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Effect of non-uniform generation and inefficient collection of electrons on the dynamic photocurrent and photovoltage response of nanostructured photoelectrodes

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Title running head: Dynamic response of nanostructured photoelectrodes

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ABSTRACT

This paper investigates how non-uniform generation and inefficient collection of electrons influence the dynamic photocurrent and photovoltage response of nanostructured photoelectrodes. The standard diffusion model theory of small amplitude light intensity modulated photocurrent (IMPS) and photovoltage (IMVS) spectroscopy is refined and generalized to an arbitrary electron generation profile, allowing straightforward coupling to any optical model. Expressions are derived for the local electron concentration, and IMPS and IMVS transfer functions, for localized, uniform, and exponential generation profiles. Both limited collection and non-uniform generation of electrons modify the photoelectrode thickness (d) dependence of the characteristic IMPS and IMVS time constants and complicate their interpretation. This can lead to significant overestimation of the electron diffusion coefficient, diffusion length and collection efficiency when using common approximate relations. With near contact electron generation, the IMPS response exhibits two time-constants, only the slower one of which corresponds to electron transport across the film and scales with d . In the presence of this effect it is possible that in case of two equally thick samples, the one with smaller electron diffusion coefficient displays apparently faster electron transport. These errors demonstrated by experimental IMPS data of pressed TiO₂ photoelectrodes can be minimized by using modulated light incident from the counter electrode side, and avoided when analyzing the ratio of IMPS at opposite directions of illumination.

KEYWORDS: dye-sensitized, photovoltaic, light absorption, recombination, collection probability, Dirac's delta

1 Introduction

Electrochemical solar cells based on nanostructured photoelectrodes is a promising approach to cost-effective utilization of solar energy. The most well known device of this type is the dye solar cell (DSC)^{1,2}. In DSC, light absorption occurs by dye molecules attached on wide-band gap semiconductor nanoparticles that form a nanoporous film. Upon light absorption, an electron is injected from the dye to the semiconductor. It thereafter travels by diffusion in the nanoparticle network until it is collected at the substrate contact or is lost via recombination reactions. The oxidized dye is regenerated by a hole transport medium, typically a liquid redox electrolyte solution, that fills the pores of the film.

The capability of the cell to produce photocurrent is described by the incident-photon-to-collected-electron efficiency (η_{IPCE}), also known as the external quantum efficiency (EQE). It is defined as the number of electrons delivered by the solar cell to the external circuit per number of photons incident on the cell, and can be expressed as a product of the partial quantum efficiencies of light harvesting (η_{LH}), electron injection (η_{INJ}) and electron collection (η_{COL})

$$\eta_{\text{IPCE}} = \eta_{\text{LH}}\eta_{\text{INJ}}\eta_{\text{COL}} = \eta_{\text{LH}}\eta_{\text{APCE}} \quad (1)$$

where further division to an optical (η_{LH}) and electrical part is achieved by defining the absorbed-photon-to-collected-electron efficiency η_{APCE} .

While the best DSCs reach η_{IPCE} over 95 %³, the photocurrent of most practical solar cells is significantly lower than what would be expected based on their optical properties. It is therefore necessary to separate and quantify experimentally the injection and collection parts of eq 1 from DSCs under realistic working conditions. This problem was

recently addressed by combining η_{IPCE} measurements with optical characterization to estimate the steady-state η_{APCE} , and using the standard electron diffusion model⁴ to decouple its η_{INJ} and η_{COL} parts⁵.

Quantifying η_{COL} is of particular interest for optimizing flexible plastic DSCs that usually suffer from poor electron transport in their low-temperature-prepared photoelectrodes, but also for fundamental investigations of the transport phenomena in disordered nanostructured photoelectrodes. Instead of the direct steady-state approach⁵, the standard practice has been to estimate η_{COL} indirectly, using dynamic techniques such as intensity modulated photocurrent (IMPS)⁶ and photovoltage (IMVS)^{7,8} spectroscopy. Interpreting the IMPS and IMVS response by the time-dependent standard diffusion model⁹ yields estimates for the electron diffusion coefficient (D) and lifetime (τ), respectively, which allows further estimation of the electron diffusion length¹⁰

$$L = \sqrt{D\tau} \quad (2)$$

The diffusion length is one of the key parameters determining η_{COL} . To make a high performance cell, L needs to be larger than the photoelectrode film thickness: when L exceeds twice the film thickness, less than 10 % of electrons generated uniformly over the film are lost by recombination at the short circuit⁵. However, it was recently shown by theoretical arguments that IMPS and IMVS are unable to yield correct estimates for the steady state values of D and τ for nanostructured semiconductor photoelectrodes, since the dynamic response is dominated by filling and emptying of a large density of trap states distributed in energy in the semiconductor band gap¹¹. This challenges the reliability of using dynamic techniques to estimate L and η_{COL} relevant to the steady state

photovoltaic performance of DSC – a question that remains to be addressed experimentally.

Investigation of this problem could be feasible by comparing η_{COL} estimates determined by dynamic and steady state measurements in same conditions. The steady state approach is based on varying the photoelectrode film thickness (d), direction of illumination, and penetration depth of light, so that L falls within the examined d range, and thus, brings about measurable photocurrent losses due to electron recombination⁵. To compare with the dynamic techniques, the effects of these conditions on the IMPS and IMVS response needs to be well understood and quantified, and this is the main purpose of the present paper.

In practical IMPS experiments, weakly absorbed light is usually used for the intensity modulation to realize roughly uniform electron generation profile in the photoelectrode film^{12,13}. Alternatively, strongly absorbed light, incident from the counter electrode side, is used to generate electrons far from the substrate contact to measure their transit time across the film^{14,15}. In both cases, recombination losses at the short circuit condition are often neglected in the data analysis, and hence, η_{COL} is implicitly assumed, or rationalized by the data, to be close to 100%.

In the present paper, we generalize the standard diffusion model theory of light intensity modulated response of nanostructured photoelectrodes to readily comply with any (arbitrary) electron generation profile. We use the theory to investigate how non-uniform generation and limited collection of electrons affect the IMPS and IMVS characteristics. The aim is to establish a clear understanding of these effects, identify problems that they induce to practical data analysis, and point out ways to avoid them.

Although the analysis of this paper neglects many details of the electron transport and recombination dynamics in nanostructured photoelectrodes, such as electron trapping, the theoretical results, demonstrated by experiments, provide a necessary background for understanding and validating more detailed electron transport theories that build on the standard diffusion model.

2 Theory

2.1 Approximate IMPS and IMVS analysis

IMPS and IMVS are used to evaluate electron transport and recombination in DSCs in order to identify materials and methods that enhance their η_{COL} . The characteristic time constant of the IMVS response^{7,8}, τ_{IMVS} , is interpreted as the electron lifetime τ , and equals with the relaxation (RC) time-constant of photoelectrode film measurable by electrochemical impedance spectroscopy¹² or photovoltage decay¹⁶ at the same conditions. The characteristic IMPS time constant, τ_{IMPS} , for its part, is a measure of the mean arrival time of photogenerated electrons at the photoelectrode substrate contact, and is related to the electron diffusion coefficient by an approximate relation¹⁴

$$D \approx a \cdot \frac{d^2}{\tau_{\text{IMPS}}} \quad (3)$$

where d is the thickness of the photoelectrode film. The proportionality constant a depends on the electron generation profile. For example, for uniform generation $a \approx 0.393$, and for generation localized at the bulk electrolyte side of the film, $a \approx 0.428$ (values determined in the present work, cf.^{14,15}). Eq 3 is widely used in the analysis of IMPS data, but it is strictly speaking valid only when recombination can be neglected¹⁷.

For cells with limited η_{COL} , loss of electrons by recombination during their transport affects τ_{IMPS} , and hence the D estimate by eq 3. Consequently, most IMPS studies do not pursue quantitative estimation of L , but rather adhere to ranking different samples by the relative magnitude of their measured τ_{IMPS} and τ_{IMVS} .

