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Intensity Modulated Photocurrent Spectroscopy (IMPS) and its Application to Perovskite Solar Cells

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Abstract

Frequency domain techniques are useful tools to characterize processes occurring on different timescales in solar cells and solar fuel devices. Intensity modulated photocurrent spectroscopy (IMPS) is one such technique that links the electrical and optical response of the device. In this review, a summary of the fundamental application of IMPS to semiconductor photoelectrodes and nanostructured solar cells is presented, with a final goal of understanding the IMPS response of the perovskite solar cell (PSC) in order to shed light on its complex physical mechanisms that generate its response. The historical application of IMPS that connects its transfer function to the charge transfer efficiency of the semiconductor electrode and subsequently the considerations of diffusive transport for the dye-sensitized solar cell is summarized. These models prioritize the association of spectral features with time constants which has led to a neglect of other absolute aspects of the spectra by the photovoltaic community. We clarify these aspects by developing the fundamental connection between the absolute value of the IMPS transfer function and the external quantum efficiency (EQE_{PV}) of a photovoltaic cell. Basic models for the solar cell are developed using kinetic equations and equivalent circuits (EC), stressing their equivalence and the advantage of the EC representation to adequately account for different capacitances in the system. A critique of the current interpretations of the PSC IMPS spectra is carried out, where time constants and their evolution are associated to characteristic transport processes of either electronic or ionic carriers within the PSC. These are clarified using the EC representation to identify that the generated characteristic processes are only related to coupling between different elements of the EC and are not reflective of transport phenomena in general. Furthermore, a general model is developed that identifies charge accumulation at the interfaces as a general feature for both low and high efficiency PSCs, whose charging/discharging resistances are the main factor in controlling the electrical response of the device. This model shows a separation of the photovoltage within the PSC that causes a reduction in its EQE_{PV} at low frequencies. Further development of the PSC will involve gaining control over the low frequency charge kinetics in the device to overcome these limitations.

1. Introduction

Since their inception in 2009,¹ perovskite solar cells (PSCs) have developed tremendously with regards to both energy conversion efficiency and device stability under ambient conditions,² with current efficiencies³ in excess of 23% for a single junction configuration and 25.2% in a tandem configuration.⁴ This growth can be related to the information obtained regarding the operation of the PSC,⁵ especially from frequency domain measurements that allow the resolution of processes of charge storage, recombination and transport over a range of timescales.

A well known frequency domain technique used to characterize solar cells is Impedance Spectroscopy (IS). IS involves the application of an AC small perturbation of voltage and measuring the subsequent AC current response, scanned over a wide range of frequencies. This allows the separation of mechanistic processes occurring on different timescales in a relatively simple manner. While IS has been very successful in identifying transport and recombination properties of dye-sensitized solar cells (DSSCs),⁶⁻⁸ the PSC has proved less fruitful. A promising complementary small perturbation technique to IS to probe the optoelectronic response of the solar cell is Intensity Modulated Photocurrent Spectroscopy (IMPS). This technique involves the application of a small perturbation of light intensity and measuring the corresponding modulated current response, scanned over a range of frequencies. In fact, IMPS was used previously to study the transport and recombination phenomena in DSSCs⁹ and also for decoupling the kinetics at semiconductor/electrolyte interfaces.¹⁰ Therefore, due to the general complexity and variability in results obtained regarding the working of PSCs in different laboratories, coupled with the rapid degradation processes currently affecting them, a viable strategy is to combine the inferences obtained from both IS and IMPS in order to generate reliable information regarding the operation of the PSC.

Firstly, a comprehensive summary of the role and interpretation of spectra obtained from IMPS in identifying surface charge transfer efficiencies for photoelectrodes and diffusion lengths and lifetimes in DSSCs is provided, focussing on the power of combining multiple small perturbation techniques to generate information about the device. The current interpretation of IMPS spectra is discussed, starting from the kinetic models of the semiconductor/electrolyte interface developed by Peter et al.¹¹ This model allows the decoupling of recombination and charge transfer to determine the charge transfer efficiency based on the association of spectral features with characteristic time constants. This was then followed by the transport-recombination model¹² for nanostructured electrodes that allowed the determination of characteristic diffusion parameters from the IMPS spectra.⁹ These studies led to arbitrary association of characteristic transport processes to interpret the IMPS spectra of devices, which are discussed extensively. Through a detailed critique that includes a basic model for the photovoltaic response in a typical solar cell, we provide an argument for focussing on the absolute values of the normalized IMPS transfer function based on its connection to the photovoltaic external quantum efficiency (EQE_{PV}). Furthermore, we stress the

importance of establishing the equivalent circuit (EC) of the system being studied in order to adequately account for all the capacitances within the system. This method identifies an arbitrary coupling between different elements in the EC that form time constants that are unrelated to characteristic transport times. Based on these developed ideas, a comprehensive electrical model of the PSC is presented that connects its EQE_{PV} , internal voltage, capacitances, resistances and their different qualities that generate the rich and unique kinetic response of the PSC.

