

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

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Supporting Information to the Paper

Impedance of Complete Dye Solar Cell

The transmission line impedance model of the DSC photoelectrode known from previous literature is summarized for reference to the discussion in the paper.

The impedance corresponding to the generalized equivalent circuit of Figure 3 is (in units $\Omega \text{ m}^2$)

$$Z_{\text{CELL}} = Z_{\text{S}} + \frac{Z_{\text{P}}(Z_{\text{CO}} + Z_{\text{TiO}_2})}{Z_{\text{P}} + Z_{\text{CO}} + Z_{\text{TiO}_2}} \quad (\text{S1})$$

The impedance of the nanostructured nanoporous photoelectrode film, Z_{TiO_2} , is of our special interest. It can be expressed according to the transmission line model as¹

$$Z_{\text{TiO}_2} = \sqrt{\frac{r_{\text{T}} r_{\text{REC}}}{1 + (i\omega/\omega_{\text{REC}})^{\beta_{\text{CPE}}}}} \coth\left((\omega_{\text{REC}}/\omega_{\text{T}})^{\beta_{\text{CPE}}/2} \sqrt{1 + (i\omega/\omega_{\text{REC}})^{\beta_{\text{CPE}}}}\right) \quad (\text{S2})$$

where

$$\omega_{\text{REC}} = (r_{\text{REC}} q_{\text{CPE}})^{-1/\beta_{\text{CPE}}} \quad (\text{S3})$$

is the characteristic frequency of the interfacial charge transfer process (electron recombination), and

$$\omega_{\text{T}} = (r_{\text{T}} q_{\text{CPE}} d^2)^{-1/\beta_{\text{CPE}}} \quad (\text{S4})$$

is the characteristic frequency of electron transport across the film. The parameters q_{CPE} and β_{CPE} are the pre-factor and exponent of the constant phase impedance element per unit volume of the electrode film (in units $\Omega \text{ m}^3$)

$$z_{\text{CPE}} = q_{\text{CPE}}^{-1} (i\omega)^{-\beta_{\text{CPE}}} \quad (\text{S5})$$

which accounts for the frequency dispersion of the capacitive element, found virtually always in EIS data. The dispersion is characterized by the value of β_{CPE} being typically in the range $0.85 < \beta_{\text{CPE}} < 0.95$.

IMPS and IMVS Time Constants

To support the discussion in the paper, brief summary of the interpretation of the measured IMPS and IMVS time constants is given in the following based on previous literature.

The IMPS and IMVS spectra exhibit usually one characteristic (angular) frequency ω_{IMPS} and ω_{IMVS} , identified as peaks in the imaginary part vs frequency plot at the frequencies $f_{\text{IMPS}} = \omega_{\text{IMPS}}/2\pi$ and $f_{\text{IMVS}} = \omega_{\text{IMVS}}/2\pi$. The characteristic frequencies correspond to time constants $\tau_{\text{IMPS}} = \omega_{\text{IMPS}}^{-1}$ and $\tau_{\text{IMVS}} = \omega_{\text{IMVS}}^{-1}$, that are further related to the dynamic electron diffusion coefficient (D_n), lifetime (τ_n), and electron diffusion length (L_n) as

$$D_n \approx a \cdot \frac{d^2}{\tau_{\text{IMPS}}} \quad (\text{S6})$$

$$\tau_n \approx \tau_{\text{IMVS}} \quad (\text{S7})$$

$$L_n = \sqrt{D_n \tau_n} \quad (\text{S8})$$

where $a \approx 0.393$ for modulated light that is absorbed very weakly by the photoelectrode.² Eqs S6 and S7 are approximate, since the measured IMPS and IMVS time constants are affected by the electron generation profile and collection efficiency.²

