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Linking optical and electrical small amplitude perturbation techniques for dynamic performance characterization of dye solar cells

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ABSTRACT: This paper unifies the analytical models used widely but thus far mostly separately for electrical and optical small amplitude perturbation measurements of nanostructured electrochemical dye solar cells (DSC): electrochemical impedance spectroscopy (EIS), intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS). The models are linked by expressing the kinetic boundary condition used for solving the time-dependent continuity equation of electrons in IMPS and IMVS analysis in terms of the series and parallel impedance components found in the complete equivalent circuit impedance model of DSC. As a result, analytical expressions are derived for potentiostatic IMPS and galvanostatic IMVS transfer functions of complete DSCs that are applicable at any operating point along the solar cell current – voltage (IV) curve. In agreement with the theory, impedance spectrum calculated as a ratio of IMVS and IMPS transfer functions measured near the maximum power point matches exactly with the impedance spectrum measured directly with EIS. Consequently, both IMPS-IMVS and EIS yield equal estimates for the electron diffusion length. The role of the chemical capacitance of the nanostructured semiconductor photoelectrode in the interpretation of the so-called RC attenuation of the IMPS response is clarified, as well as the capacitive frequency dispersion in IMPS and IMVS.

KEYWORDS: Dye-sensitized, photovoltaic, electron transport, recombination, generation, photocurrent transient, photovoltage transient

1. INTRODUCTION

Nanostructured semiconductor solar cells have emerged as a promising option for low-cost photovoltaic solar electricity generation. Contrary to the conventional pn-junction devices where the primary steps of photovoltaic energy conversion – light absorption, charge transport, and charge collection – take place in the same semiconductor material phase, in a nanostructured solar cell these processes are separated to different material phases, with the result that some of the costly purity requirements of the active materials and the processing techniques are relaxed.

A classic example is the nanostructured electrochemical dye solar cell (DSC).^{1, 2} DSCs have validated efficiency record of 10.4 %³ and good long term stability.⁴ Their low cost materials, printability to flexible substrates and unique design possibilities with respect to color and semi-transparency makes them attractive option for building integrated photovoltaics (BIPV) such as facade elements as well as consumer applications such as solar chargers for portable electronics.

The operation of DSC is based on light-induced charge separation at an interface between a liquid redox electrolyte or a solid hole conductor and nanoparticles of a wide-band gap semiconductor oxide, most commonly TiO_2 , that form a nanostructured nanoporous photoelectrode. At this interface, a monolayer of dye absorbs photons and injects electrons to the conduction band of the TiO_2 particle, which is followed by transport of the electrons by diffusion through the nanoparticle film to the collecting contact.

One of the most remarkable features of the DSCs is that practically all photogenerated electrons can be collected from the highly disordered random network of interconnected semiconductor nanoparticles before they recombine with electron acceptors species in the hole conducting medium surrounding the nanoparticles.^{1, 5, 6} The basic reason for this is that the transport of electrons is much faster than their recombination. However, clarifying the physical mechanisms that determine the result of this kinetic competition has remained an active, and sometimes controversial, subject of experimental and theoretical investigations.

Central in these investigations has been an extensive use of dynamic opto-electrical techniques based on small amplitude modulation of the steady state, namely electrochemical impedance (EIS),⁷⁻⁹ intensity modulated photocurrent (IMPS)^{10, 11} and intensity modulated photovoltage spectroscopy (IMVS)^{12, 13}. In EIS, the AC current response to an AC voltage modulation is measured as a function of the modulation frequency, whereas IMPS and IMVS involve measuring the dynamic photocurrent and photovoltage response of the cell to small amplitude light intensity modulation.

Although it has been shown both theoretically¹³⁻¹⁵ and experimentally^{13, 16, 17} that these techniques give similar dynamic information on the electron transport and recombination, their development has evolved virtually independently: some researchers have focused on EIS while others have used mainly IMPS and IMVS. There has also been a difference in the data analysis techniques used: while it is customary to analyze EIS data with equivalent circuit models,^{7, 8} the IMPS and IMVS response has been interpreted using models based on differential equations.^{11, 18-20} Yet, there is no fundamental reason for this, since also equivalent circuit modeling is based on differential equations, and hence, both approaches must give the same mathematical expressions. In fact, as pointed out earlier,²¹ the EIS, IMPS and IMVS techniques are related by definition simply as

$$Z_{\text{CELL}} = \frac{F_{\text{IMVS, CELL}}^*}{F_{\text{IMPS, CELL}}^*} \quad (1)$$

where Z_{CELL} is the solar cell impedance, and $F_{\text{IMVS, CELL}}^*$ and $F_{\text{IMPS, CELL}}^*$ are the IMVS and IMPS transfer functions of the solar cell measured respectively galvanostatically and potentiostatically at the same conditions as EIS.²¹

However, due to the lack of a mathematical model applicable for analysis of the IMPS and IMVS data along the whole current – voltage (IV) curve of a complete DSC, the IMPS and IMVS techniques have been applied previously almost exclusively only at respectively short and open circuit conditions. On the other hand, voltage and current dependent EIS has become a standard practice. The purpose of the present paper is to open also IMPS and IMVS technique for similar analysis, by establishing a mathematical link between the equivalent circuit modeling of EIS and differential equation modeling of IMPS and IMVS in light of eq 1, following an approach similar to Bay and West.¹⁵ The result is a quantitative analytical model that unifies the EIS, IMPS and IMVS techniques with each other and with the steady-state-state solar cell IV measurements.

In contrast to recent numerical simulations of the non-linear electron transport and recombination in DSC,^{19, 20, 22-27} the IMPS and IMVS modeling here uses linear approximations to arrive at analytical solutions that can be directly compared with the widely used equivalent circuit impedance model of DSC.

2. THEORETICAL BACKGROUND

Before going to the IMPS and IMVS modeling that is the main topic of the paper, it is worthwhile to write down the basic definitions of the EIS, IMPS and IMVS transfer functions, point out their relation to the IV curve, and briefly summarize the equivalent circuit impedance model of DSC, since we want to express the IMPS and IMVS model in exact consistency with it.

2.1. Opto-electrical Transfer Functions and Their Relation to the IV curve

In the EIS measurement, a small amplitude sinusoidal voltage modulation $V_{\text{CELL,AC}}(\omega, t)$ is superimposed on a constant steady state cell voltage V_{CELL} and the resulting AC current density $i_{\text{AC}}(\omega, t)$ is recorded as a function of the modulation frequency (ω). The cell impedance is defined as the ratio of the AC voltage and current

$$Z_{\text{CELL}}(\omega) = \frac{V_{\text{CELL,AC}}(\omega, t)}{i_{\text{CELL,AC}}(\omega, t)} \quad (2)$$

In intensity modulated photocurrent spectroscopy (IMPS) the solar cell is held at constant voltage (potentiostatic control) and the AC current response $i_{\text{CELL,AC}}(\omega, t)$ caused by light intensity modulation is measured and correlated by the AC photon flux signal $\Phi_{\text{AC}}(\omega, t)$ by defining the IMPS transfer function as

$$F_{\text{IMPS, CELL}}^*(\omega) = \frac{i_{\text{CELL,AC}}(\omega, t)}{q_e \Phi_{\text{AC}}(\omega, t)} \quad (\text{at potentiostatic control}) \quad (3)$$

where q_e is the electron charge. The intensity modulated photovoltage spectroscopy (IMVS) for its part, is carried out at constant DC cell current (galvanostatic control), and the AC voltage signal $V_{\text{CELL,AC}}(\omega, t)$ caused by light intensity modulation is recorded and contrasted with the AC photon flux

$$F_{\text{IMVS, CELL}}^*(\omega) = \frac{-V_{\text{CELL,AC}}(\omega, t)}{q_e \Phi_{\text{AC}}(\omega, t)} \quad (\text{at galvanostatic control}) \quad (4)$$

Since the modulation amplitude in the measurements is small enough to maintain linearity of the response, eqs 2 – 4 define complex transfer functions in the frequency domain. These transfer functions describe the dynamics of physical processes related to photocurrent and photovoltage generation in the cell.