2. The method of IMPS

2.1. IMPS basic definitions

The photovoltaic external quantum efficiency EQE_{PV} is a relationship between the collected electrical current j_e and ϕ , the incident spectral photon flux, at a wavelength λ . It is convenient to express the spectral flux in the units of electrical current

$$j_\phi = q\phi \quad (1)$$

where q is the elementary charge. The EQE_{PV} of a solar cell is given by

$$EQE_{PV}(\lambda) = \frac{j_e(\lambda)}{j_\phi(\lambda)} \quad (2)$$

Integration of the EQE_{PV} composed with the incident spectral flux over the range of wavelengths of illumination yields the photocurrent j_{sc} of the solar cell.

A closely related quantity to the EQE_{PV} is the IMPS transfer function. Formally, IMPS involves the measurement of a modulated extracted current density $\tilde{j}_e$ upon the application of a small perturbation of modulated photon flux $\tilde{\phi}$ over a wide range of frequencies, generally between 10^{-2} - 10^6 Hz, as indicated in Figure 1. This photon flux is usually monochromatic and is superimposed on top of a steady state extracted current density $\bar{j}_e$ due to an input steady state photon current density $\bar{j}_\phi$, where steady state values are indicated by an overbar.

Figure 1 The variables involved in the calculation of the IMPS transfer function Q . A small perturbation of photon flux expressed as a current density is applied from a given steady state of photon current density $\bar{j}_\phi$ and extracted current density $\bar{j}_e$ (blue point),

and the corresponding modulated current density is recorded. The low frequency limit of the transfer function is also shown.

The IMPS transfer function Q is then calculated as¹³

$$Q(\omega) = \frac{\tilde{j}_e(\omega)}{\tilde{j}_\phi(\omega)} \quad (3)$$

It can be seen in Equation 3 that Q is a current-to-current ratio and hence is dimensionless. IMPS can be measured under any given DC bias voltage or light intensity. The data is generally represented either in the form of a Q -plane plot, which is a plot of the real part of the IMPS transfer function $Q'(\omega)$ versus the negative imaginary part $-Q''(\omega)$, or in terms of the evolution of Q' versus frequency.

The notation Q is applied to the expression of IMPS normalized as in Equation 3, that emphasizes the connection to the EQE_{PV} as discussed later. There are alternative traditional names for the IMPS transfer function presented in different units, such as H , as the spectral data were mainly used to evaluate kinetic time constants, rather than absolute values.

2.2. The connection of EQE to IMPS

In the analysis of small perturbation techniques, the low frequency limit of the transfer function takes a special significance, since it relates directly to the steady-state characteristic of the input-output signals in the device. In the case of IS, it is well known that the low frequency resistance is the inverse derivative of the j-V curve. Similarly, in the case of IMPS, a connection occurs to the steady state current-illumination curve, as discussed in general by Bertoluzzi and Bisquet in Ref. 13 and described for perovskite solar cells by Ravishankar et al.¹⁴ This is summarized in the following paragraphs.

The extracted current density can be expanded in a Taylor series using the small perturbation condition ($\bar{j}_\phi \gg \tilde{j}_\phi$) as

$$j_e(\bar{j}_\phi + \tilde{j}_\phi) = \bar{j}_e + \frac{d\bar{j}_e}{d\bar{j}_\phi} \tilde{j}_\phi + \frac{d^2\bar{j}_e}{d\bar{j}_\phi^2} \tilde{j}_\phi^2 \dots \quad (4)$$

By ensuring a linear response, we get the low frequency (LF) limit of the transfer function as

$$Q(0) = \frac{d\bar{j}_e}{d\bar{j}_\phi} \quad (5)$$

Figure 2 Schematic of the experimental setup used for measuring the EQE_{PV} of a solar

cell. An AC pulse of monochromatic radiation arrives on the sample, which is at a steady state of DC illumination. The frequency of the AC pulse is determined by the chopper and the current response is measured. Reproduced with permission from Ref. 15. Copyright 2013, AIP Publishing.

By comparing Equation 3 and 5, it is observed that the IMPS transfer function is in fact a quantity closely related to the EQE_{PV} of the solar cell. In order to understand this clearly, we consider the traditional method of EQE_{PV} measurement, termed the *differential spectral response method*,¹⁵ whose setup is shown in Figure 2. The solar cell is kept under a DC background light intensity, followed by measurement of the solar cell response to an AC perturbation of monochromatic light intensity, whose frequency is determined by a mechanical chopper or by an AC driving current to the light source. Generally, this frequency is of the order of a few tens-hundreds of Hertz. We can then define the transfer function of the differential spectral response method as¹⁵

$$EQE_{PV-DIFF} = \frac{d\bar{J}_e}{dJ_\phi}(\omega_{chopper}) \quad (6)$$

It can be seen that by comparing Equations 5 and 6 that the LF limit of the IMPS transfer function is in fact the EQE_{PV} as obtained from the differential spectral response method with the chopper frequency tending to zero,

$$EQE_{PV-DIFF IMPS} = \frac{d\bar{J}_e}{dJ_\phi}(\omega \rightarrow 0) = Q'(0) \quad (7)$$

In addition, a steady state EQE can be defined from the absolute values of input and output currents as

$$EQE_{PV-SS} = \frac{\bar{J}_e}{J_\phi} \quad (8)$$

It must be noted that $EQE_{PV-DIFF}$ can also be obtained by differentiating the quantity $\bar{J}_e(J_\phi)$ plotted in the graph of Equation 8.