According to a conventional model of DSC dynamics, interpretation of the measured time constants is complicated by the fact that they are dominated (slowed down) by multiple electron trapping and de-trapping event, expressed by the following equations³

$$D_n = \left(1 + \frac{c_{\mu,\text{trap}}}{c_{\mu,\text{CB}}} \right)^{-1} D_0 \quad (\text{S9})$$

$$\tau_n = \left(1 + \frac{c_{\mu,\text{trap}}}{c_{\mu,\text{CB}}} \right) \tau_0 \quad (\text{S10})$$

where $c_{\mu,\text{trap}}$ and $c_{\mu,\text{CB}}$ are the chemical capacitances corresponding to occupation of trap and conduction band states, and D_0 and τ_0 are the diffusion coefficient and lifetime of electrons in the conduction band. The total chemical capacitance of the photoelectrode, used in the impedance model (eqs 22 and S2 – S5) is $c_{\mu} = c_{\mu,\text{trap}} + c_{\mu,\text{CB}}$.

Eqs S9 and S10 have an important consequence: the D_n and τ_n estimated by dynamic measurements cannot be used to predict the steady state cell performance that is dictated by D_0 and τ_0 , unless the conduction band and trap chemical capacitances are determined independently by experiments.³ This problem is presently unresolved largely

because typically only one capacitance value for the photoelectrode, namely c_{μ} , can be measured at given conditions for example with EIS. Nevertheless, under the assumption behind eqs S9 and S10, namely that direct electron recombination from the traps and transport between the traps is negligible, the product of D_n and τ_n is not influenced by electron trapping,³ and hence, can be used to correctly estimate the steady state electron diffusion length $L_0 = (D_0 \tau_0)^{1/2}$, provided that both D_n and τ_n are measured at the same electron trap occupancy,⁴ or care is taken to correct the data for a difference in it.⁵ This is good news, since the estimate for L_0 can then be used to interpret and predict steady state performance data such as the incident-photon-to-collected-electron efficiency (IPCE)^{6,7} or the IV curve.^{7,8}

In this paper we use the short hand notations $D = D_n$ and $\tau = \tau_n$. *I.e.* in the dynamic modeling (EIS, IMPS, IMVS), D and τ refer to the trapping affected apparent electron diffusion coefficient and lifetime.

Solution for Arbitrary Optical Conditions and Properties

Solution for electron continuity equation (A1 with eqs A2 – A6 in the Appendix of the paper) in the general case of an arbitrary electron generation profile, meaning arbitrary optical conditions and properties of the cell, is given in the following for reference to the next section (originally derived in ref.²).

The AC modulated excess electron density is

$$n_{AC}(x, \omega, t) = N(x, \omega)e^{i\omega t} \quad (S11)$$

the amplitude of which is

$$N(x, \omega) = \int_0^d f_{LH}(\xi) N_{\delta}(x, \xi, \omega) d\xi \quad (S12)$$

where

$$N_{\delta}(x, \xi, \omega) = \frac{\delta\Phi_{DC}\eta_{INJ}}{\gamma D} \left[\cosh(\gamma(d-\xi)) \frac{\gamma D \cosh(\gamma x) + k_{EXT} \sinh(\gamma x)}{\gamma D \sinh(\gamma d) + k_{EXT} \cosh(\gamma d)} - \sinh(\gamma(x-\xi)) u(x-\xi) \right] \quad (S13)$$

is the solution of the same problem for localized (Delta function) generation at $x = \xi$,

$$\gamma = \sqrt{\frac{1}{D} \left(\frac{1}{\tau} + i\omega \right)} \quad (S14)$$

is a parameter related to the frequency dependent distribution (relaxation) of the electron density (Note: $\gamma = L^{-1}$ at $\omega = 0$), and $u(x-\xi)$ is the unit step function. Analytical expressions for the solution, namely $N(x, \omega)$ in eq S11, for different cases of electron generation profile were given and investigated in detail in ref.².