The relation (eq 1) of the IMPS, and IMVS techniques to the EIS and the solar cell IV curve follows directly from eqs 2 – 4, and can be understood with help of Figure 1. When the IMPS and IMVS transfer functions are measured at potentiostatic and galvanostatic conditions respectively, and with the same light modulation amplitude and wavelength in both cases, they constitute the orthogonal components of the cell impedance²¹. The impedance for its part corresponds to the differential resistance R_{CELL} of the IV curve (at the limit of zero frequency), *i.e.* its slope of the IV curve at the point $(V_{\text{CELL}}, i_{\text{CELL}})$ where the measurements are taken

$$Z_{\text{CELL}}(\omega = 0) = \frac{\partial V_{\text{CELL}}}{\partial i_{\text{CELL}}} = R_{\text{CELL}} \quad (5)$$

According to the sign convention of the present paper, and consistently with positive R_{CELL} , the short circuit current density (i_{sc}) of the cell is positive and the open circuit voltage (V_{oc}) is negative. Increase

of light intensity causes thus an increase in the current ($i_{\text{CELL,AC}} > 0$) in the potentiostatic IMPS measurement, but decreases the cell voltage ($V_{\text{CELL,AC}} < 0$) in the galvanostatic IMVS experiment (Figure 1). Nevertheless, it is customary and convenient to plot IMVS spectra in the positive real part – negative imaginary part quadrant of the complex plane, so we add minus sign in eq 4, which places all the three transfer functions of eq 1 in the same quadrant. Since the above considerations do not involve any assumptions of the type or properties of the solar cell, eq 1 is valid for any solar cell irrespective of its materials and photovoltaic conversion mechanism.

The relation between the solar cell IV curve and R_{CELL} , measurable with EIS *e.g.* as a function of current density ($i = i_{\text{CELL}}$) can be written as^{8, 28, 29}

$$V_{\text{CELL}}(i_{\text{CELL}}) = V_{\text{OC}} + \int_0^{i_{\text{CELL}}} R_{\text{CELL}}(i) di \quad (6)$$

Physical modeling of the differential resistance of each cell component contributing to R_{CELL} allows one to derive values for physical parameters through analysis of experimental EIS data and to predict their effect on the IV curve and cell efficiency.^{8, 9, 29} Eq 1 implies that the same must be possible also with IMPS and IMVS. The main goal of the present paper is work out the mathematical equations required for doing it in practice.

Figure 1. Relation of the IMPS, IMVS and EIS techniques to each other and to the steady state solar cell IV curve (black continuous line). The black dotted lines represent the steady state limit of the IV curve due to modulation of the incident light intensity. The colored arrows show the corresponding modulation of cell current and voltage in IMPS (red, solid and dashed arrows indicating respectively increasing and decreasing light intensity), IMVS (blue), and EIS (green).

2.2. Equivalent Circuit Modeling of EIS

In the standard equivalent circuit impedance model of DSC,^{7-9, 29} shown in Figure 2, hindrance of charge transport in the material phases and charge transfer across their interfaces is represented by resistances, and accumulation of charge is accounted for by capacitive circuit elements. Of particular importance to the present paper is the transmission line impedance model³⁰, developed to describe the photoelectrode of the DSC applications by Bisquert *et al.*^{7, 8, 31} The model is summarized in more detail *e.g.* in Appendix I of ref.²⁹ and in the Supporting Information of the present paper.

Figure 2. Equivalent circuit impedance model of the dye solar cell. r_T ($\Omega \text{ m}$) is the electron transport resistivity, and r_{REC} ($\Omega \text{ m}^3$) and c_μ ($\Omega \text{ m}^3$) the electron recombination resistance and chemical capacitance per unit volume. R_{CO} ($\Omega \text{ m}^2$) and C_{CO} (F m^{-2}) are the contact resistance and capacitance at the interface between the conducting substrate and the TiO_2 film; R_{SU} ($\Omega \text{ m}^2$) and C_{SU} (F m^{-2}) the charge transfer resistance and double layer capacitance at the substrate-electrolyte interface; R_{CE} ($\Omega \text{ m}^2$) and C_{CE} (F m^{-2}) the charge transfer resistance and double layer capacitance at the counter electrode-electrolyte interface. Z_D ($\Omega \text{ m}^2$) is the electrolyte diffusion impedance at the counter electrode and R_s ($\Omega \text{ m}^2$) the Ohmic series resistance of the cell including contributions from the sheet resistance of the substrates, resistivity of the electrolyte and electrical contacts and wiring of the cell.

2.3. Differential Equation Modeling of IMPS and IMVS

The differential equation model used for the IMPS and IMVS modeling in this paper is summarized in the Appendix. While it has become recently clear that accurate description of the electron transport and recombination characteristics of DSCs requires numerical modeling that takes explicitly into account non-linear electron recombination,^{19, 20, 22-27} electron trapping and detrapping effects,^{19, 20, 25, 26} and even dye regeneration and ionic transport in the electrolyte,^{25, 32} the present modeling is based on the conventional linear electron continuity equation that neglects these effects. The reason for this choice is that we seek analytical solutions that can be directly compared with the standard EIS equivalent circuit

model of DSC^{7, 8, 31} which is subject to the same assumptions. At the same time the resulting analytical expressions for the IMPS and IMVS transfer functions of the complete solar cell are readily applicable to fitting to experimental data for parameter estimation, similar to the standard practice of using equivalent circuits to analysis EIS data.

It should be nevertheless kept in mind that due to the linear assumption, some errors will be introduced in the fitted parameter values depending on how well the assumption are applicable at the actual measurement conditions. The magnitude of these errors and their importance for practical performance evaluation of DSC are presently under keen investigations giving both support for and criticism against the applicability of the linear assumption.^{17, 20, 22-24, 33, 34} The analytical solutions presented here serve as a point of comparison for such investigations. Indeed, eqs A8 and A9 are the general expressions for the IMPS and IMVS transfer functions of the nanostructured TiO₂ photoelectrode film, and thus applicable to any electron transport model, including numerical models.

What brings us to main topic of the present paper is the fact that the IMPS and IMVS transfer function defined by eqs A8 and A9 are actually not measurable from a complete DSC since the equations neglect the effect of the additional impedance components in the solar cell. The main goal of the paper is to link the time-dependent differential equation model of the photoelectrode to the full equivalent circuit impedance model of DSC so that the IMPS and IMVS transfer functions for the complete solar cell can be found.

3. RESULTS AND DISCUSSION

3.1. Effect of Series and Parallel Impedances on the IMPS and IMVS Response

Figure 3. Simplified equivalent circuit transfer function model of the dye solar cell.

Looking at the equivalent circuit model of DSC (Figure 2) we can see that there are additional impedance components connected in series and in parallel with the nanostructured TiO₂ film, as represented more generally by the simplified circuit in Figure 3. To model the complete solar cell IMPS

and IMVS responses, we need to understand how they influence the boundary condition (eq A2) used for solving the time-dependent continuity equation of electrons in the photoelectrode film.

As mentioned in the previous section, the IMPS measurement is taken under external potentiostatic control of the solar cell. This means that while the light intensity is modulated and causes an AC photocurrent to flow in the cell, the cell voltage V_{CELL} is kept precisely at a fixed value with the help of a potentiostat, meaning that AC component of the cell voltage is always exactly zero: $V_{\text{CELL,AC}} = 0$. IMVS measurement for its part is taken under galvanostatic control keeping the cell current constant, so that the AC cell current remains exactly zero: $i_{\text{CELL,AC}} = 0$. The effect of the series and parallel impedances is that they prevent applying externally an exact potentiostatic and galvanostatic control of the photoelectrode film itself. To understand how this influences the IMPS and IMVS response, it is useful to build a mental picture of the situation.

