

Comment on “Diffusion Impedance and Space Charge Capacitance in the Nanoporous Dye-Sensitized Electrochemical Solar Cell” and “Electronic Transport in Dye-Sensitized Nanoporous TiO₂ Solar Cells—Comparison of Electrolyte and Solid-State Devices”

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Two recent papers published in *The Journal of Physical Chemistry B*,^{1,2} represent a new contribution to the ongoing discussion regarding interpretation of the impedance characteristics of the dye-sensitized, liquid-junction photovoltaic (DSLJPV) cell using nanostructured titanium dioxide (NS TiO₂) photoanodes. From a perspective of improving the performance of the solar device, it is important to appreciate whether the resulting description of the transient behavior of the DSLJPV cell is relevant for the cell operation under practical, steady-state conditions.

In the early stage of investigation and development of the DSLJPV cell, it has been assumed that due to the small size (in the range of 10–20 nm) of individual TiO₂ particles, which are unable to withstand any significant electrical potential gradient, the electron transport across the NS TiO₂ film should be dominated by diffusion, driven by the electron concentration gradient.^{3,4} The “electron diffusion model” was largely used as the basis for interpretation of transient photocurrent^{4,5} and intensity-modulated photocurrent spectroscopic^{6–10} measurements, involving the DSLJPV cell, including the present studies,^{1,2} which were intended to elucidate the charge transport through the NS TiO₂ film. The role of the electrolyte filling the pores of the NS film was, in general, restricted to screening the electrons flowing across the network of TiO₂ particles.^{5,11–14} In this context, the whole system, which consists of the TiO₂ network and the electrolyte within the film, has been treated as a single effective medium.¹⁴ Another way to account for the effect of the electrolyte considers treating the electron diffusion through the NS TiO₂ film in terms of an ambipolar diffusion model.¹⁵

All of these approaches apparently overlook the real nature of the NS TiO₂ photoanode which is a typical three-dimensional electrode^{16,17} with a large porosity (ca. 60%) and a thickness (in the range of 10 μm) that is much larger than the sizes of the pores and of the individual particles. Like any other three-dimensional electrode, the NS TiO₂ electrode includes two coincidental (superposed) continua, i.e., an electronically conducting solid matrix (the network of interconnected TiO₂ nanoparticles) and an ionic conductor (the electrolyte filling the pores of the NS TiO₂ film). Bearing this in mind, let us examine the operation of a DSLJPV cell under steady-state conditions following the scheme represented in Figure 1.

In the space separating the platinum cathode from the NS TiO₂ photoanode, the current, flowing in the direction x perpendicular to the electrode surface, is carried by the ions of the electrolyte (typically Li⁺ and I[−]). Once it reaches the outer photoanode|electrolyte interface, the ionic current starts to be progressively converted, via the charge-transfer reaction, into

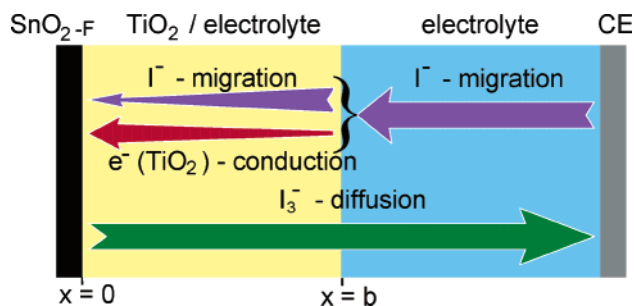


Figure 1. Schematic representation of the main ionic and electronic fluxes involved in the operation of the dye-sensitized liquid-junction photovoltaic cell under steady-state conditions.

the electronic current within the NS TiO₂ matrix. The latter process must, in any case, be completed close to the back contact at which the current is collected as an electronic current. Assuming that (i) there is an overall conservation of charge and no accumulation of charges within the NS TiO₂ photoanode and (ii) Ohm's law applies to both the solid and liquid phases, we can express the total current density, I , as the sum of I_{sol} , an ionic current density, and I_{TiO_2} , an electronic current density. Given condition (i), the sum $I_{\text{sol}} + I_{\text{TiO}_2}$ is independent of x (i.e., the distance from the back contact), whereas with increasing distance in depth of the NS TiO₂ photoanode, the current passes progressively from the electrolyte to the NS TiO₂ matrix. To summarize, we can write the total steady-state current density (referred to a projected cross sectional area of the electrode perpendicular to the axis x) as¹⁶