Based on these time constants, the electron collection efficiency can be estimated roughly as^{12,18}

$$\eta_{\text{COL}} \approx 1 - \frac{\tau_{\text{IMPS}}}{\tau_{\text{IMVS}}} \quad (4)$$

but also this relation is accurate only for relatively high values of η_{COL} ¹⁸. Hence, neither eq 3 nor 4 are particularly suitable for accurate evaluation of dynamic electron transport and collection in practical DSCs that show limited η_{COL} , or for quantitative comparison to the steady state methods⁵ that work best when η_{COL} is low.

In this paper, we use the time-dependent standard diffusion model to investigate the failure of eqs 3 and 4 due to non-uniform electron generation and limited electron collection. We start by reviewing and slightly reformulating the diffusion model for IMPS and IMVS analysis, and summarize the analytical results for different electron generation profiles.

2.2 *Time-dependent standard diffusion model with small amplitude light intensity modulation*

The theoretical framework for the present work is the well established one-dimensional differential equation model for the electron generation, transport and recombination in a nanostructured semiconductor photoelectrode permeated with a redox electrolyte (called hereafter the diffusion model), summarized in Appendix A. We should emphasize that,

among other details of electron transport and recombination dynamics, this model explicitly neglects electron trapping that in reality can dominate experimental IMPS and IMVS response. However, it turns out to be necessary to generate thorough understanding of the characteristics of this simple model to support development and experimental verification of more complex models.

In IMPS and IMVS, the dynamic response of the cell to a small amplitude sinusoidal modulation of the incident light intensity is measured as a function of the angular modulation frequency ω . The incident photon flux Φ constitutes a monochromatic modulated (AC) part Φ_{AC} superimposed on a constant background (DC) part Φ_{DC}

$$\Phi(\omega, t) = \Phi_{DC} + \Phi_{AC}(\omega, t) = \Phi_{DC}(1 + \delta e^{i\omega t}) \quad (5)$$

where the modulation depth δ is typically set less than 0.1 to maintain linearity of the response.

As the incident light beam traverses the photoelectrode film its intensity is attenuated by light absorption, and hence the local absorption rate varies with position in the film. To treat this formally, we define the spatial light harvesting efficiency $f_{LH}(x)$, with units m^{-1} , as the probability per unit length that a photon incident on the cell is absorbed at the position x within the photoelectrode film, with $x = 0$ at the substrate contact. f_{LH} defines the light absorption profile and is related to the overall light harvesting efficiency η_{LH} as

$$\eta_{LH} = \int_0^d f_{LH}(x) dx \quad (6)$$

where d is the photoelectrode film thickness. By defining η_{LH} with respect to the photon flux incident externally on the photoactive area of the cell, f_{LH} includes all optical effects and losses relevant to the optical conditions in question.

The spatial electron generation rate is assumed equal to the spatial light absorption rate that scales linearly with the incident photon flux Φ ($\text{m}^{-2}\text{s}^{-1}$), multiplied by a position-independent electron injection efficiency,

$$g(x, t) = \eta_{\text{INJ}} \Phi(\omega, t) f_{\text{LH}}(x) \quad (7)$$

The spatial distribution of electron generation is thus defined by f_{LH} , whereas its time-dependence follows the light modulation.

2.3 IMPS transfer function

The IMPS transfer function (F_{IMPS}^*) has been defined earlier as the ratio of the harmonically modulated incident photon flux (excitation) and the resulting photocurrent density i_{AC} of the cell (response)

$$F_{\text{IMPS}}^*(\omega) = \frac{i_{\text{AC}}(\omega, t)}{q_e \Phi_{\text{AC}}(\omega, t)} = \frac{D}{\Phi_{\text{AC}}(\omega, t)} \cdot \frac{\partial n_{\text{e,AC}}(0, \omega, t)}{\partial x} = \frac{D}{\delta \Phi_{\text{DC}}} \cdot \frac{\partial N(0, \omega)}{\partial x} \quad (8)$$

where we have used eqs 5 and A5 and the Fick's law of diffusion (see Appendix A for notation). At the limit of small modulation amplitude at the steady state and short circuit condition, eq 8 is equal to the differential IPCE of the cell

$$\eta_{\text{IPCE,DIF}} = \frac{1}{q_e} \frac{\partial i_{\text{SC}}}{\partial \Phi_{\text{DC}}} = \eta_{\text{LH}} \eta_{\text{INJ}} \eta_{\text{COL,DIF}} \quad (9)$$

where i_{SC} is the steady state short circuit current density, $\eta_{\text{COL,DIF}}$ the differential electron collection efficiency, and q_e the elementary charge. In reality, the short circuit current of DSC may not be exactly linear with the incident light intensity^{5,10,19}, meaning that $\eta_{\text{IPCE,DIF}}$ varies with the intensity, and differs from the absolute η_{IPCE} that is defined instead as

$$\eta_{\text{IPCE}} = \frac{i_{\text{SC}}}{q_e \Phi_{\text{DC}}} = \eta_{\text{LH}} \eta_{\text{INJ}} \eta_{\text{COL}} \quad (10)$$

The light intensity dependence of $\eta_{\text{IPCE,DIF}}$ is considered to be solely due to $\eta_{\text{COL,DIF}}$, whereas η_{LH} and η_{INJ} can be normally assumed intensity independent. Eqs 9 and 10 imply that the quantum efficiency of electron generation $\eta_{\text{GEN}} = \eta_{\text{LH}} \eta_{\text{INJ}}$ acts as a frequency-independent scaling factor for the photocurrent output. Hence, instead of eq 8, it is useful to define the IMPS transfer function as the frequency dependent differential electron collection efficiency

$$F_{\text{IMPS}}(\omega) = \frac{F_{\text{IMPS}}^*(\omega)}{\eta_{\text{LH}} \eta_{\text{INJ}}} = \frac{D}{\delta \Phi_{\text{DC}} \eta_{\text{LH}} \eta_{\text{INJ}}} \cdot \frac{\partial N(0, \omega)}{\partial x} \quad (11)$$

that at the steady state short circuit condition equals the differential electron collection efficiency (cf. eq 9)

$$\eta_{\text{COL,DIF}} = F_{\text{IMPS}}(\omega \rightarrow 0, k_{\text{EXT}} \rightarrow \infty) \quad (12)$$

This IMPS definition (eq 11) is ideal for systematic analysis of the electron collection problem and will be used throughout the present paper.

2.4 IMVS transfer function

The IMVS transfer function (F_{IMVS}^*) relates the dynamic excitation of the incident photon flux to the AC photovoltage (V_{AC}) that is further related to the electron concentration at the substrate contact

$$F_{\text{IMVS}}^*(\omega) = \frac{V_{\text{AC}}(\omega, t)}{q_e \Phi_{\text{AC}}(\omega, t)} = \frac{n_{\text{e,AC}}(0, \omega, t)}{q_e \Phi_{\text{AC}}(\omega, t)} \cdot \left(\frac{\partial V}{\partial n_e} \bigg|_{x=0} \right) = \frac{N(0, \omega)}{\delta \Phi_{\text{DC}} C_e(0)} \quad (13)$$

by the differential (chemical) capacitance (per unit volume) of the photoelectrode, C_e

$$C_e = q_e \frac{\partial n_e}{\partial V} \quad (14)$$

In DSC, C_e is a specific property of the photoelectrode – electrolyte material system. It is also a function of the electron concentration^{12,20}, and hence, its value at the substrate contact, $C_e(0)$ depends on the operating conditions of the cell. Nevertheless, it does not affect the frequency dependence of eq 13, but only its magnitude. For the present theoretical investigations, it is therefore more practical to define the IMVS transfer function based on electron concentration at the contact

$$F_{\text{IMVS}}(\omega) = \frac{n_{e,\text{AC}}(0, \omega, t)}{\eta_{\text{LH}} \eta_{\text{INJ}} \Phi_{\text{AC}}(\omega, t)} = \frac{N(0, \omega)}{\delta \Phi_{\text{DC}} \eta_{\text{LH}} \eta_{\text{INJ}}} \quad (15)$$

where we also account for the quantum efficiency of electron generation in analogy with the IMPS definition (eq 11).