Imagine first, that we were somehow able assign potentiostatic control directly on the photoelectrode film, *i.e.* $V_{\text{TiO}_2, \text{AC}} = 0$. This would mean that also the electron density in the TiO_2 film at the contact would be fixed to its steady state value, as illustrated in Figure 4a. To maintain the electron density constant, all excess photogenerated electrons arriving at the contact would have to be rapidly extracted to the external circuit. In terms of the kinetic boundary condition (eq A2) this would correspond to $k_{\text{EXT}} = \infty$. This condition has been traditionally thought to describe the short circuit condition,^{11, 18} but actually describes potentiostatic condition. Remember that the modeling of the small amplitude response is done only for the AC part of the electron density generated by the modulated light beam, and hence, the DC part can describe any steady state condition, such as any voltage polarization of the photoelectrode. Hence, if Z_S and Z_P were negligible, the traditional solutions for short-circuit-IMPS^{11, 18} would correctly describe any potentiostatic IMPS experiment.

The same applies to the IMVS measurements. Having galvanostatic control directly on the photoelectrode film would mean that the AC component of the photogenerated current at the contact would be zero, $i_{\text{TiO}_2, \text{AC}} = 0$. This means that the slope of the excess electron density at the contact would be fixed to its steady state value as shown in Figure 4b. In practice, no excess AC light induced electrons would be extracted from the film. This corresponds to $k_{\text{EXT}} = 0$ in eq A2, which is traditionally considered as the open circuit condition of the cell, but actually describes galvanostatic condition.

However, what happens in reality is the following. When an AC light modulation induced photocurrent flows in the cell during potentiostatic IMPS measurement, an AC voltage drop ($V_{S, \text{AC}} + V_{\text{CO, AC}}$) is induced over the series and contact impedances, Z_S and Z_{CO} in Figure 3. Since in the external potentiostatic control the total cell voltage is held exactly zero ($V_{\text{CELL, AC}} = 0$), an AC voltage equal but opposite to the voltage drop in Z_S and Z_{CO} is induced over the photoelectrode film. In other words, while the whole cell is potentiostatically controlled, the photoelectrode film is not, *i.e.* $V_{\text{TiO}_2, \text{AC}} \neq 0$. As a result,

not all excess AC light induced electrons are extracted from the film, which decreases the AC photocurrent output of the film, corresponding to decrease in the AC variation of the slope in the electron density (Figure 4c). Since finite $V_{\text{TiO}_2, \text{AC}}$ is present also at the interface between the photoelectrode substrate and the electrolyte, an AC parallel current $i_{\text{P}, \text{AC}}$ flows through it, to the direction opposite to the photocurrent $i_{\text{TiO}_2, \text{AC}}$. This further decreases the AC photocurrent output of the cell, depending on the magnitude of Z_{P} (Figure 3).

In the IMVS measurement there is a similar situation: even if the external AC cell current is fixed to zero galvanostatically ($i_{\text{CELL}, \text{AC}} = 0$), there is AC photocurrent flowing through the photoelectrode contact, and *via* Z_{P} and Z_{CO} , due to photogenerated electrons leaking to the electrolyte at the substrate – electrolyte interface. This additional loss of electrons decreases their density at the TiO_2 film contact (Figure 4d), which decreases the AC photovoltage $V_{\text{TiO}_2, \text{AC}}$ of the film and thus the whole cell, $V_{\text{CELL}, \text{AC}}$. In other words, where the series impedances prevented potentiostatic control of the photoelectrode in the IMPS measurement, the finite parallel impedance prevents its galvanostatic control in the IMVS experiment.

It becomes evident that the series and parallel impedance components determine how the externally controlled and measured cell current and voltage translate to the current flowing in the photoelectrode film and the voltage at its contact, and thus need to be taken into account in the modeling of the whole cell IMPS and IMVS responses. In the following, we show that this can be done simply by replacing the kinetic boundary condition (eq A2) with one related to these impedance components. This needs to be done separately for the potentiostatic IMPS and galvanostatic IMVS measurement conditions.

Figure 4. Schematic illustration of the modulation of the excess electron density n_e in the photoelectrode film in potentiostatic IMPS and galvanostatic IMVS experiments. The thick line represents the steady state n_e and the thin dotted lines its modulation (at the limit of zero frequency). If exact external control of a) photoelectrode voltage and b) current of the photoelectrode film would be possible, n_e and its slope at the contact would be fixed to their steady state values in the IMPS and IMVS measurements, respectively. However, in real complete DSC, the parallel and series impedances Z_P , Z_S and Z_{CO} in Figure 3 prohibit this, and as a result, modulation of n_e , and its slope, occurs at the contact both in the IMPS and IMVS experiments. This modifies the IMPS and IMVS responses as described in the text.

3.2. IMPS of Complete DSC Under Potentiostatic Control

It follows from basic analysis of the circuit in Figure 3 that, when $V_{CELL,AC} = 0$, the AC photocurrent of the TiO_2 photoelectrode can be expressed in terms of the AC voltage over it as

$$i_{TiO_2,AC} = - \left(\frac{Z_P Z_S}{Z_P + Z_S} + Z_{CO} \right)^{-1} V_{TiO_2,AC} \quad (7)$$

The minus sign in the above equation comes from the fact that while $i_{TiO_2,AC} > 0$, $V_{TiO_2,AC} < 0$ in the IMPS measurement, as it is also in the IMVS measurement (see Figure 4c and d and Figure 1). Expressing in this equation $i_{TiO_2,AC}$ with the Fick's law of diffusion and using the relation of $V_{TiO_2,AC}$ to the chemical capacitance at the photoelectrode contact (eq A10), we arrive at the following equation

$$D \frac{\partial N(x, \omega)}{\partial x} \Big|_{x=0} = \left(\frac{Z_p Z_s}{Z_p + Z_s} + Z_{co} \right)^{-1} \frac{N(0, \omega)}{c_\mu(0)} \quad (8)$$

Now, bearing in mind eq A7, we can see that the above equation is identical to the kinetic boundary condition (eq A2) with the difference that the parameter k_{EXT} is replaced with an expression that contains the three impedance components of Figure 3 and the chemical capacitance at the photoelectrode contact:

$$k_{EXT, IMPS} = \left(\frac{Z_p Z_s}{Z_p + Z_s} + Z_{co} \right)^{-1} \frac{1}{c_\mu(0)} \quad (9)$$

It thus follows very conveniently that the existing and well known solutions of the time-dependent diffusion model of the photoelectrode film, with the kinetic boundary condition,^{11, 18} are entirely valid for potentiostatic IMPS measurements of complete DSCs, even in the presence of arbitrary series and parallel impedances.

The physical background of the rate constant k_{EXT} has been rarely discussed in the literature. It was originally speculated that the extraction of electrons from the photoelectrode film could be controlled by some potential dependent kinetic mechanism,¹¹ but this seems to disagree with the fact that the contact between the nanostructure TiO_2 film and the conducting substrate has normally very low bias independent resistance and may be assumed Ohmic by nature, except with ITO-PET and some metal substrates.^{35, 36} Eq 9 shows that k_{EXT} need not be related to any specific kinetic charge transfer mechanism, but instead can be explained more generally by other internal impedance components of the solar cell. Eq 9 thus gives k_{EXT} an exact yet general physical interpretation. Any non-negligible³⁶ and possibly voltage-dependent contact resistance^{37, 38} can be introduced in it through Z_{co} .

One reason why k_{EXT} has received little attention is that it has not been needed in practice: the IMPS and IMVS techniques have been applied almost exclusively at the short circuit and open circuit conditions where k_{EXT} disappears from the model solutions explicitly, when it is assigned the values $k_{EXT} \rightarrow \infty$ in IMPS and $k_{EXT} = 0$ in IMVS. However, as already discussed, these conditions fail due to the series and parallel impedances.