Proof that “IMVS/IMPS = EIS” in Arbitrary Optical Conditions

Using eqs 10, 11, 14 and A11, the ratio of the IMVS and IMPS transfer functions of the complete cell can be expressed in terms of the IMVS transfer function of the photoelectrode film

$$\frac{F_{\text{IMVS,CELL}}^*(\omega)}{F_{\text{IMPS,CELL}}^*(\omega)} = \frac{Z_p + Z_s}{Z_p + Z_{\text{CO}}} \cdot \frac{1}{c_\mu(0)k_{\text{EXT,IMPS}}} \cdot \frac{F_{\text{IMVS,TiO}_2}^*(k_{\text{EXT,IMVS}}, \omega)}{F_{\text{IMVS,TiO}_2}^*(k_{\text{EXT,IMPS}}, \omega)} \quad (\text{S15})$$

On the right hand side we have the ratio of two IMVS transfer functions that use different value for the kinetic parameter k_{EXT} – one corresponding to a galvanostatic IMVS experiment and the other corresponding to a potentiostatic IMPS experiment, taken at the same conditions and at the same point on the solar cell IV curve. Using eq A9, we can express these IMVS transfer functions in terms of the electron density at the photoelectrode contact

$$\frac{F_{\text{IMVS,CELL}}^*(\omega)}{F_{\text{IMPS,CELL}}^*(\omega)} = \frac{Z_p + Z_s}{Z_p + Z_{\text{CO}}} \cdot \frac{1}{c_\mu(0)k_{\text{EXT,IMPS}}} \cdot \frac{N(0, \omega, k_{\text{EXT,IMVS}})}{N(0, \omega, k_{\text{EXT,IMPS}})} \quad (\text{S16})$$

According to the solution of the electron diffusion model for arbitrary optical conditions (eqs S12 – S14), the electron density at the contact is

$$N(0, \omega, k_{\text{EXT}}) = \frac{\delta\Phi_{\text{DC}}\eta_{\text{INJ}}}{\gamma\mathcal{D} \sinh(\gamma d) + k_{\text{EXT}} \cosh(\gamma d)} \cdot \int_0^d f_{\text{LH}}(\xi) \cosh(\gamma(d - \xi)) d\xi \quad (\text{S17})$$

In the above equation, the integral expression is independent of k_{EXT} , and hence, it cancels out when we use eq S17 in eq S16. This leaves us with the following expression

$$\frac{F_{\text{IMVS,CELL}}^*(\omega)}{F_{\text{IMPS,CELL}}^*(\omega)} = \frac{Z_p + Z_s}{Z_p + Z_{\text{CO}}} \cdot \frac{1}{c_\mu(0)k_{\text{EXT,IMPS}}} \cdot \frac{\gamma\mathcal{D} \sinh(\gamma d) + k_{\text{EXT,IMPS}} \cosh(\gamma d)}{\gamma\mathcal{D} \sinh(\gamma d) + k_{\text{EXT,IMVS}} \cosh(\gamma d)} \quad (\text{S18})$$

that contains only electrical parameters – all parameters related to the optical model, including the incident light intensity and the electron injection efficiency, have cancelled out. Thus the result and what follows is valid for any optical conditions, properties or model of the solar cell (provided that the assumptions of the present models apply).

Inserting the expressions for k_{EXT} from eqs 9 and 13, eq S18 can be rearranged to

$$\frac{F_{\text{IMVS,CELL}}^*(\omega)}{F_{\text{IMPS,CELL}}^*(\omega)} = Z_s + \frac{Z_p [Z_{\text{CO}} + (c_\mu(0)\gamma\mathcal{D})^{-1} \coth(\gamma d)]}{Z_p + Z_{\text{CO}} + (c_\mu(0)\gamma\mathcal{D})^{-1} \coth(\gamma d)} \quad (\text{S19})$$

This is identical to the expression for the solar cell impedance (eqs S1 and S2), provided that the impedance of the nanostructured photoelectrode film can be expressed as

$$Z_{\text{TiO}_2} = (c_\mu(0)\gamma\mathcal{D})^{-1} \coth(\gamma d) \quad (\text{S20})$$

Inserting γ from eq S14 it can be modified to

$$Z_{\text{TiO}_2} = \frac{L}{Dc_{\mu}(0)} \frac{1}{\sqrt{1+i\omega\tau}} \coth\left(\frac{d}{L}\sqrt{1+i\omega\tau}\right) \quad (\text{S21})$$

where

$$L = \sqrt{D\tau} \quad (\text{S22})$$

is the electron diffusion length.