Finally, we point out that in the case of the kinetic boundary condition (eqs A2a, A7a), the IMPS and IMVS transfer functions are related in a particularly simple manner. Since the photocurrent and thus the IMPS transfer function are proportional to the electron concentration at the substrate contact (cf. eqs A7a and 11):

$$F_{\text{IMPS}}(\omega) = \frac{k_{\text{EXT}}}{\delta \Phi_{\text{DC}} \eta_{\text{LH}} \eta_{\text{INJ}}} N(0, \omega) \quad (16)$$

the transfer functions are related as

$$F_{\text{IMPS}}^*(\omega) = C_e(0) k_{\text{EXT}} F_{\text{IMVS}}^*(\omega) \quad (17)$$

$$F_{\text{IMPS}}(\omega) = k_{\text{EXT}} F_{\text{IMVS}}(\omega) \quad (18)$$

This means that if experimental conditions are arranged corresponding to a finite constant k_{EXT} , it makes no difference to the dynamic information whether one measures the IMPS or the IMVS response. In practice this can be realized simply by using an external

measure resistor in series with the cell, the current and voltage over which are naturally proportional to each other. Usually however, IMPS is measured at the short circuit and IMVS at the open circuit condition and this distinction will be adopted also here. Owing to the different value of k_{EXT} , the dynamic response is characteristically different in these cases.

2.5 Measurable IMPS and IMVS response

To simplify the present theoretical investigations, two factors affecting the experimentally measured IMPS and IMVS response are neglected.

Firstly, while the IMPS transfer function is defined here as a frequency-dependent collection efficiency (eq 11), experimental IMPS data is actually measured with respect to the photocurrent density (eq 8) and include therefore the quantum efficiency of electron generation, $\eta_{\text{GEN}} = \eta_{\text{LH}}\eta_{\text{INJ}}$, as an unknown factor (eq 9). This causes a scaling problem in the interpretation of the measured IMPS data, as discussed below. The scaling factor in the measured IMVS data is correspondingly $\eta_{\text{LH}}\eta_{\text{INJ}}/C_e(0)$ (cf. eqs 13 and 14).

Secondly, the measured IMPS response (but not IMVS) of the photoelectrode film is attenuated due to impedance of other cell components, an effect known as RC attenuation^{6,21,22}. The photocurrent signal measured in the external circuit ($F_{\text{IMPS,EXT}}^*$) is

$$F_{\text{IMPS,EXT}}^*(\omega) = F_A(\omega)F_{\text{IMPS}}^*(\omega) \quad (19)$$

where F_{IMPS}^* is the non-attenuated response given by eq (8) and F_A the attenuation factor that can be written generally as

$$F_A(\omega) = \frac{Z_p(\omega)}{Z_p(\omega) + Z_s(\omega)} \quad (20)$$

where Z_S and Z_P are the impedances connected respectively in series and parallel with the photoelectrode film. In practice, the main contribution to Z_S is the Ohmic series resistance R_S of the cell, whereas Z_P is given by the combined capacitance C_{PE} of the photoelectrode film and the substrate – electrolyte interface, the latter dominating close to short circuit condition. The RC attenuation may dominate the high-frequency end of the IMPS response^{6,21,23}, but can be accounted for by measuring F_A independently by impedance spectroscopy at the same conditions, and minimizing R_S and C_{PE} by cell design.

2.6 Solutions for different electron generation profiles

Having defined the theoretical framework we turn to the main topic of the paper, namely, theoretical analysis of the effect of the electron generation profile, film thickness and electron diffusion length on IMPS and IMVS response. To determine expressions for the IMPS and IMVS transfer functions (eqs 15 and 16), eq A6 needs to be solved for the AC part of the electron concentration, $N(x, \omega)$. We begin by considering an arbitrary spatially varying electron generation.

2.6.1 Arbitrary generation

Since eq A6 is a linear ordinary differential equation, it follows from the principle of superposition that the solution of eq A6 for any arbitrary generation term $G(x)$ (eq A4) can be obtained readily as

$$N(x) = \int_0^d f_{LH}(\xi) N_\delta(x, \xi) d\xi \quad (21)$$

where N_δ is the solution of eq A6 for a Dirac's δ -function generation, given by eq 23 below. The mathematical derivation of this result is provided as Supporting Information.

The result means that determining the local electron concentration profile, as well as the IMPS and IMVS transfer functions, for any $f_{\text{LH}}(x)$, is a task as easy as performing the integration in eq 21. For an $f_{\text{LH}}(x)$ not too complicated, as in all the cases of the present paper, this integration is straightforward analytically. More generally, one may find it sufficient and convenient to work with eq 21 numerically, irrespective of whether an analytical solution exists or not. Particularly useful this will be in cases where one is restricted to numerical $f_{\text{LH}}(x)$ data, e.g. from optical simulations.

In essence, eq 21 couples the standard diffusion model to any optical model describing spatial variation of photon flux in the photoelectrode film. In the following, we summarize briefly the analytical results for certain generation profiles of practical and theoretical interest, and discuss some limiting cases.

2.6.2 Localized generation

In the purely theoretical case of localized electron generation, the spatial light harvesting efficiency is

$$f_{\delta}(x, \xi) = \eta_{\text{LH}} \delta(x, \xi) \quad (22)$$

where $\delta(x, \xi)$ is the Dirac's delta function localized at $x = \xi$. The solution N_{δ} of eq A6 for the localized generation term (eqs A4 and 22) is

$$N_{\delta}(x, \xi) = \frac{\delta\Phi_{\text{DC}} \eta_{\text{LH}} \eta_{\text{INJ}}}{\gamma D} \left[\cosh(\gamma(d - \xi)) \frac{\gamma D \cosh(\gamma x) + k_{\text{EXT}} \sinh(\gamma x)}{\gamma D \sinh(\gamma d) + k_{\text{EXT}} \cosh(\gamma d)} - \sinh(\gamma(x - \xi)) u(x - \xi) \right] \quad (23)$$

where

$$\gamma = \sqrt{\frac{1}{D} \left(\frac{1}{\tau} + i\omega \right)} \quad (24)$$

and $u(x - \xi)$ is the unit step function. The mathematical derivation of eq 23 is given as Supporting Information.

IMPS

The IMPS transfer function at the short circuit becomes (eqs 16 and 23 with $k_{\text{EXT}} \rightarrow \infty$)

$$F_{\text{IMPS,SC},\delta} = \frac{\cosh(\gamma(d - \xi))}{\cosh(\gamma d)} \quad (25)$$

As the locus of generation approaches the collecting contact ($\xi = 0$) the IMPS response becomes unity, and the dynamic photocurrent response is pushed to high frequencies, whereas for localized generation at the electrolyte side of the film

$$F_{\text{IMPS,SC},\delta} = \frac{1}{\cosh(\gamma d)} \quad (\xi = d) \quad (26)$$

Eq 26 has a particularly useful interpretation. In the limit of steady state ($\omega \rightarrow 0$) it gives the (differential) spatial electron collection efficiency²⁴

$$\eta_{\text{COL,DIF},\delta}(\xi) = \frac{\cosh\left(\frac{d - \xi}{L}\right)}{\cosh\left(\frac{d}{L}\right)} \quad (27)$$

This is the probability at which electron injected to the film at $x = \xi$ will reach the collecting contact by diffusion before being lost by recombination. The overall collection efficiency of electrons generated in the film according to a profile $f_{\text{LH}}(x)$ is then nothing else but the weighted average of the spatial collection efficiency¹²

$$\eta_{\text{COL}} = \frac{\int_0^d f_{\text{LH}}(x) \eta_{\text{COL,DIF},\delta}(x) dx}{\int_0^d f_{\text{LH}}(x) dx} \quad (28)$$

This is a consequence of the fact that in our model, the electrons perform pure Fickian diffusion, i.e. their transport is independent of their local concentration.