To form the expression for the IMPS transfer function of the complete DSC, one merely needs to express the AC current of the complete cell in terms of the AC current of the photoelectrode, based on the circuit of Figure 3, and use eq 3 to obtain

$$F_{IMPS, CELL}^*(\omega) = F_A(\omega) F_{IMPS, TiO_2}^*(k_{EXT, IMPS}, \omega) \quad (10)$$

where

$$F_A(\omega) = \frac{Z_p(\omega)}{Z_p(\omega) + Z_s(\omega)} \quad (11)$$

is the so-called the “RC attenuation factor” of the IMPS response,^{11, 18, 39} and $k_{\text{EXT,IMPS}}$ is given by eq 9. Compared to the specific approximate expressions for F_A in the literature,^{11, 39} Eq 11 includes all impedance components of complete DSC equivalent circuit (Figure 2), while being general to allow introduction of other components as well.

Eq 10 shows that the internal impedance components of the solar cell affect the measured IMPS response of the cell in two ways. Firstly, through the attenuation factor (eq 11), and secondly, through the boundary condition at the photoelectrode contact (eq 9). Note that this boundary condition is in fact dynamic, since the series and parallel impedances are generally frequency dependent, but this seemingly complex situation becomes correctly accounted for by eq 9.

Potentiostatic IMPS experiments can be carried out at any point along the solar cell IV curve. The link provided by eq 9 makes thus all the pre-existing IMPS theories and experiments, used so far only at the short circuit conditions, applicable at any point along the solar cell IV curve.

3.3. IMVS of Complete DSC Under Galvanostatic Control

Following similar analysis as above for IMPS, we can write the nonzero AC flux of electrons flowing in the galvanostatic IMVS measurement from the photoelectrode film to the electrolyte *via* the impedance components Z_{CO} and Z_{P} as

$$D \frac{\partial N(x, \omega)}{\partial x} \bigg|_{x=0} = \left(\frac{1}{Z_{\text{P}} + Z_{\text{CO}}} \right) \frac{N(0, \omega)}{c_{\mu}(0)} \quad (12)$$

Comparison of the above equation to eq A2, keeping in mind eq A7, shows that the kinetic boundary condition is again valid, but in this case the parameter k_{EXT} is given by

$$k_{\text{EXT,IMVS}} = \left(\frac{1}{Z_{\text{P}} + Z_{\text{CO}}} \right) \frac{1}{c_{\mu}(0)} \quad (13)$$

an is thus different from the expression for potentiostatically controlled IMPS experiment (eq 9).

In this case, because no AC current flows through the series impedance, the whole AC cell voltage drops at the photoelectrode and equals that of the parallel impedance, $V_{\text{CELL,AC}} = V_{\text{P,AC}}$. For the same reason, all AC photocurrent flows through the parallel impedance, $i_{\text{TiO}_2, \text{AC}} = i_{\text{P,AC}}$. It thus follows from the circuit of Figure 3 that the IMVS transfer function measurable from a complete DSC can be expressed in terms of the IMVS transfer function of the photoelectrode as

$$F_{\text{IMVS, CELL}}^*(\omega) = \frac{Z_{\text{P}}}{Z_{\text{P}} + Z_{\text{CO}}} F_{\text{IMVS, TiO}_2}^*(k_{\text{EXT,IMVS}}, \omega) \quad (14)$$

where $k_{\text{EXT,IMVS}}$ is given by eq 13. Alternatively, using eq A11 it can be expressed in terms of the IMPS transfer function of the photoelectrode as

$$F_{\text{IMVS, CELL}}^*(\omega) = Z_p F_{\text{IMPS, TiO}_2}^*(k_{\text{EXT, IMVS}}, \omega) \quad (15)$$

where one must take care to insert $k_{\text{EXT, IMVS}}$ from eq 13 instead of $k_{\text{EXT, IMPS}}$ as the kinetic boundary condition. This may seem odd at first sight, but remember that $F_{\text{IMPS, TiO}_2}^*$ simply represents the dynamic current of the photoelectrode film at given condition (here external galvanostatic control, thus evoking $k_{\text{EXT, IMVS}}$), which is related to the cell voltage (represented by $F_{\text{IMVS, CELL}}^*$) by eq 15 when $i_{\text{CELL, AC}} = 0$ (cf. Figure 3).

With eqs 9, 10, 11, 13, 14 and 15 any model describing the IMPS and IMVS transfer functions of DSC that uses the kinetic boundary condition (eq A2) can be coupled to any equivalent circuit impedance model of the complete solar cell that can be reduced to the general circuit of Figure 3. Appendix gives the solutions for the basic optical model of DSC that is most interesting for practical applications.

3.4. Correspondence of the IMVS/IMPS and EIS models

It is shown in the Supporting Information that even in the case of arbitrary optical conditions eq 1 is valid for the general expressions of the IMVS and IMPS transfer functions, and that their ratio yields the following expression for the impedance of the photoelectrode film based on the diffusion model

$$Z_{\text{TiO}_2} = \frac{L}{Dc_\mu(0)} \frac{1}{\sqrt{1+i\omega\tau}} \coth\left(\frac{d}{L} \sqrt{1+i\omega\tau}\right) \quad (16)$$

where

$$L = \sqrt{D\tau} \quad (17)$$

is the electron diffusion length. This is indeed the impedance expression that can be derived consistently from both the diffusion model and the transmission line model of the photoelectrode film,⁴⁰ demonstrating the correspondence of the two modeling regimes.

As known from the previous works,⁴¹⁻⁴⁴ an exact correspondence of parameters between the models is provided by the chemical capacitance c_μ per unit volume of the photoelectrode (F m^{-3}) according to the following relations

$$D = (r_T c_\mu)^{-1} \quad (18)$$

$$\tau = r_{\text{REC}} c_\mu \quad (19)$$

$$L = \sqrt{D\tau} = \sqrt{\frac{r_{\text{REC}}}{r_T}} = d \sqrt{\frac{R_{\text{REC}}}{R_T}} \quad (20)$$

where $R_{\text{REC}} = r_{\text{REC}}/d$ and $R_T = r_T d$ are the measured recombination and transport resistances in units $\Omega \text{ m}^2$. However, the general form of the transmission line impedance model of the photoelectrode (eq S2 in the Supporting Information) uses constant phase element (CPE) in place of the chemical capacitance

to account for the frequency dispersion observed typically in experimental EIS data. Let us therefore arrange the transmission line impedance expression to include the chemical capacitance explicitly.

The CPE is defined as

$$z_{\text{CPE}} = q_{\text{CPE}}^{-1} (i\omega)^{-\beta_{\text{CPE}}} \quad (21)$$

where q_{CPE} and β_{CPE} are the CPE pre-factor and exponent. The equivalent capacitance (in units Fm^{-3}) of an electrochemical interface modeled by the parallel connection of the CPE element and a charge transfer resistance (in this case r_{REC}) is^{28, 29, 45}

$$c_{\mu} = (q_{\text{CPE}})^{1/\beta_{\text{CPE}}} (r_{\text{REC}})^{1/\beta_{\text{CPE}} - 1} \quad (22)$$

This relation is obtained by requiring that the RC-relaxation time constant of the parallel resistance – capacitance and resistance – CPE circuits are equal. Rearranging we get an expression for the CPE pre-factor

$$q_{\text{CPE}} = c_{\mu}^{\beta_{\text{CPE}}} (r_{\text{REC}})^{\beta_{\text{CPE}} - 1} \quad (23)$$

Using this relation, eqs S3 and S4 in the Supporting Information, and eqs 18 – 20, the transmission line impedance expression of the photoelectrode (eq S2 in the Supporting Information) can be arranged to a form that contains only the diffusion model parameters, and the CPE exponent β_{CPE} that is responsible for the frequency dispersion

$$Z_{\text{TiO}_2} = \frac{L}{Dc_{\mu}} \frac{1}{\sqrt{1 + (i\omega\tau)^{\beta_{\text{CPE}}}}} \coth\left(\frac{d}{L} \sqrt{1 + (i\omega\tau)^{\beta_{\text{CPE}}}}\right) \quad (24)$$