Eq 41 is indeed the expression for the photoelectrode impedance, that can be derived from the diffusion model of Section 2.3, or alternatively from the transmission line impedance model of the photoelectrode film.⁹

Determination of the Instrumental Calibration Factor in IMVS/IMPS Ratio Measurements

Prior to instrument calibration, the calculated IMVS/IMPS ratio based on the raw data given by an old version of the CIMPS system by ZAHNER-Elektrik GmbH & Co.KG was consistently *ca.* 2.5 – 2.7 higher than the measured impedance, irrespective of the type of solar cell or the measurement conditions. This error is a technical feature originating most likely from a deviation in scaling in our old CIMPS system version with the EPot due to the hardware routing of the measurement signals. The error was found to be absent in the latest version of the CIMPS system and in separate measurements using PGSTAT302N potentiostat controlled by NOVA software (Metrohm Autolab B.V.).

The calibration of the CIMPS system used here was done by measuring a silicon photodiode at the same conditions at open circuit, with and without an additional 1.1 kΩ resistor in series with the photodiode. Figure S1 shows the measured data. While the impedance was correctly shifted by 1.1 kΩ along the real axis, the IMVS/IMPS ratio shifted by a factor CF * 1.1 kΩ, where CF = 2.53 is the calibration factor. The calibration measurement data are given as Supplementary Information.

Consistently with the calibration factor, raw measured IMVS/IMPS ratio was a factor of 2.5 – 2.7 times higher independent of the measured solar cell sample or measurement condition (data not shown). This was true both for the real and imaginary part of the IMVS/IMPS ratio, which indicates that either the IMVS or IMPS signal processing was subject to a scaling error in the used measurement system.

The apparent variation in the scaling error (2.5 – 2.7) is most likely due to drift in the solar cell operation between consecutive EIS, IMPS and IMVS measurements. Figure S2 shows the drift observed during the measurement of the data reported in Figure 6 and 7 in the paper. The reason for the drift can be *e.g.* change in the cell temperature (illumination, Ohmic heating), potential induced changes at TiO₂ – dye – electrolyte interface (ion adsorption and re-organization of the Helmholtz double layer), proton intercalation into TiO₂, etc.