It is worth mentioning that the spatial collection efficiency should be useful also for estimating the fraction of electrons lost by recombination in charge extraction experiments^{25,26}. In that case the generation profile in eq 28 is replaced by the electron concentration profile established in the film prior to the extraction step.

IMVS

The IMVS transfer function for the localized generation at the open circuit condition ($k_{\text{EXT}} \rightarrow 0$) is

$$F_{\text{IMVS, OC}, \delta} = \frac{\cosh(\gamma(d - \xi))}{\gamma D \sinh(\gamma d)} \quad (29)$$

In the special case of near-contact generation this reduces to

$$F_{\text{IMVS, OC}, \delta} = \frac{1}{\gamma D} \coth(\gamma d) \quad (\xi = 0) \quad (30)$$

and for the generation at the opposite end of the film to

$$F_{\text{IMVS, OC}, \delta} = \frac{1}{\gamma D \sinh(\gamma d)} \quad (\xi = d) \quad (31)$$

Interestingly, the IMVS response for δ -generation at the contact (eq 30) has exactly the same mathematical form as the general transmission line impedance describing transport and interfacial transfer of electrons in porous electrode films²⁷. Indeed, the diffusion model is equivalent to a transmission line model²⁸. The exact correspondence of eq 30 to impedance arises from the fact that in both cases, electron current is injected to the film at the same location where the potential is measured, i.e. at the contact. For the same reason, eq 31 does not correspond to impedance.

2.6.3 Uniform generation

In the case of uniform light absorption, the electron generation is constant over the photoelectrode film. If in this hypothetical case, we fix the light harvesting efficiency to η_{LH} , the spatial light harvesting efficiency becomes

$$f_{\text{UNI}}(x) = \frac{\eta_{\text{LH}}}{d} \quad (32)$$

and the modulated spatial electron concentration is

$$N_{\text{UNI}}(x) = \frac{\delta\Phi_{\text{DC}}\eta_{\text{INJ}}\eta_{\text{LH}}}{d\gamma^2 D} \left[\sinh(\gamma d) \frac{\gamma D \cosh(\gamma x) + k_{\text{EXT}} \sinh(\gamma x)}{\gamma D \sinh(\gamma d) + k_{\text{EXT}} \cosh(\gamma d)} - \cosh(\gamma x) + 1 \right] \quad (33)$$

IMPS

The short circuit IMPS transfer function for the uniform electron generation is then

$$F_{\text{IMPS,SC,UNI}} = \frac{1}{\gamma d} \tanh(\gamma d) \quad (34)$$

It is noteworthy that in the limit $L \gg d$, the IMPS response for the uniform generation (eq 34) becomes mathematically equivalent to the finite-length Warburg impedance of diffusion²⁹

$$F_{\text{IMPS,SC,UNI}} = \frac{1}{\sqrt{is}} \tanh(\sqrt{is}) \quad ; \quad s = \frac{\omega d^2}{D} \quad (L \gg d) \quad (35)$$

whereas in the limit $L \ll d$, it approaches the form of the Gerischer impedance

$$F_{\text{IMPS,SC,UNI}} = \frac{F_G}{\sqrt{1+i\omega\tau}} \quad ; \quad F_G = \frac{L}{d} \quad (L \ll d) \quad (36)$$

that is a good model for the impedance of a porous charge transfer electrode when $L \ll d$ ²⁷. This is of course no coincidence since as already mentioned, both the IMPS response and impedance follow from the same electron transport problem²⁸.

Note also that in the limit of poor electron collection ($L \ll d$), the steady state value of F_{IMPS} , i.e. the (differential) electron collection efficiency, is given by the ratio of the diffusion length to the film thickness (eq 36). In other words, the usual conception, that only those electrons that are generated within distance L from the contact will be collected, is a good approximation when (but only when) $L \ll d$.

IMVS

The open circuit IMVS transfer function for its part, becomes for the uniform generation

$$F_{\text{IMVS, OC, UNI}} = \frac{1}{dD\gamma^2} \quad (37)$$

that simplifies further to

$$F_{\text{IMVS, OC, UNI}} = \frac{1}{d} \cdot \left(\frac{1}{\tau} + i\omega \right)^{-1} \quad (38)$$

Eq 38 represents a perfect semicircle in the complex plane, characterized by a single time constant, the electron lifetime τ . This is understandable since for uniform generation and no collection (open circuit), the electron concentration remains always constant over the film and hence, electron diffusion does not play a role in the dynamic response.

2.6.4 Exponential generation

A more realistic model for the IMPS and IMVS response of DSC is obtained when the electron generation is assumed exponential corresponding to absorption of monochromatic light according to the Beer-Lambert law. Depending whether the modulated light is incident on the photoelectrode (PE) or counter electrode (CE) side, the spatial light harvesting efficiency is

$$f_{\text{PE}}(x) = T_{\text{TCO}}(1 - R_{\text{PE}})\alpha_{\text{D}}e^{-\alpha x} \quad (\text{PE side illumination}) \quad (39)$$

$$f_{\text{CE}}(x) = T_{\text{CE}}T_{\text{EL}}(1 - R_{\text{PE}})\alpha_{\text{D}}e^{\alpha(x-d)} \quad (\text{CE side illumination}) \quad (40)$$

where α_{D} and α are respectively the monochromatic light absorption coefficient of the dye and the total monochromatic absorption coefficient of the photoelectrode film, including e.g. light absorption by the triiodide ions in the electrolyte within the pores of the film. T_{TCO} , T_{CE} and T_{EL} are the transmittances of the photoelectrode substrate, the counter electrode and the bulk electrolyte layer, respectively, and R_{PE} is the reflectance of the photoelectrode film⁵.

Analytical integration of eq 21 for these exponential profiles yields results that are equivalent to those derived earlier⁶, with the difference that here, we explicitly include optical losses in the expressions. This being the case, it suffices only to briefly summarize the results according to our notation.

At the PE side illumination,

$$N_{\text{PE}}(x) = \frac{T_{\text{TCO}}(1 - R_{\text{PE}})\alpha_{\text{D}}\delta\Phi_{\text{DC}}\eta_{\text{INJ}}}{\gamma D(\gamma^2 - \alpha^2)} \left[\gamma(A_{\text{PE}}D - 1)\cosh(\gamma x) + (A_{\text{PE}}k_{\text{EXT}} + \alpha)\sinh(\gamma x) + \gamma e^{-\alpha x} \right] \quad (41)$$

where

$$A_{\text{PE}} = \frac{\gamma \sinh(\gamma d) - \alpha \cosh(\gamma d) + \alpha e^{-\alpha d}}{\gamma D \sinh(\gamma d) + k_{\text{EXT}} \cosh(\gamma d)} \quad (42)$$

and the electron concentration at the collecting contact is

$$N_{\text{PE}}(0) = \frac{T_{\text{TCO}}(1 - R_{\text{PE}})\alpha_{\text{D}}\delta\Phi_{\text{DC}}\eta_{\text{INJ}}}{\gamma^2 - \alpha^2} A_{\text{PE}} \quad (43)$$

The solution for the CE side illumination is obtained by replacing α with $-\alpha$ in eqs 41 and 42 and multiplying thereafter by $\exp(-\alpha d)$ (cf. eq 40):

$$N_{\text{CE}}(x) = \frac{T_{\text{CE}} T_{\text{EL}} (1 - R_{\text{PE}}) \alpha_{\text{D}} \delta \Phi_{\text{DC}} \eta_{\text{INJ}}}{\gamma D (\gamma^2 - \alpha^2)} \left[\gamma (A_{\text{CE}} D - 1) \cosh(\gamma x) + (A_{\text{CE}} k_{\text{EXT}} - \alpha) \sinh(\gamma x) + \gamma e^{\alpha x} \right] e^{-\alpha d} \quad (44)$$

where

$$A_{\text{CE}} = \frac{\gamma \sinh(\gamma d) + \alpha \cosh(\gamma d) - \alpha e^{\alpha d}}{\gamma D \sinh(\gamma d) + k_{\text{EXT}} \cosh(\gamma d)} \quad (45)$$

and the electron concentration at the contact is

$$N_{\text{CE}}(0) = \frac{T_{\text{CE}} T_{\text{EL}} (1 - R_{\text{PE}}) \alpha_{\text{D}} \delta \Phi_{\text{DC}} \eta_{\text{INJ}}}{\gamma^2 - \alpha^2} A_{\text{CE}} e^{-\alpha d} \quad (46)$$