Comparing this to eq 16 we can note two differences. The first is obviously the CPE exponent. The comparison shows that the frequency dispersion modeled by it enters the solution of the diffusion model in a way that can be interpreted as a distribution of time-constants (dynamic electron lifetimes) centered at τ .⁴⁶ The frequency dispersion does not affect the steady state solution ($\omega = 0$), and hence, its absence in the diffusion model does not hamper applicability to steady state data. Nevertheless, since the CPE element is often necessary in the impedance model to achieve good fits to measured impedance spectra, it must in such cases have an effect on the measured IMPS and IMVS responses as well. This can be taken into account in all the solutions for the dynamic IMPS and IMVS responses by replacing eq A8 with

$$\gamma = L^{-1} \sqrt{1 + (i\omega\tau)^{\beta_{\text{CPE}}}} \quad (25)$$

It is worth mentioning that the distribution of time constants, originating from the CPE behavior, is not the reason why the IMPS responses cannot be described well by a single RC time constant, in other words, it is not the reason why the IMPS transfer function is typically a distorted arc in the complex plane plot rather than a semi-circle. The shape of the IMPS arc is mainly a geometrical effect of the

electron diffusion in the film,¹⁸ represented by the transmission line. The frequency dispersion by CPE is an additional effect to this macroscopic geometric dispersion, and its microscopic origin is not well understood.

The second difference is related to the chemical capacitance. To match eq 24 exactly with eq 16 the chemical capacitance (per unit volume) has to be assigned with its value at the substrate contact: $c_{\mu}(0)$. This is an important point that highlights the condition at which the diffusion model and the transmission line model can be considered physically consistent, in addition to being merely mathematically equivalent. The diffusion model allows the electron density to vary, whereas the transmission line model does not, as it assumes that the resistance and capacitance parameters have constant values along the transmission line. Physical consistency between the models is reached only when the electron density is constant in the whole film. In practice, this is obtained close to open circuit condition, unless leakage current through R_{SU} (cf. Figure 2) is substantial, or whenever the electron diffusion length is much longer than the film thickness, *i.e.* the transport of the electrons is much faster than their recombination. This issue is discussed in more detail elsewhere.^{29, 41}

3.5. Experimental Verification

As mentioned in Section 2.1, the simple relation between EIS, IMPS and IMVS transfer functions (eq 1) is valid for any kind of solar cell. In this Section we verify this experimentally for DSC.

The measured solar cell was one reported in our previous publication.⁴⁷ The cell was a conventional sandwich type glass substrate DSC with organic liquid electrolyte. The nanostructured photoelectrode was 9 μm thick room-temperature compressed TiO_2 nanoparticle film (geometric area 0.24 cm^2) that was sintered at 450 $^{\circ}\text{C}$ for 60 min.

EIS, IMPS and IMVS measurements carried out on the solar cell at low light intensity, using IM6 Impedance Measurement Unit (Zahner Elektrik GmbH & Co.KG). The light source was four red LEDs controlled by EPot external potentiostat and CIMPS software. The LEDs provided both the DC bias light and its small amplitude AC modulation. The light was incident from the PE side. The EIS and IMPS measurements were taken potentiostatically at $V_{\text{CELL}} = -0.7$ V, whereas IMVS was measure galvanostatically at a current that produced $V_{\text{CELL}} = -0.7$ V. In EIS the modulation amplitude was 10 mV, and the light intensity modulation in IMPS and IMVS was 10 % of the bias intensity. To account for possible drift in IV curve during switching from one measurement to another, five cycles of four consecutive measurements (IMPS, EIS, IMVS, EIS) were taken following right after each other. The transfer function ratio IMVS/IMPS was calculated for each neighboring pair of IMVS and IMPS spectra (nine in total). Note that knowledge of the exact light intensity is not important to these experiments,

because the DC light intensity and any optical calibration factors cancel out when calculating the IMVS/IMPS ratio.

After calibration of the CIMPS system, the IMVS/IMPS ratio spectra derived from separate IMVS and IMPS measurement at the same conditions overlapped almost exactly, as predicted by eq 1. A small 6 % constant factor difference remaining was attributed to a small error in the calibration factor and drift in the data during consecutive EIS, IMVS and IMPS measurements (See Supporting Information). In Figure 5 and Figure 6 this small error is corrected for to emphasize the fact that the shape of the IMVS/IMPS ratio spectra matches exactly with the impedance spectrum of the cell measured at the same conditions. The correspondence is excellent over the whole frequency range from 100 mHz to 10 kHz, and verifies eq 1 experimentally.

Figure 5. Complex plane plots of a) EIS, b) IMVS and c) IMPS transfer functions of a DSC measured at $V_{\text{CELL}} = -0.7\text{V}$ under illumination ($i_{\text{SC}} = 0.58 \text{ mA cm}^{-2}$, $V_{\text{OC}} = -0.78 \text{ V}$, $FF = 0.77$). Red LEDs were used to provide both the DC bias light and its small amplitude AC modulation. The light was incident from the PE side. The error bars represent the minimum and maximum values at each frequency, caused by drift during the consecutive EIS, IMVS and IMPS measurements (cf. Figure S2). In figure a) the measured IMVS/IMPS spectrum was divided by a constant factor 2.7, corresponding to an instrument calibration factor. The inset in figure a) is a magnification close to the origin, showing the characteristic feature of electron transport: a linear part with unit slope.

Figure 6. Imaginary part spectra of a) EIS, b) IMVS and c) IMPS measurements corresponding to Figure 5. The spectra peak at the characteristic frequency which is for IMVS ca. 2 Hz, corresponding to apparent electron lifetime $\tau_{\text{IMVS}} = 80$ ms, and for IMPS ca. 21 Hz, corresponding to apparent electron transport time $\tau_{\text{IMPS}} = 7.6$ ms.

The impedance spectrum displays characteristic features typical to a DSC. The peak in the imaginary part of impedance at ca. 2 Hz (Figure 6a) corresponding to the large semicircle in the complex plane plot (Figure 5a) arises from interfacial electron transfer (recombination) at the TiO_2 – electrolyte interface of the nanostructured photoelectrode film. Note the exact correspondence to the peak in the imaginary part of IMVS in Figure 6b. As shown before for open circuit conditions,^{13, 16, 17} this match is expected since both EIS and IMVS measure the electron recombination dynamics at this frequency range, hence giving same dynamic information (trapping influenced electron lifetime).

The IMPS spectrum peaks at much higher frequencies, around 20 – 30 Hz (Figure 6c), which means that electron transport from the film to the contact is much faster than their recombination in the film. Consistently with this, the impedance spectrum shows a linear part in the complex plane plot at high frequencies (inset in Figure 5a), which is a fingerprint of reasonably good quality photoelectrode where the electron diffusion length exceeds the film thickness.^{7, 40} The linear transport part in the impedance spectrum appears at the same frequency range as the IMPS response (Figure 6a and Figure 6c), confirming their common origin, namely electron diffusion in the film.

Another way of showing the correspondence of the IMVS and IMPS data to EIS, is to estimate the electron diffusion length from the measured data using eqs 7 – 9 for IMPS and IMVS and eqs 45 for EIS. Assuming uniform light absorption in the film ($a = 0.393$ in eq 7), and using the known film thickness ($d = 9 \mu\text{m}$), and the time-constants $\tau_{\text{IMVS}} = 80$ ms and $\tau_{\text{IMPS}} = 7.6$ ms estimated from Figure 6, the IMPS-IMVS-based estimate for the diffusion length is $L_n = 18 \mu\text{m}$. For the EIS based estimate, the

electron recombination resistance can be read from Figure 5a as the width of the large semicircle ($R_{\text{RECA}}^{-1} = 1680 \Omega$, where A is the geometric photoelectrode area) and the transport resistance as three times the real axis projection of the linear part at high frequencies ($R_{\text{TA}}^{-1}/3 = 120 \Omega$), which gives $L = 19 \mu\text{m}$. This agrees well with the value derived separately from the IMPS and IMVS spectra. This agreement has been reported also by Wang and Peter.¹⁷

3.5.1. Experimental Evidence from the Literature

In addition to the above result, there is some direct experimental evidence on the effect of series impedance components on the IMPS response of DSC in the literature.

