrons and electrostatic interaction modulates the ion concentration in the pores of the TiO_2 network. Because of the presence of three different charged species in the electrolyte and one in the TiO_2 , this action is certainly more complex than in the solid-state DSSC or in the base region of a pn-junction solar cell where we have only electrons and holes. The qualitative outcome, however, is as expected: Tuning the concentration of counter charges (Li^+ ions in the DSSC, majority carriers in the base of the pn-junction) allows one to turn a capacitive behavior into an inductive one. According to our opinion, this latter experiment is a rather convincing proof of the concept that over a wide range of voltages the junction capacitance of a DSSC is dominated by a diffusion capacitance (may it be in its capacitive or in its inductive version) in a very close analogy to what is observed in pn-junctions.

We note here that a recent investigation of the effective I_3^- diffusion constant in the nanoporous TiO_2 medium¹² finds that diffusion limitation in a DSSC with 0.05 M I_2 and 0.5 M LiI occurs at a limiting current density $J_{\text{lim}} = 60 \text{ mA cm}^{-2}$, hence, well above the short circuit current density of a DSSC. This is why we observe a diffusion capacitance and not an inductance in a standard DSSC. The transition to an inductive behavior is just expected when the screening of electrons in the TiO_2 by the ions in the electrolyte becomes insufficient.

In summary, there appears to be a series of features well-known from solid-state device physics that are about to be re-discovered in the frame of the DSSC. Some of these features are obviously common to *all* solar cells, because all solar cells are devices that translate a photogenerated nonequilibrium of charge carriers into electrical power. This does not imply that there were no important details in the DSSC that are unique to this type of device. Any progress in explaining these properties using a well-defined scientific terminology will have also a strong feedback on our overall understanding of photovoltaics.

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- (19) Though details of the numerical simulations are not important for the basic aspects discussed in this reply, we here give some information on the input parameters for the simulations. The absorber material in this simulation has a thickness of $1 \mu\text{m}$, a band gap energy $E_g = 1.4 \text{ eV}$, a carrier lifetime $\tau = 10 \mu\text{s}$, and effective densities of states in the conduction and valence band $N_{\text{CV}} = 10^{20} \text{ cm}^{-3}$. The absorption constant α corresponds to that of a direct semiconductor with $\alpha = 5 \times 10^4 \text{ cm eV}^{-1/2} (h\nu - E_g)^{1/2}$. The Fermi energy is in the middle of the absorber material, and therefore, the contact (Schottky) barrier Φ_b between the contact metals and the adjacent semiconductor layers is $\Phi_b = 0.7 \text{ eV}$ for the transition of electrons from the n-type layer to the metal contact as well as for the holes when leaving the p-type layer towards the metal. Note that, for symmetry reasons, only the choice of a lower band gap absorber material enables us to decrease the contact barrier because of $\Phi_b = E_g/2$. A flat band solar cell with an absorber band gap $E_g = 1.0 \text{ eV}$ would have negligible fill factor losses.
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- (25) We interpret the “time-scale” argument in comment 31 of ref 16 along the same lines: In the DSSC, we cannot afford an increase of the collection time τ_c by a factor of $\exp(0.8 \text{ V}/0.026 \text{ V}) \approx 0.23 \times 10^{14}$ without having serious losses of the output power. This argument, however, applies only as long as we are tempting to extract charge carriers from the device. Therefore, the argument is not valid under open circuit conditions because here $\tau_c = \infty$, by definition.
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