IMPS

Noting that for the exponential generation profiles (eqs 39 and 40), η_{LH} is obtained from eq 6, the IMPS transfer functions for the PE and CE illumination are obtained by using eqs 43 and 46 in eq 16:

$$F_{\text{IMPS,PE}} = \frac{\alpha k_{\text{EXT}}}{(\gamma^2 - \alpha^2)(1 - e^{-\alpha d})} A_{\text{PE}} \quad (47)$$

$$F_{\text{IMPS,CE}} = \frac{\alpha k_{\text{EXT}}}{(\gamma^2 - \alpha^2)(1 - e^{-\alpha d})} A_{\text{CE}} e^{-\alpha d} \quad (48)$$

which at the short circuit ($k_{\text{EXT}} \rightarrow \infty$) reduces to

$$F_{\text{IMPS,SC,PE}} = \frac{\alpha^2}{(\gamma^2 - \alpha^2)(1 - e^{-\alpha d})} \cdot \left(\frac{\gamma}{\alpha} \tanh(\gamma d) + \frac{e^{-\alpha d}}{\cosh(\gamma d)} - 1 \right) \quad (49)$$

$$F_{\text{IMPS,SC,CE}} = \frac{\alpha^2 e^{-\alpha d}}{(\gamma^2 - \alpha^2)(1 - e^{-\alpha d})} \cdot \left(\frac{\gamma}{\alpha} \tanh(\gamma d) - \frac{e^{\alpha d}}{\cosh(\gamma d)} + 1 \right) \quad (50)$$

IMVS

The IMVS transfer function follows from the above IMPS expressions directly by eq 18. At the open circuit ($k_{\text{EXT}} \rightarrow 0$), the IMVS responses are therefore

$$F_{\text{IMVS, OC, PE}} = \frac{\alpha}{D(\gamma^2 - \alpha^2)(1 - e^{-\alpha d})} \cdot \left(1 - \frac{\alpha}{\gamma} \coth(\gamma d) + \frac{\alpha}{\gamma} \frac{e^{-\alpha d}}{\sinh(\gamma d)} \right) \quad (51)$$

$$F_{\text{IMVS, OC, CE}} = \frac{\alpha e^{-\alpha d}}{D(\gamma^2 - \alpha^2)(1 - e^{-\alpha d})} \cdot \left(1 + \frac{\alpha}{\gamma} \coth(\gamma d) - \frac{\alpha}{\gamma} \frac{e^{\alpha d}}{\sinh(\gamma d)} \right) \quad (52)$$

3 Results and discussion

Next we investigate in detail the characteristics of the IMPS and IMVS transfer functions with respect to variation of the photoelectrode film thickness, generation profile and diffusion length. This is done first qualitatively in terms of the characteristic shapes and trends in the IMPS and IMVS spectra, and thereafter quantitatively in terms of the characteristic time constants, τ_{IMPS} and τ_{IMVS} , and estimation of L and η_{COL} .

Unless otherwise stated, the following standard set of parameters is used throughout the paper: $d = 30 \text{ } \mu\text{m}$, $1/\alpha = 5 \text{ } \mu\text{m}$, $L = 10 \text{ } \mu\text{m}$, $\tau = 16 \text{ ms}$, i.e. $(2\pi\tau)^{-1} = 10 \text{ Hz}$, and $D = 6.25 \cdot 10^{-6} \text{ m}^2/\text{s}$.

3.1 Characteristics of the IMPS and IMVS spectra

3.1.1 Localized and uniform generation

The extreme cases of localized (δ -function) and uniform (flat) generation profiles (Figures 2 and 3) are ideal for illustrating the characteristics of the time-dependent diffusion model.

IMPS

The IMPS response is typically dominated by a single time constant that varies with the photoelectrode film thickness or locus of generation (Figure 2). However, the response is never a perfect semicircle in the complex plane, but exhibits marked frequency dispersion

that can be identified as a flattened arc (Figure 2a), spiraling to the origin (Figures 2a and 2b), or a 45° slope at the high frequencies (Figure 2c).

These effects can be understood by realizing that the IMPS spectrum is effectively a measure the number and arrival time of electrons reaching the collecting contact^{6,9,21}: The spiraling occurs at the frequency scale where the transport time of electrons from the point of generation to the contact is slow enough to cause a phase difference over 90° between the photocurrent and the light intensity signals. In the case of uniform generation, a distribution of mean arrival times corresponding to electrons generated at different distances from the contact, gives rise to the 45° slope in the complex plane plot.

According to our definition, the steady state limit of the IMPS response equals $\eta_{\text{COL,DIF}}$, and is hence always less than unity. Since in our example L is fixed to 10 μm , η_{COL} decreases due to recombination losses as the film thickness or the distance of generation increases from 1 μm to 28 μm (Figures 2a-c). For $d = 1 \mu\text{m}$, the uniform generation (Figure 2c) yields an IMPS response of the finite-length Warburg type (eq 35), whereas for $d = 28 \mu\text{m}$ the spectrum adopts the Gerischer form (eq 36). However, in practice these spectra have very similar shapes, the main differences being the characteristic frequency and the steady state limit of the real part. We will return to this important point later.

When $L \gg d$ (Supporting Information, Figure S3), $\eta_{\text{COL,DIF}} \approx 1$ (100 %), and hence the IMPS spectra for the uniform generation, and localized generation at the electrolyte side of the film, adopt a constant d -independent shape in the complex plane, and only the characteristic frequency is sensitive to d .

IMVS

The IMVS spectrum is always characterized by a single dominant time constant, but similar to IMPS, the response may spiral to the origin in the complex plane (Figures 3a and 3b). This occurs markedly in the case of δ -generation when $L < d$, and is associated with decrease of the low frequency limit and shift of the response to smaller frequencies, as d increases. These effects are due to the fact that when electrons are generated farther from the contact, a smaller fraction of them are able to *visit* the contact prior to their recombination, and the arrival time of those that make it, is delayed due to the longer distance.

The IMVS response with uniform generation is always a perfect semicircle in the complex plane, as evident from eq 38. Also when $L \gg d$ (Supporting Information, Figure S4), the IMVS response yields a perfect semicircle for all cases of spatial generation, and is characterized by a time constant equal to electron lifetime τ . This results from the fact that when $L \gg d$, diffusion is fast enough to distribute the electrons uniformly over the film thickness in a timescale much shorter than τ , irrespective of the generation profile.

Like IMPS, the IMVS response is thus governed by the time-dependent re-distribution of the non-uniformly generated electrons in the photoelectrode film by diffusion, and their detection at the contact³⁰.

3.1.2 Exponential generation

Exponential light absorption by Beer-Lambert law is a good approximation for a homogenous photoelectrode subject to negligible scattering and back-reflection of light, and has been the model of choice in practically all previous studies. The IMPS and IMVS responses are now weighted sums of the localized responses spanning over the film

thickness (Figures 2a and 3a), the weighting function being the exponential generation profile (eq 21).

Since the qualitative effects of d , L , and the generation profile (influenced now by α) on the IMPS and IMVS response have been discussed by others^{6,21}, we make here only one important remark on the IMPS response.

Appearance of two IMPS time-constants with PE illumination

An interesting feature of the IMPS response is that when the electron generation is biased towards the collecting contact, the IMPS response can exhibit two time-constants, as originally noticed by Cao et. al⁹. In Figure 4 we have fixed $1/\alpha = 5 \mu\text{m}$ and increase the film thickness gradually, while $L = 10 \mu\text{m}$ or $100 \mu\text{m}$. For the thinnest film with $d = 1 \mu\text{m}$, light is not attenuated much ($1/\alpha = 5 \mu\text{m}$) and $L \gg d$, and hence, the result is close to that of uniform generation with ideal electron collection, eq 35 (cf. Figures 4a and 4b vs 2c). As d increases, the generation profile becomes gradually more biased towards the contact. This causes the IMPS response to separate into a fast (high frequency) component ω_1 , and a slow (low-frequency) component ω_2 , that for $L = 100 \mu\text{m}$, are clearly distinguished in the spectrum as two separate arcs in the complex plane plot (Figures 4b) and as two peaks (time constants) in the imaginary part vs frequency plot (Figures 4f).