Liu *et al.*⁴⁸ reported that the measured IMPS time constant decreased systematically when current collector grid was deposited on the conducting substrate, Pt was deposited on the TCO glass at the counter electrode, or the distance between the photo and counter electrodes was reduced. These effects are understandable in light of the present paper, since the modifications decrease respectively R_s , R_{CE} and R_D (Figure 2), which contribute to the series impedance Z_s (Figure 3) and thus affect the IMPS response (eqs 28 – 30). Also the negligible effect of the current collectors and Pt on the IMVS time constant reported by Liu *et al.* is expected, since Z_s does not affect the IMVS response (eqs 32 – 33). Interestingly, contrary to the present theory, decrease in the IMVS time constant was observed upon thinning the electrode gap. The reason may be an increase in the tri-iodide concentration: at given illumination, electrons are transferred from the electrolyte to the TiO_2 by photoexcitation of the dye, resulting in production of excess I_3^- at the open circuit under illumination. This excess I_3^- is diluted to a higher concentration the thinner the electrolyte is, which promotes faster electron recombination with I_3^- .

IMPS response has been also shown to slow down considerably when the DC current of the cell is limited by ionic diffusion in the electrolyte, giving rise to an additional time constant corresponding and spiraling of the IMPS response to positive imaginary values.^{49, 50} This is at least qualitatively consistent with the present model that predicts attenuation of the IMPS response when Z_s becomes high due to increase of electrolyte diffusion impedance Z_D near the electrolyte diffusion limited condition.

3.6. Final Remarks

3.6.1. EIS vs IMPS and IMVS Techniques

An important difference between the EIS, IMVS and IMPS techniques regarding practical applications is that the time constants measured with IMPS and IMVS cannot be readily to predict the steady state operation and performance of the solar cell,¹⁴ whereas EIS yields directly such information as it gives the internal cell resistances that are directly related to the solar cell IV curve (eq 6, and refs.⁸,

^{28, 29}). As discussed by Bisquert *et al.*,⁴⁴ this difference can be understood by the general relation, $\tau = RC$, between time-constant (τ), resistance (R) and capacitance (C). While IMPS and IMVS are normally interpreted in terms of time-constants, EIS yields separately the corresponding resistance and capacitance, *i.e.* twice as much information as IMPS and IMVS. This is due to the practical reason that in the IMPS and IMVS analysis half of the measured data are usually omitted, namely the real part of the response spectra, and only the imaginary part is used for estimating time constants, as in Figure 6. Doing so in IMPS, information is lost on how much photocurrent is produced (*i.e.* the differential IPCE, *cf. e.g.* ref.¹⁸) and attention is paid only on how fast it follows the photoexcitation. Correspondingly in IMVS, information on the magnitude of the photovoltage modulation is lost when the focus is only on the photovoltage relaxation time.

If also the real part of the IMPS and IMVS spectra was analyzed, a more complete picture of the solar cell function would be obtained, but this would require accounting for the light harvesting and electron injection efficiencies to quantify the AC electron generation rate (eqs A12 and A13). However, taking the ratio of the potentiostatic IMPS and galvanostatic IMVS responses, the photomodulation component cancels out, leaving just the relation between the produced AC current and voltage, which is equal to cell impedance (eqs 1 – 4). It is interesting to note with this regards that combinations of photocurrent and photovoltage transient measurements are sometimes used to estimate the photoelectrode chemical capacitance.^{51, 52} The fact that same results are obtained as with EIS⁵² is understandable in light of eq 1.

3.6.2. Role of the Photoelectrode Capacitance in the RC Attenuation of the IMPS Response

Voltage dependent IMPS^{11, 16} and equivalent small amplitude photocurrent transient measurements⁵³ have shown that the IMPS time constant increases (photocurrent response slows down) as the solar cell is biased from the short circuit towards the open circuit. The reason for this has been explained to be increasing RC-attenuation due to the photoelectrode (chemical) capacitance c_μ increasing with voltage.^{11, 52-54} In fact, this has been considered to set an experimental limitation to the IMPS technique, restricting its use only to short circuit conditions, where the RC attenuation is less pronounced and dominated by the capacitance of the substrate – electrolyte interface.^{11, 16, 52-54} Furthermore, the substrate dominated RC attenuation can be corrected for by determination of the attenuation factor (eq 11) by separate EIS measurements.^{11, 39, 52, 53} A question thus arises can the IMPS response be corrected also for the RC-attenuation caused by c_μ elsewhere along the IV curve, by removing its contribution from the measured transport time, as sometimes attempted?⁵⁴

Eq 11 shows that the attenuation factor is in fact independent of c_μ that instead affects the IMPS response *via* the boundary condition, eq 9. However, the value entering the expression is not the capacitance of the whole film (in units Fm^{-2}), but the chemical capacitance *per unit volume* (Fm^{-3}), at

the contact, $c_\mu(0)$. After all, electron density in the film is turned to externally measurable voltage only at the contact. Moreover, when eqs 9 and 13 and the relation $Dc_\mu(0) = r_T(0)^{-1}$ (eq 18) are used in the general solution of modulated electron density (eq S13 in the Supporting Information), or in the final analytical expressions for the IMPS and IMVS transfer functions (eqs A19 – A22), $c_\mu(0)$ cancels out, leaving just the electron transport resistance $r_T(0)$ (a steady state parameter) explicitly in the expressions. This means that c_μ influences the IMPS and IMVS transfer functions only through the frequency dependent term γ (eq 25 with eqs 18 and 19), just like it does for the impedance (eq 24).

These observations evidence the general theoretical result of Bisquert and Vikhrenko:¹⁴ the chemical capacitance of the photoelectrode film is an inseparable property of the dynamic electron transport (diffusion) in the film, and affects the IMPS and IMVS response through the value of the dynamic electron diffusion coefficient D_n (eqs S6 and S9) and lifetime τ_n (eqs S7 and S10; remember our notation $D = D_n$ and $\tau = \tau_n$ in this paper). Its influence on the electron transport time cannot thus be removed to yield a more accurate, chemical-capacitance-independent transport time, unless the capacitance (or density) of the conduction band electrons can be distinguished experimentally from that of the trapped electrons (eq 10), which nevertheless is not possible based solely on EIS, IMVS, and IMPS data.¹⁴

The best way to deal with c_μ in the dynamic transport measurements is to determine the electron transport resistance r_T instead. This can be done by IMPS using eqs S6 and 18 with additional information on c_μ at the same measurement conditions, or directly by equivalent circuit fitting of EIS data. Unlike the dynamic transport time, r_T is a steady state parameter that is directly related to the solar cell performance. The same applies to the recombination resistance r_{REC} (measurable by EIS) and τ_n measurable both by IMVS and EIS.^{14, 44}

3.6.3. Complementary Nature of IMPS, IMVS and EIS

The above discussion shows that EIS can give the same, and more useful, information on the DSC operation than IMPS, but this does not mean that the IMPS technique would be dispensable. For example, at the short circuit condition, EIS fails to give information on the electron transport, since the photoelectrode impedance is very high, but IMPS works well yielding estimates for D_n . Also when $L < d$ (bad solar cell), r_T and r_{REC} , as well as c_μ become immeasurable by EIS (the so called Gerischer impedance case, cf. Appendix I of ref.²⁹ for discussion of this issue). Yet, estimates for D_n , τ_n and L may be attainable even in such a case by careful model based IMPS and IMVS analysis.¹⁸

It would be fruitful to identify other conditions where the complementary nature of the IMPS, IMVS and EIS techniques gives better resolution of the DSC performance characteristics than a single

technique alone. This can be done by a parametric study using the mathematical results of the present paper.

