Reply to Comments on "Diffusion Impedance and Space Charge Capacitance in the Nanoporous Dye-Sensitized Electrochemical Solar Cell"

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Reply to Dr. Gregg's Comment. The first assumption in this comment is not correct where it is stated that we have treated the DSSC as a pn-junction. One just has to look at the boundary conditions, i.e., eq 5 in our paper. We like to give credit to Shockley's work because the physical effect is in essence identical but we have used appropriate boundary conditions for the DSSC and not for a pn-junction. The second statement in this comment is also incorrect where it is implied that a different physical result would emerge if one would carry out the calculations after introducing the definition of a chemical potential (compare the equation given in the comment). One can see this point easily by going back to the equations, e.g. in Shockley's papers, before the definition of a chemical potential is introduced. The physical content of the result is identical. The following physical argument in the comment where it is assumed that a macroscopic concentration gradient would be established in the DSSC by the primary separation of electrons and holes is also wrong. The fact is overlooked here that the colloidal network is 3-dimensional with random orientations of the vectors connecting an injected electron with a left-behind hole. Moreover, the injected electrons can be screened by the ionic environment because the diameters of the colloidal network are in the nm range. The final comment is also incorrect. The photogeneration of electron−hole pairs produces a shift in the quasi-Fermi levels. This effect is of course necessary but not sufficient for setting up a large photovoltage. Setting up a large photvoltage requires an effective separation of photogenerated electrons and holes across a macroscopic interface. For this, one needs either a dark potential, a band offset, or both to drive effectively charge separation against the increasing photovoltage. A large photovoltage can be generated in the case of a sufficiently slow recombination even in the absence of such a driving force at the interface, provided the interface is semi-permeable, i.e., only the electrons can cross the interface. The latter case has been investigated by Pichot and Gregg.[1] Their experiment did not address, however, efficient solar power conversion, and neither a high photocurrent nor a good fill factor were addressed. In contrast to the above case for achieving efficient solar power conversion, a sufficient driving force is mandatory at the interface.

Reply to Dr. Bisquert's Comment. This comment also appears to confuse the fact that we give credit to Shockley's work since he has treated in essence the physical effect of interest with the use of identical boundary conditions. It is sufficient to just take a look at eq 5 in our paper. Thus, we are a little puzzled by the lengthy explanation leading to the boundary conditions for the dye-sensitized electrochemical solar cell that we have already used (our eq 5). The following general statement is completely incorrect: A reflecting boundary condition (our eq 5) is not unique to DSSC. The literature on the available different types of solid-state solar cells shows several different realizations of a reflecting boundary condition for the minority carriers. For high efficiency cells, this is a standard feature.

Reply to Dr. Augustynski's Comment. We cannot recognize a physical model in this comment. It is true of course that a proper microscopic model should do a better job in principle with respect to understanding finer details than a diffusion model. This comment, however, does not offer a microscopic model. The latter requires massive numerical simulations, e.g., to obtain an average by calculating a sufficient number of all of the possible realizations of a random walker in the colloidal network where also the filling of traps and recombination reactions (with oxidized dyes and oxidized redox ions) have to be introduced. Efforts are currently being made in this direction, e.g., by Dr. Nelson's group at the Imperial College; however, it is not clear yet how much work is necessary to establish details for sure that show meaningful deviations from the predictions of a diffusion model. The main point of our paper is simply to elucidate the physical nature of the apparent huge capacitance that has been erroneously ascribed to the TiO_2 network turning into a metal under light exposure in the dye-sensitized electrochemical solar cell. The notion of metallic behavior for the TiO_2 network under forward bias or under light exposure is simply incorrect, and the essence of what is really going on in such an impedance measurement can be seen from our paper. One should be careful not to obscure the real issues when discussing the obvious shortcomings of the diffusion model. The basic physical results in this and our preceding paper on the dye-sensitized solar cell do not depend on finer details. Our first paper states that setting up an efficient photovoltage in the presence of recombination reactions requires a driving force for effective electron−hole separation against the increasing photovoltage. If the recombination is sufficiently slow the photovoltage can be set up, but for obtaining efficient solar power conversion, compare reply to Dr. Gregg's comment, one needs a driving force across the macroscopic interface, here the SnO_2:F/TiO_2 interface, i.e., a dark potential or a band offset or both. Our second paper shows that there is no transition to a metallic TiO_2 network in the DSSC, neither under light corresponding to one sun nor in the investigated range of the forward bias in the dark. The true capacitance has been measured and is shown in our paper. These are the issues that we have addressed, and we cannot identify any statement in the comment that is relevant to these issues.

References and Notes

(1) Pichot, F.; Gregg, B. A. *J. Phys. Chem. B* **2000,** *104,* 6−10.