Since we are accustomed to analyze IMPS data in terms of a single time constant $\tau_{\text{IMPS}} = 1/\omega_{\text{IMPS}}$, we are led to ask, which of these two time constants is the correct one, i.e. related to the electron diffusion coefficient and film thickness by eq 3. It turns out that it is the slower component ω_2 : Note from Figure 4f that ω_1 is independent of d , whereas ω_2

moves to smaller frequencies with increasing d , i.e. it slows down, as would be expected by eq 3.

Cao et. al related the slower component to “buildup of the electron concentration gradient in the film to a steady-state value”⁹. This interpretation is unfortunate since both electron concentration and its gradient are irrelevant for electron transport by pure Fickian diffusion: concentration gradients and their dynamic evolution are merely a *consequence* of the distribution of the photogenerated electrons by Brownian motion and their extraction at the substrate contact.

The appearance of two time-constants can be explained instead by two distinct transport lengths. The faster component is related to electrons that diffuse directly to the contact and the slower component to those that find their way to the opposite direction and are reflected back at edge of the film (Figure 1). Consistently with this interpretation, the d dependence of ω_2 (Figure 4f) follows fairly well the characteristic IMPS frequency with the CE illumination (Figure 4h).

Two separate components are only rarely found in IMPS experiments^{9,15,23,31,32} and may be alternatively explained by RC attenuation^{6,22,23}. Unfortunately however, the presence of only one distinguishable τ_{IMPS} does not imply that it is unaffected by non-uniform generation. Comparison of Figures 4a and 4b shows that when $L < d$, the slow component ω_2 is attenuated due to recombination of electrons during their transport almost twice across the film, and in the limit $L \ll d$, the IMPS spectrum approaches the Gerischer shape characterized by only one apparent τ_{IMPS} . Comparing Figures 4e and 4f reveals that this time constant belongs to the fast component ω_1 , and hence, its

application in eq 3 for quantitative estimation of D leads to an error. This error will be quantified below.

IMVS

The IMVS spectra for the exponential generation are qualitatively similar to those of Figure 3 and are hence provided as Supporting Information (Figure S5). In all cases the spectra are dominated by a single time constant τ_{IMVS} , that yet, is somewhat affected by the non-uniform generation when $L < d$, as discussed below.

3.2 IMPS time constant and estimation of the electron diffusion coefficient

Figure 5 shows the effect of the photoelectrode film thickness on the IMPS and IMVS time constants for different cases of spatial generation when $L = 10 \text{ } \mu\text{m}$. The time-constants were extracted from calculated spectra as the reciprocal of the angular frequency corresponding to the minimum of the imaginary part.

The main feature is that the IMPS response is always slower with the CE illumination compared to the PE illumination, owing to the longer mean transport distance of collected electrons. For the same reason, this difference amplifies as the characteristic light penetration depth $1/\alpha$ decreases.

Two factors complicate the interpretation of τ_{IMPS} by eq 3 (Figure 5a). The first is that the d dependence of τ_{IMPS} follows eq 3 only when $d \ll L$; for thicker films, the dependence of τ_{IMPS} on d is much weaker than d^2 , and in the limit $d \gg L$, τ_{IMPS} becomes independent of d . The limiting value of τ_{IMPS} depends on $1/\alpha$ and L for the exponential generation profiles, while it is an L -independent constant, ca. 0.58τ , with the uniform generation (data not shown). This is due to electron recombination. The effective

transport distance is now determined roughly by L rather than d , which makes the transport appear faster than it really is. The second, and more dramatic effect, is the appearance of the shorter time-constant $1/\omega_1$ that begins dominating the IMPS response for sufficiently thick films with PE illumination and small $1/\alpha$. This is due to the electron transport distance being determined mainly by $1/\alpha$ instead of d or L ²¹.

Both of these factors lead to an overestimation of D by eq 3. The error is larger for the PE illumination, increases with d , and is at worst more than one order of magnitude in our example (Figure 6a). Obviously, these effects can bias quantitative evaluation of the electron transport, unless care is taken to ensure the validity of eq 3 for the samples under study. Moreover, the problem of two IMPS time constants can potentially compromise even relative comparison (ranking) of two samples by their apparent (dominant) τ_{IMPS} . This point is demonstrated by Figure 7 where we compare five series of optically identical cases of photoelectrode films having equal τ but different D , and thus different L . The adjacent traces of τ_{IMPS} vs d cross each other so that there is a range of d values where the sample with smaller D exhibits apparently faster electron transport, i.e. lower τ_{IMPS} .

It is important to notice that while the transition of τ_{IMPS} from $1/\omega_2$ to $1/\omega_1$ is clear and abrupt when plotted vs d (Figure 7), it is much less discernible by the features of the IMPS spectrum (Figures 4a and 4e). In practice, it would be hard to identify which of the components, ω_1 or ω_2 , dominates a measured IMPS spectrum, unless a series of samples with systematically varied d is measured.

The problem is much smaller when the electron generation is uniform or biased towards the CE side (Figure 7b-c). Consequently, investigations of electron transport

kinetics by dynamic photocurrent measurements should be preferable done with CE illumination. In addition, the slower response with CE illumination minimizes also problems due to electron thermalization¹⁵ and RC attenuation.

3.3 IMVS time constant and estimation of the electron diffusion length

The characteristic IMVS time constant is usually assumed independent of d and equal to the electron lifetime τ . As already mentioned, this is indeed the case if electron generation is uniform or $L \gg d$. If on the other hand the generation is non-uniform and $L < d$, relaxation of the spatial photogenerated electron concentration by diffusion occurs in the time scale longer than τ and renders τ_{IMVS} dependent on the generation profile. As shown in Figure 5b, biasing the generation towards the contact by PE side illumination decreases τ_{IMVS} , whereas the opposite occurs with the CE side illumination. Quantitatively, the effect is however rather modest, introducing no more than $\pm 50\%$ error in our case. Furthermore, with the PE illumination, $0.56 < \tau_{\text{IMVS}}/\tau < 1$, irrespective of L and the steepness of the generation profile.

Figure 6b shows L estimated by eq 2 using the τ_{IMVS} data of Figure 5b and the estimated diffusion coefficients D_{EST} of Figure 6a. Due to their opposite dependence on the generation profile, the errors embedded in these data compensate partially each other when forming L . However, the errors in D_{EST} largely dominate over those in τ_{IMVS} , leading to significant, up to a factor of four overestimation of L .

3.4 Estimation of the electron collection efficiency

Faced with these problems we should consider their impact on the quantitative estimation of the electron collection efficiency (Figure 8a). There are several routines for deriving estimates for η_{COL} in practice. Firstly, with known d and α , we could calculate it directly by the diffusion model (eqs 49 and 50 with $\omega = 0$) using the measured values of D_{EST} (eq 3) and τ_{MVS} . Figure 8b shows that this method leads to systematic overestimation of η_{COL} by up to 40 %-units, corresponding to up to 400% relative error at the CE illumination for $d = 3L$. Secondly, we could apply the widely used eq 4 using directly the τ_{MPS} and τ_{MVS} data. Interestingly, this simple method is more accurate, with absolute error less than 15 %-units, and relative errors up to 200% at the CE illumination (Figure 8c).

While for the both methods, the relative errors are less than 10% when $L > d$, more accurate methods are obviously needed to cover the low collection regime $L < d$. In principle, complex nonlinear least square fitting of complete IMPS spectrum can yield simultaneously estimates for all unknown model parameters³¹. Although this is mathematically straightforward, great care needs to be taken in practice to confirm sensitivity of the fit to individual parameters, while allowing for some inaccuracy in the experimental data and the model.