3.6.4. Assumption of Linear Electron Recombination Kinetics

The IMPS and IMVS model discussed here is based on the linear time-dependent electron continuity equation (eq A1) and this choice was motivated in Section 2.3. The results obtained are nevertheless useful also in the case of non-linear electron recombination. The non-linearity affects only the continuity equation, for which eq A2 (with eqs 9 and 13) is the correct boundary conditions for potentiostatic IMPS and galvanostatic IMVS techniques or their equivalent time-domain counterparts^{19, 52, 55}, even in the non-linear case. Moreover, it has been shown that eq A1 is formally valid for the analysis of small amplitude responses when homogenous background generation rate and density of electrons in the films is assumed, even in the case of non-linear recombination,^{24, 34} and non-negligible direct electron recombination with oxidized dye molecules.³⁴ Such conditions can be approximately found close to open circuit condition using weakly absorbed bias light.

4. CONCLUSIONS

The paper unified the analytical models widely used for analyzing experimental electrochemical impedance spectroscopy (EIS), intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) data. The main conclusions of the paper can be summarized as follows.

Simple general relation between EIS, IMPS and IMVS, eq 1, follows directly from the definition of the corresponding transfer functions and is valid for any solar cell or measurement condition in the limit of small modulation amplitude where linear response can be assumed. This means that the three techniques yield very similar dynamic information and can be considered complementary to each other. Here, the relation was verified both theoretically and experimentally for nanostructured electrochemical dye solar cells.

The EIS, IMPS, and IMVS models can be linked by expressing the kinetic boundary condition of the time-dependent continuity equation of electrons used in the IMPS and IMVS modeling in terms of series and parallel impedances found in the equivalent circuit impedance model of the complete solar cell. This also gives the kinetic boundary condition an unambiguous yet general physical interpretation.

It has been previously shown how EIS data can be linked to steady state current – voltage (IV) data of DSC using a common model based only on physical parameters.²⁹ The present paper links the IMPS and IMVS techniques to the same model by providing analytical expressions for potentiostatic IMPS and

galvanostatic IMVS transfer functions of complete DSCs applicable at any point along the IV curve. The result is a complete analytical dynamic-static opto-electrical model for DSCs.

The so-called RC attenuation of the IMPS response originates from all internal impedance components of the solar cell connected in series and parallel with the photoelectrode, and does not depend on the chemical capacitance of the nanostructured semiconductor photoelectrode film. As known from previous works of Bisquert *et al.*,^{14, 43} the chemical capacitance is an inseparable property of the dynamic electron transport and recombination in film. Its influence on the measured dynamic electron diffusion coefficient and lifetime cannot be corrected for based solely on EIS, IMPS and IMVS data.

Capacitive frequency dispersion of the constant phase element (CPE) type enters the IMPS and IMVS transfer functions similar to impedance and can be interpreted as a distribution of relaxation times (dynamic electron recombination time) as distinct from the frequency dispersion due to the electron diffusion process described by the transmission line model.

The theoretical linking of the EIS, IMPS, and IMVS techniques in this paper provides a basis for investigating whether conditions can be found where the complementary nature of the three techniques comes together to give more accurate description of the DSC operation than obtained with single technique alone.

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Supplementary Information available: Summary based on previous literature of the transmission line impedance model of complete DSCs, interpretation of the IMPS and IMVS time constant and the solution for eq A1 in the general case of arbitrary optical conditions. Proof that eq 1 hold for this general solution and yields an expression for the photoelectrode impedance identical to that of the transmission line model. Details and experimental data on the determination of the instrumental calibration factor in IMVS/IMPS ratio measurements and drift during the measurements.

5. APPENDIX

Time-dependent Differential Equation Model of IMPS and IMVS

The standard analytical model for the IMPS and IMVS responses is based on solving the time dependent continuity equation for the excess electron density n_e in the nanostructured photoelectrode film¹¹

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

where D and τ are respectively the electron diffusion coefficient and lifetime, and $g = g(x, t)$ the local rate of electron generation. Note that the total electron density is $n = n_e + n_0$ where n_0 is the equilibrium electron density in the dark. The basic assumptions needed for analytical solution are that D and τ are constants independent of electron density and position in the film, and that the electron recombination is linear with electron density. See Section 2.3 for discussion on the implications of these assumptions.

The model is most commonly solved subject to a kinetic boundary at the substrate contact ($x = 0$)¹¹

$$D \frac{\partial n_e}{\partial x} \bigg|_{x=0} = k_{\text{EXT}} n_e(0, t) \quad \text{for all } t \quad (\text{A2})$$

where k_{EXT} is the rate constant for electron extraction from the film. This rate constant is discussed in Section 3.1 and 3.2 and given a physical interpretation in terms of the impedance components of the complete solar cell, linking thus mathematically the IMPS/IMVS model to the EIS model.

At the far edge of the film a reflecting boundary condition is applied

$$\frac{\partial n_e}{\partial x} \bigg|_{x=d} = 0 \quad \text{for all } t \quad (\text{A3})$$

where d is the photoelectrode film thickness. The generation term

$$g(x, t) = \eta_{\text{INJ}} \Phi(t) f_{\text{LH}}(x) \quad (\text{A4})$$

depends on the incident photon flux Φ ($\text{m}^{-2}\text{s}^{-1}$), the quantum efficiency of electron injection η_{INJ} , and the spatial light harvesting efficiency $f_{\text{LH}}(x)$ that has units m^{-1} and defines the electron generation profile in the photoelectrode film.¹⁸ In the IMPS and IMVS experiments one is interested only on the modulated part of the photon flux

$$\Phi_{\text{AC}}(\omega, t) = \delta \Phi_{\text{DC}} e^{i\omega t} \quad (\text{A5})$$

where Φ_{DC} is the DC bias photon flux and δ the modulation depth that is typically kept below 0.1 (10 %) to maintain linearity of the response. The time-dependent electron generation rate becomes thus (eqs A4 and A5)

$$g_{\text{AC}}(x, t) = G(x) = \eta_{\text{INJ}} \delta \Phi_{\text{DC}} f_{\text{LH}}(x) e^{i\omega t} \quad (\text{A6})$$

The solution for eq A1 with this generation term can be written as

$$n_{\text{AC}}(x, \omega, t) = N(x, \omega) e^{i\omega t} \quad (\text{A7})$$

where N is the local frequency-dependent amplitude of the modulated excess electron density.

The IMPS transfer function of the TiO₂ photoelectrode film is obtained from eqs 3, A5, and A7 using the Fick's law of diffusion

$$F_{\text{IMPS, TiO}_2}^*(\omega) = \frac{D}{\delta\Phi_{\text{DC}}} \left(\frac{\partial N(x, \omega)}{\partial x} \Big|_{x=0} \right) \quad (\text{A8})$$

whereas the IMVS transfer function of the photoelectrode

$$F_{\text{IMVS, TiO}_2}^*(\omega) = \frac{N(0, \omega)}{\delta\Phi_{\text{DC}} c_\mu(0)} \quad (\text{A9})$$

is obtained from eq 4 by noting that the electron density and the voltage measurable at the PE contact are related to each other by the chemical capacitance of the TiO₂ film per unit volume (Fm⁻³)

$$c_\mu(0) = -q_e \frac{\partial n_e(0)}{\partial V_{\text{TiO}_2}} = -q_e \frac{N(0, \omega)}{V_{\text{TiO}_2, \text{AC}}} \quad (\text{A10})$$

at the contact ($x = 0$). (Note: There is a sign error in the corresponding eq 14 in ref.¹⁸.) Here, the voltage over the TiO₂ film is defined as the difference between the electrical potential (ϕ) at the contact vs the electrical potential in the electrolyte $V_{\text{TiO}_2} = \phi_{\text{TiO}_2}(x = 0) - \phi_{\text{EL}}(x = d)$, and is thus negative at the open circuit condition of the cell. The same applies to cell voltage: $V_{\text{CELL}} = \phi_{\text{PE}} - \phi_{\text{CE}}$. According to the definitions of eqs A8 and A9 both IMPS and IMVS transfer functions have positive real part at the limit of zero frequency.