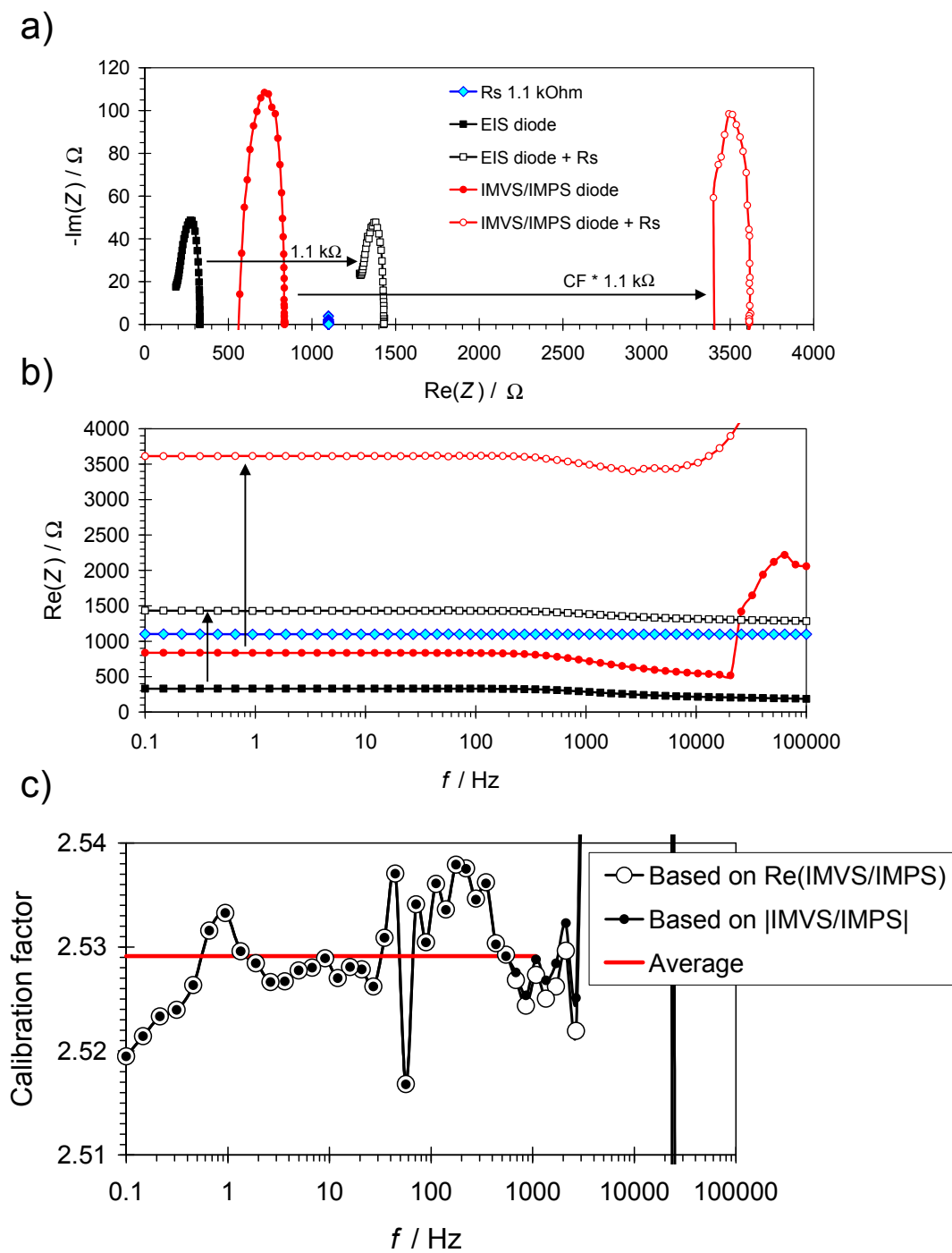


Figure S1. Calibration of the IMPS and IMVS measurement system. a) Complex plane and b) real part vs frequency of the measured impedance spectra and calculated IMVS/IMPS ratio spectra from a silicon photodiode with or without a 1.1 k Ω series connected resistor. c) Calibration factor calculated based on the effect of the additional series resistor on the magnitude or real part of the IMVS/IMPS ratio.

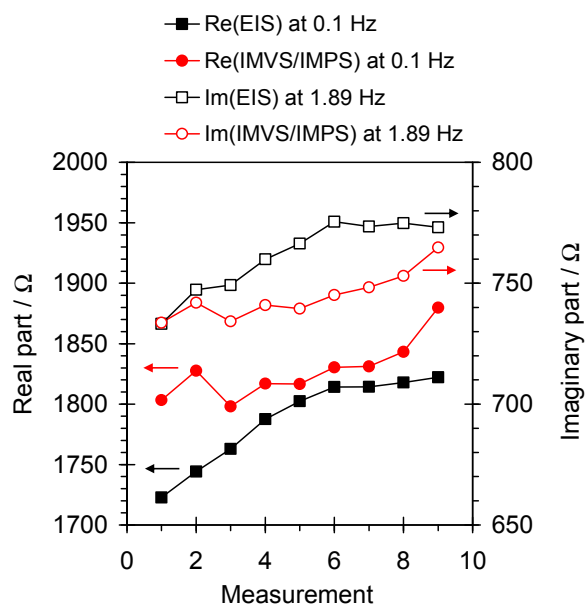


Figure S2. Drift in the EIS and IMVS/IMPS ratio spectra during the consecutive IMPS, EIS and IMVS measurements.

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