Ideally, as many model parameters as possible should be determined independently, which is straightforward for d and α . Estimating further τ by τ_{MVS} , and the RC attenuation factor (eq 20) by impedance spectroscopy, at the same conditions, leaves D , and an unknown scaling factor (see Chapter 2.5 above) as the free parameters for the fitting¹⁷. Assuming that the diffusion model is valid, estimation of τ by τ_{MVS} remains as

the only source of error that, nevertheless, can bring about overestimation of η_{COL} by up to 8 %-unit when $d = 3L$, while the error is smaller at the PE illumination (Figure 8d).

3.5 *Scaling problem of IMPS response*

The above results show that when $\eta_{\text{COL}} \ll 1$, the IMPS response is sensitive to τ , and thus, simultaneous estimation of D and τ should in principle be possible by fitting the diffusion model to a measured IMPS spectrum. The similarity of the spectral shapes of the IMPS response (Figure 4) means however that this sensitivity is based mainly on the value of the low frequency limit of the spectrum. For this reason, τ , L , and η_{COL} , cannot be determined reliably from a single IMPS measurement in practice.

This is why IMVS is commonly used in conjunction with IMPS to provide an independent estimate for τ , to be used as a fixed parameter in the IMPS fitting^{17,21}. Using IMVS data (measured at open circuit) to interpret IMPS data (measured at short circuit) is however complicated by the significant concentration dependence of the electron transport and recombination kinetics^{6,17}. The mean concentration is lower at the short circuit than at the open circuit. Hence, to determine τ corresponding to the short circuit IMPS, the IMVS needs to be measured at lower light intensity, using e.g. charge extraction method^{25,26} to establish an appropriate point of comparison in terms of electron concentration. Alternatively, transport measurements can be taken close to open circuit condition, where the electron concentration is fairly uniform over the whole film²², but with the price that the validity of the data for describing short circuit performance becomes questionable.

3.6 IMPS-ratio

To alleviate the IMPS scaling problem, we can, however, use exact analogy with the steady-state IPCE-ratio method⁵, i.e. measure IMPS for both illumination directions and define correspondingly a new dynamic performance characteristic (cf. eqs 8, 11, 39, and 40)

$$F_{\text{IMPS,SC,CE/PE}} = \frac{F_{\text{IMPS,SC,CE}}}{F_{\text{IMPS,SC,PE}}} = \frac{\eta_{\text{LH,PE}}}{\eta_{\text{LH,CE}}} \cdot \frac{F_{\text{IMPS,SC,CE}}^*}{F_{\text{IMPS,SC,PE}}^*} = \frac{T_{\text{TCO}}}{T_{\text{CE}} T_{\text{EL}}} \cdot \frac{F_{\text{IMPS,SC,CE}}^*}{F_{\text{IMPS,SC,PE}}^*} \quad (53)$$

that may be called IMPS-ratio.

Since η_{INJ} and the absorptance of the photoelectrode film are independent of the illumination direction, they cancel out in eq 53, provided that same monochromatic light wavelength is used in both cases. As a result, the unknown scaling factor in the IMPS-ratio is a ratio of transmittances (optical losses) that can be measured independently. Note that the IMPS-ratio is also independent of the absolute calibration of the light intensity, which simplifies the experiments and improves their accuracy.

The IMPS-ratio facilitates simultaneous determination of D and τ in the case when recombination losses are non-negligible, at least at the CE illumination. At the limit of low frequencies, the IMPS-ratio equals the IPCE-ratio that gives an estimate for L when d and α are known⁵. The frequency dependence of the IMPS-ratio for its part, contains the required additional information for factoring L into D and τ (eq 2) by fitting eq 53 (with eqs 49 and 50) to experimental $F_{\text{IMPS,SC,CE}}^*/F_{\text{IMPS,SC,PE}}^*$ data, with known values of T_{TCO} , T_{CE} , and T_{EL} .

It is essential to realize that this method produces D and τ estimates that are inherently consistent with the steady state limit (the IPCE-ratio). In other words, experimental

investigation of the correspondence between the steady state and dynamic electron transport characteristics needs to be based on other criteria than comparing L and η_{COL} evaluated by the diffusion model based on IMPS and IPCE data. One possible criterion could be quantitative consistency of τ estimates based on the IMPS-ratio and IMVS measured at the same conditions, while varying systematically d , α and the illumination direction.

3.7 *Experimental demonstration*

The problem due to non-uniform generation and limited collection of electrons is clearly demonstrated by the IMPS data of DSCs in Figure 9. The preparation of these cells is described in ref.⁵ where the steady state photocurrent limiting factors of the same batch of cells was studied by spectral IPCE and optical measurements. In brief, the cells were conventional sandwich type glass substrate DSCs with organic liquid electrolyte. The nanostructured photoelectrode films (3 – 22 μm thick) had 1 – 6 room-temperature compressed TiO_2 nanoparticle layers, and were either used as such (“pressed-only”), or after additional heat-treatment (sintering) at 450 $^\circ\text{C}$ for 60 min (“sintered”). The two types of cells had equal optical properties, while the pressed-only cells exhibited roughly 50 % lower short circuit photocurrent due to lower η_{COL} ⁵.

In the IMPS measurements, taken at the short circuit, the cells were illuminated from the photoelectrode side using 640 nm light from a red LED that provided both DC bias intensity (10.5 mW/cm^2) and its small amplitude AC modulation. All the measured IMPS spectra were characterized by only one distinguishable time-constant, and the RC attenuation was insignificant, as confirmed by impedance measurements.

Figure 9 shows that in the sintered films, the measured τ_{MPS} increases roughly linearly with film thickness. Compared to this, τ_{MPS} is higher in thin pressed-only films. This is expected due to the absence of high-temperature sintering that is normally used to induce neck growth between the TiO_2 nanoparticles: electron diffusion is slower through narrower interparticle contacts³³. However, as d increases, τ_{MPS} saturates to a constant value in the pressed-only films, so that at 22 μm , electron transport appears equally fast with and without sintering. This is unexpected, and demonstrates that conclusions on electron transport based on measured τ_{MPS} can be significantly influenced by the photoelectrode thickness in the DSC samples.

In this case, the light penetration depth ($1/\alpha$) was between 7 μm and 10 μm for 640 nm light, while the steady state diffusion length was less than 5 μm in the pressed-only films⁵. These values place the pressed-only films firmly in the region where both limited electron collection and near contact generation are expected to have a significant influence on the measured τ_{MPS} (Figure 5a). Both effects likely play a role in the saturation of the τ_{MPS} with d in Figure 9.

3.8 *Final remarks*

While the standard diffusion model investigated here is able to capture the main characteristics of electron transport and accumulation in nanostructured photoelectrodes^{2,4,5}, it has the deficiency that it does not account for the strong electron concentration dependence of its key parameters, D and τ , observed with the dynamic techniques^{2,6,9,17}, and explained by the so-called multiple trapping model of electron transport and recombination^{6,11}. For this reason, the theoretical results presented here are

not directly valid for experimental IMPS and IMVS data. For example, even the approximate estimation of η_{COL} with eq 4 is sensible only with τ_{IMPS} and τ_{IMVS} data that correspond to the same electron concentration³⁴, and the thickness dependence of τ_{IMPS} (eq 3) is likely affected also by the spatial variation of the electron concentration in the film at the short circuit condition.

Nevertheless, the present results show how non-uniform generation and limited collection of electrons is expected to influence the IMPS and IMVS response, and illuminate the pitfalls that they induce to practical data analysis. We point out that more complicated models that take explicitly into account e.g. thermalization¹⁵ and trapping^{6,15,33-36} of electrons, nanoparticle grain³³ and film³⁶ morphology, or ambipolar nature of the electron diffusion³⁷, build on the standard diffusion model, and hence, are inherently subject to all phenomena discussed here. The effect of these phenomena on the IMPS and IMVS response is often ignored in the practical data analysis, which can compromise the validity of data interpretation as discussed above.