Note that when the IMPS and IMVS transfer functions are calculated using the same value for k_{EXT} , they are related to each other simply as¹⁸

$$F_{\text{IMPS, TiO}_2}^*(k_{\text{EXT}}, \omega) = c_\mu(0) k_{\text{EXT}} F_{\text{IMVS, TiO}_2}^*(k_{\text{EXT}}, \omega) \quad (\text{A11})$$

which can be seen by comparing eqs A8 and A9 in light of eq A2. This relation proves useful in the mathematical derivations of this paper.

Complete Solar Cell IMPS and IMVS Transfer Functions in the Case of Simple Optical Model with Monochromatic Modulated Light

According to a basic optical model of DSC (cf. eqs 6, 39 and 40 of ref.¹⁸) the local AC modulated electron generation rate is

$$g_{\text{AC, PE-side}}(x) = \delta\Phi \eta_{\text{INJ}} T_{\text{TCO}} [1 - r_{\text{PE}}] \alpha_{\text{D}} e^{-\alpha x} \quad (\text{A12})$$

when the light is incident from the side of the collecting contact of the photoelectrode (PE illumination) and

$$g_{\text{AC, CE-side}}(x) = \delta\Phi \eta_{\text{INJ}} T_{\text{CE}} T_{\text{EL}} [1 - r_{\text{PE}}] \alpha_{\text{D}} e^{\alpha(x-d)} \quad (\text{A13})$$

when the light comes from the opposite direction (CE illumination). These expressions assume that the harmonic small amplitude light modulation is provided by monochromatic light absorbed in the

photoelectrode film exponentially according to the Beer-Lambert law as determined by a single value for the absorption coefficient α . This is the normal case when *e.g.* laser or LED is used as a light source for the modulated beam, in addition to a DC background illumination that can be any kind of light.

The IMPS transfer functions of the photoelectrode film for these two cases have been reported elsewhere.¹⁸ According to the definition of eq 3 they can be expressed as (from eqs 6, 11, 39, 40, 42, 45, 47 and 48 of ref.¹⁸)

$$F_{\text{IMPS, TiO}_2, \text{PE-side}}^*(\omega) = T_{\text{TCO}} [1 - r_{\text{PE}}] \alpha_{\text{D}} \eta_{\text{INJ}} (\gamma^2 - \alpha^2)^{-1} k_{\text{EXT}} A_{\text{PE-side}} \quad (\text{A14})$$

$$F_{\text{IMPS, TiO}_2, \text{CE-side}}^*(\omega) = T_{\text{CE}} T_{\text{EL}} [1 - r_{\text{PE}}] \alpha_{\text{D}} \eta_{\text{INJ}} (\gamma^2 - \alpha^2)^{-1} e^{-\alpha d} k_{\text{EXT}} A_{\text{CE-side}} \quad (\text{A15})$$

where

$$A_{\text{PE-side}} = \frac{\gamma \sinh(\gamma d) - \alpha \cosh(\gamma d) + \alpha e^{-\alpha d}}{\gamma D \sinh(\gamma d) + k_{\text{EXT}} \cosh(\gamma d)} \quad (\text{A16})$$

$$A_{\text{CE-side}} = \frac{\gamma \sinh(\gamma d) + \alpha \cosh(\gamma d) - \alpha e^{\alpha d}}{\gamma D \sinh(\gamma d) + k_{\text{EXT}} \cosh(\gamma d)} \quad (\text{A17})$$

and γ is given by

$$\gamma = \sqrt{\frac{1}{D} \left(\frac{1}{\tau} + i\omega \right)} \quad (\text{A18})$$

or eq 25.

Now, using eqs A14, A15, and 9 – 11 we can find the corresponding expressions for the complete solar cell. The IMPS transfer function of the complete DSC for the PE side illumination is

$$F_{\text{IMPS, CELL, PE-side}}^*(\omega) = \frac{Z_{\text{P}}}{Z_{\text{P}} + Z_{\text{S}}} \cdot \frac{T_{\text{TCO}} [1 - r_{\text{PE}}] \alpha_{\text{D}} \eta_{\text{INJ}} [\gamma \sinh(\gamma d) - \alpha \cosh(\gamma d) + \alpha e^{-\alpha d}]}{(\gamma^2 - \alpha^2) \left[\left(\frac{Z_{\text{P}} Z_{\text{S}}}{Z_{\text{P}} + Z_{\text{S}}} + Z_{\text{CO}} \right) c_{\mu}(0) \gamma D \sinh(\gamma d) + \cosh(\gamma d) \right]} \quad (\text{A19})$$

and for the CE illumination

$$F_{\text{IMPS, CELL, CE-side}}^*(\omega) = \frac{Z_{\text{P}}}{Z_{\text{P}} + Z_{\text{S}}} \cdot \frac{T_{\text{CE}} T_{\text{EL}} [1 - r_{\text{PE}}] \alpha_{\text{D}} \eta_{\text{INJ}} [\gamma \sinh(\gamma d) + \alpha \cosh(\gamma d) - \alpha e^{\alpha d}] e^{-\alpha d}}{(\gamma^2 - \alpha^2) \left[\left(\frac{Z_{\text{P}} Z_{\text{S}}}{Z_{\text{P}} + Z_{\text{S}}} + Z_{\text{CO}} \right) c_{\mu}(0) \gamma D \sinh(\gamma d) + \cosh(\gamma d) \right]} \quad (\text{A20})$$

The corresponding IMVS transfer functions can be obtained from eqs 13 and 15 with eqs A14 and A15.

The result for the PE side illumination is

$$F_{\text{IMVS, CELL, PE-side}}^*(\omega) = \frac{Z_p \cdot \frac{T_{\text{TCO}} [1 - r_{\text{PE}}] \alpha_D \eta_{\text{INJ}} [\gamma \sinh(\gamma d) - \alpha \cosh(\gamma d) + \alpha e^{-\alpha d}]}{(\gamma^2 - \alpha^2) [(Z_p + Z_{\text{CO}}) c_{\mu}(0) \gamma D \sinh(\gamma d) + \cosh(\gamma d)]}}{Z_p \cdot \frac{T_{\text{TCO}} [1 - r_{\text{PE}}] \alpha_D \eta_{\text{INJ}} [\gamma \sinh(\gamma d) - \alpha \cosh(\gamma d) + \alpha e^{-\alpha d}]}{(\gamma^2 - \alpha^2) [(Z_p + Z_{\text{CO}}) c_{\mu}(0) \gamma D \sinh(\gamma d) + \cosh(\gamma d)]}} \quad (\text{A21})$$

and for the CE illumination

$$F_{\text{IMVS, CELL, CE-side}}^*(\omega) = \frac{Z_p \cdot \frac{T_{\text{CE}} T_{\text{EL}} [1 - r_{\text{PE}}] \alpha_D \eta_{\text{INJ}} [\gamma \sinh(\gamma d) + \alpha \cosh(\gamma d) - \alpha e^{\alpha d}] e^{-\alpha d}}{(\gamma^2 - \alpha^2) [(Z_p + Z_{\text{CO}}) c_{\mu}(0) \gamma D \sinh(\gamma d) + \cosh(\gamma d)]}}{Z_p \cdot \frac{T_{\text{CE}} T_{\text{EL}} [1 - r_{\text{PE}}] \alpha_D \eta_{\text{INJ}} [\gamma \sinh(\gamma d) + \alpha \cosh(\gamma d) - \alpha e^{\alpha d}] e^{-\alpha d}}{(\gamma^2 - \alpha^2) [(Z_p + Z_{\text{CO}}) c_{\mu}(0) \gamma D \sinh(\gamma d) + \cosh(\gamma d)]}} \quad (\text{A22})$$

Table of contents entry

Electrochemical impedance spectroscopy (EIS), and intensity-modulated photocurrent (IMPS) and photovoltage (IMVS) spectroscopies used for performance characterization of dye solar cells are linked under a common model explaining their fundamental relation.

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