$$I = I_{\text{sol}} + I_{\text{TiO}_2}$$

and

$$\frac{dI_{\text{sol}}}{dx} + \frac{dI_{\text{TiO}_2}}{dx} = 0$$

where the boundary conditions are

$$I_{\text{TiO}_2} = 0 \quad \text{at } x = b$$

$$I_{\text{TiO}_2} = I \quad \text{at } x = 0$$

The charge-transfer current (formally, the current density gradient), I^* , associated in the present case with the photoelectrochemical reaction, is given by

$$-\frac{dI_{\text{sol}}}{dx} = \frac{dI_{\text{TiO}_2}}{dx} = I^*$$

The actual current distribution within a three-dimensional electrode will depend on a series of features including the effective conductivities (i.e., taking into account the average tortuosity of the film) of (i) the NS TiO₂ matrix and (ii) the electrolyte, and (iii) the kinetics of the charge-transfer reaction. In particular, an effective conductivity of the electrolyte that is much larger than that of the solid phase will lead to the increase of the charge-transfer current close to the back contact, whereas the opposite situation will impede the current penetration inside the three-dimensional structure.

Importantly, whatever the actual values of the above parameters, the electronic current will grow (and the ionic current

will decrease) going from the outer surface of the TiO₂ film toward the back contact as shown schematically in Figure 1. Such a situation is consistent with the electron concentration profile within the TiO₂ network growing toward the back contact, which is in obvious contradiction with the postulated electron transport by diffusion. In the absence of the driving force for electron diffusion, the flux of electrons toward the back contact may only occur by migration. This therefore implies the presence of the electrical potential gradient across the whole NS TiO₂ network. In parallel, there must also be a potential gradient within the electrolyte to drive the ionic component, I_{sol} , of the current. In the case of a conventional (in the absence of illumination) electrochemical process, the amount of the charge-transfer current, I^* , is a function of the potential difference between the solid phase and the electrolyte at any point x within the three-dimensional electrode.

For our present case of a three-dimensional photoanode, the charge-transfer current will also, obviously, (perhaps mainly) be affected by the number of incident photons absorbed by the dye sensitized film, i.e., this will depend on its absorption coefficient and the light intensity (a simplified approach here may consist of considering the amount of absorbed light as affecting the charge-transfer resistance through the photoanode). At first sight, this should result in an uneven current distribution across the NS TiO₂ electrode. Considering, for example, the DSLJPV cell illuminated from the side of the photoanode substrate, one can expect (in the absence of other correcting factors) the local value of the charge-transfer current being large close to the back contact, following the light absorption profile. This implies that a significant portion of the total current has to be carried out deep into the NS TiO₂ film by the ions of the electrolyte.

In this context, the absence of the supporting electrolyte from the solution constitutes an important advantage as the anion of the actual electrolyte, I^- , (which also acts as the redox species) is transported toward the reaction site by migration. One realizes immediately, in this regard, that both the nature of redox species reacting at the photoanode (anionic or cationic) as well as the transport numbers of the electrolyte ions will affect the current distribution within the three-dimensional NS TiO₂ electrode. Although the transport of I^- ions in depth of the TiO₂ film is not expected to lead to any significant diffusion limitation, this will no longer be the case of the oxidized component of the redox couple, I_3^- . In fact, as shown schematically in Figure 1, the I_3^- anions will have to diffuse toward the platinum cathode. The latter process appears clearly as the principal diffusion limitation in the DSLJPV cell.

The actual concentration profile of I_3^- anions within the NS TiO₂ photoanode will affect the cell operation in two ways. The larger the concentration gradient, the more rapid the transport

of the I_3^- ions toward the cathode will be. However, a large local concentration of the I_3^- ions will also favor the back (recombination) reaction, involving the triiodide and the TiO₂ electrons. This recombination process will also be affected by the electrical potential difference between the solid (the TiO₂ network) and liquid (the electrolyte) phases. Considering, the large driving force associated with the forward charge-transfer events, i.e., the electron injection from the adsorbed excited dye to the TiO₂ particles and the reaction of the oxidized dye molecule with iodide ions, it appears plausible that the local potential difference will primarily influence the net charge-transfer current through the backward processes.

As both the current and potential distribution within the NS TiO₂ photoanode may be expected to determine to a significant extent the performance of the DSLJPV device, there is a clear need to reexamine its operation from the above delineated perspective of an electrochemical cell. This should include, in particular, the effects of the variable film porosity and those of the conductivities of the electrolyte and of the TiO₂ network.

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