4 Conclusions

The standard diffusion model of light intensity modulated photocurrent and photovoltage response of nanostructured photoelectrodes was generalized to an arbitrary electron generation profile, and applied to investigate how non-uniform generation and inefficient electron collection affect the IMPS and IMVS response.

These effects can be understood by time-dependent redistribution of the photo-generated electrons by diffusion and their arrival at the collecting contact. The arrival time depends not only on the electron diffusion coefficient, but also on the effective collection distance that is influenced by the diffusion length and light penetration depth,

when they are significantly shorter than the film thickness. This modifies the thickness dependence of the characteristic IMPS and IMVS time-constants, complicates their interpretation, and can potentially lead to significant overestimation of the electron diffusion coefficient, diffusion length and collection efficiency by well-known approximate relations.

When electron generation is strongly biased to the collecting contact, the IMPS response can exhibit two components, the faster one corresponding to electron diffusion directly to the contact and the slower one to electrons that were reflected from the other end of the film. The influence of the fast component is difficult to distinguish by the shape of the IMPS spectrum, especially when electron collection is limited, but can be minimized by using modulated light incident from the counter electrode side.

A new dynamic performance characteristic, IMPS-ratio, facilitates simultaneous estimation of electron diffusion coefficient, lifetime, and diffusion length at the short circuit condition by alleviating the scaling problem of the experimental IMPS spectra.

The present theory and analysis provides a background for quantitative IMPS and IMVS investigation of practical dye solar cells that show limited electron collection and non-uniform light absorption.

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Supporting Information Available: Derivation of eqs 21 and 23. IMPS and IMVS spectra corresponding to Figures 2 and 3 but with $L = 100 \mu\text{m}$ (Figures S3 and S4).

IMVS spectra for exponential generation (Figure S5). This information is available free of charge via the Internet at <http://pubs.acs.org>.

5 Appendix A

The time-dependent standard diffusion model involves solving the continuity equation for excess photogenerated electrons in the semiconductor, treating the film as a homogenous isotropic effective medium,

$$\frac{\partial n_e}{\partial t} = D \frac{\partial^2 n_e}{\partial x^2} - \frac{n_e}{\tau} + g \quad (\text{A1})$$

where D and τ are respectively the electron diffusion coefficient and lifetime, $g = g(x, t)$ is the local electron generation rate, and $n_e = n_e(x, t)$ is the local excess electron concentration defined as $n_e = n - n_0$, where n is the total electron concentration and n_0 the equilibrium electron concentration in the dark. The model assumes that D and τ are constants, i.e. independent of the electron concentration and position in the film. The boundary conditions relevant to the problem are^{6,7}

$$D \frac{\partial n_e}{\partial x} \Big|_{x=0} = k_{\text{EXT}} n_e(0, t) \quad (\text{A2a})$$

$$\frac{\partial n_e}{\partial x} \Big|_{x=d} = 0 \quad (\text{A2b})$$

where d is the photoelectrode film thickness, and k_{EXT} is the kinetic rate constant for electron extraction at the substrate contact (see Figure 1). While the boundary condition at the contact can be alternatively formulated based on fixed electron concentration or flux at $x = 0$, the kinetic formulation is particularly convenient, since it simultaneously covers both the open and short circuit condition. Setting $k_{\text{EXT}} = 0$ corresponds to the open

circuit, whereas the short circuit condition is found in the limit $k_{\text{EXT}} \rightarrow \infty$, corresponding to a situation where the substrate acts as a perfect sink for the excess electrons.

The general solution of eq A1 can be found by separation of variables. Due to linearity of eq A1 it suffices to solve it for the modulated part only. The steady state solution is then readily obtained by setting $\omega = 0$. Writing the modulated generation rate as

$$g_{\text{AC}}(x, t) = G(x)e^{i\omega t} \quad (\text{A3})$$

where

$$G(x) = \delta\Phi_{\text{DC}}\eta_{\text{INJ}}f_{\text{LH}}(x) \quad (\text{A4})$$

and $f_{\text{LH}}(x)$ is the spatial light harvesting efficiency in eq 6, the AC solution of eq A1 will be of the form

$$n_{\text{e,AC}}(x, \omega, t) = N(x, \omega)e^{i\omega t} \quad (\text{A5})$$

where $N = N(x, \omega)$ is the frequency dependent complex electron concentration that satisfies (cf. eqs A1-A2b)

$$\left(\frac{1}{\tau} + i\omega\right)N - D\frac{\partial^2 N}{\partial x^2} = G \quad (\text{A6})$$

subject to the boundary conditions

$$D\frac{\partial N}{\partial x}\Big|_{x=0} = k_{\text{EXT}}N(0, \omega) \quad (\text{A7a})$$

$$\frac{\partial N}{\partial x}\Big|_{x=d} = 0 \quad (\text{A7b})$$

Eqs A6-A7b provide the basis for the analysis of the small amplitude periodic photocurrent and photovoltage response.

Figure Captions

Figure 1. Geometry of the one-dimensional electron generation-collection problem with exponential generation profiles. Two transport lengths can be distinguished when the generation is strongly biased towards the collecting contact: 1. diffusion directly to the contact, 2. diffusion to the opposite direction and reflection from the edge of the film.

Figure 2. Effect of film thickness (d) and locus of generation (ξ) on the IMPS spectra for different cases of spatial electron generation. (a,d) localized generation at $x = \xi$ when d is fixed to 30 μm ; (b,e) localized generation at the far edge of the film ($x = \xi = d$); (c,f) uniform generation. The arrows show the direction of increasing ξ or d .

Figure 3. IMVS spectra for localized and uniform electron generation. See Figure 2 for descriptions. The IMVS spectra are normalized by dividing each spectrum by the steady state limit of the IMVS response for uniform illumination with the same τ and d (eq 38).

Figure 4. Effect of film thickness (d) on the IMPS spectra for exponential generation profiles with fixed light penetration depth $1/\alpha = 5 \mu\text{m}$ and electron lifetime $\tau = 16 \text{ ms}$, $(2\pi\tau)^{-1} = 10 \text{ Hz}$. Figures (a-d) show the complex plane plots and (e-h) the corresponding imaginary component spectra, showing the effect of the illumination direction (PE- vs CE-side) and electron diffusion length L (10 μm vs 100 μm). The arrows show the direction of increasing d .

Figure 5. Effect of the film thickness and locus of generation on (a) IMPS time constant, and (b) IMVS time constant. Three cases of exponential generation with PE illumination

(continuous lines) and CE illumination (dashed lines) with different light penetration depth ($1/\alpha$) are shown in colors.

Figure 6. Effect of the film thickness and locus of generation on (a) relative electron diffusion coefficient estimated by eq 3 using τ_{IMPS} from Figure 5a, and (b) relative electron diffusion length estimated by eq 2 using D_{EST} and τ_{MVS} from Figures 5a and 5b.

Figure 7. Comparison of the photoelectrode thickness dependence of the IMPS time constant for hypothetical, optically identical photoelectrode samples with equal τ but different L . (a) Illumination from the photoelectrode side, (b) Illumination from the counter electrode side, (c) uniform illumination.

Figure 8. Effect of the film thickness and locus of generation on the electron collection efficiency. (a) The exact values by the diffusion model using $D = 6.25 \cdot 10^{-6} \text{ m}^2/\text{s}$ and $\tau = 16 \text{ ms}$ ($L = 10 \text{ }\mu\text{m}$), and (b) errors introduced by estimating $D = D_{\text{EST}}$ (Figure 6a) and $\tau = \tau_{\text{MVS}}$ (Figure 5b). (c) Error introduced by using eq 4. (d) Minimum error corresponding to fitting the complete IMPS spectrum, using a fixed estimated value $\tau = \tau_{\text{MVS}}$ (Figure 5b).

Figure 9. Measured IMPS time constant as a function of film thickness in dye solar cells having pressed TiO_2 photoelectrode films with, or without, additional sintering at $450 \text{ }^\circ\text{C}$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 7

Figure 9

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