In order for a proper matching of these quantities, certain considerations need to be met in the experimental study. In several instances, due to the fact that a modulated driving current to the LED is required to generate the modulated photon flux, the measured output of the IMPS setup is the ratio of modulated extracted current versus the input current that drives the LED (j_{LED}), which therefore requires a transformation in order to obtain the IMPS transfer function as defined in Equation 3. For simplicity, we derive the value of this scaling factor at a modulation frequency of zero, which is subsequently applicable to the whole range of frequencies. The first step involves measuring the output light intensity I of the LED with wavelength λ for different j_{LED} values, using the responsivity R (W/A) of a calibration photodiode. The slope p is then calculated at each measured point as

$$p(\bar{I}) = \frac{d\bar{J}_{LED}}{d\bar{I}}(\bar{I}) \quad (9)$$

Using Equation 9, the current density corresponding to an amplitude perturbation of

10% in light intensity is set as an input for each DC light intensity at which IMPS is measured. The ratio of the extracted current versus input light intensity at zero modulation frequency can then be expressed as

$$\frac{d\bar{J}_e}{d\bar{I}} = \frac{d\bar{J}_e}{dJ_{LED}} \times p(\bar{I}) \quad (10)$$

Using the relation between photon intensity and photon current density, we have

$$d\bar{I} = d\bar{J}_\phi \times \left(\frac{hc}{q\lambda}\right) \quad (11)$$

where h is Planck's constant and c is the speed of light. Combining Equations 10 and 11, we obtain the relation

$$Q(0) = \frac{d\bar{J}_e}{dJ_\phi} = \frac{d\bar{J}_e}{dJ_{LED}} \times \left(\frac{hcp(\bar{I})}{q\lambda}\right) \quad (12)$$

Therefore, the output transfer function as measured by the IMPS setup is scaled by a factor of $(hcp(\bar{I})/q\lambda)$ to obtain the IMPS transfer function Q .

Figure 3 (a) IMPS equivalent circuit of the basic solar cell model with series resistance R_s , external DC voltage $\bar{V}_{ext}$, chemical capacitance C_μ , recombination resistance R_{rec} , DC current source $\bar{J}_\phi$. The modulated voltage source $\hat{V}_{ext}$ for an IS measurement and modulated current source $\hat{J}_\phi$ for an IMPS measurement are also shown. (b) Z-plane IS response and (c) Q-plane IMPS response of the circuit shown in (a) with the intercepts

and characteristic frequency values denoted.

3. IMPS Modelling

3.1. Basic Solar Cell

In this section, we develop the IMPS response of a simple solar cell, shown in Figure 3(a), from the kinetic equations to understand its connection to the steady state response and to get a fundamental understanding regarding the role of the resistances in determining the EQE_{PV} of the device. We assume a solar cell of length L with electrons as minority carriers, with electron and hole selective contacts at $x = 0$ and $x = L$ respectively. The transport equation is then given by

$$\frac{dn}{dt} = \frac{1}{q} \frac{dj_e}{dx} + G - U \quad (13)$$

where j_e is the current density of electrons and G and U are the generation and recombination terms, respectively. We assume the transport of electrons is excellent, therefore a very small gradient in concentration of electrons is required to drive the current. Therefore, n is position independent, and we can integrate Equation 13 over the length of the semiconductor L to yield

$$\frac{dn}{dt} = \frac{j_e(L) - j_e(0)}{qL} + G - U \quad (14)$$

We consider the current for the electrons to be blocked at $x = L$, and we have

$$j_e(L) = 0 \quad (15)$$

Combining Equations 14 and 15, we have

$$\frac{dn}{dt} = -\frac{j_e}{qL} + \frac{j_\phi}{qL} - U \quad (16)$$

At steady state, assuming total absorption, we have

$$\bar{j}_e = \bar{j}_\phi - qL\bar{U} \quad (17)$$

where $\bar{j}_{rec} = qL\bar{U}$ is the recombination current density. The steady state collection efficiency EQE_{PV-SS} , defined in Equation 8, is then given by

$$EQE_{PV-SS} = 1 - \frac{qL\bar{U}}{\bar{j}_\phi} \quad (18)$$

Therefore, the steady state collection efficiency is reduced from unity by the ratio of the recombination current density to the photogenerated current density. We now differentiate Equation 17 to get the $EQE_{PV-DIFF}$, as defined in Equation 7, as

$$EQE_{PV-DIFF} = \left(1 + qL \frac{d\bar{U}}{d\bar{j}_e}\right)^{-1} \quad (19)$$

The differential collection efficiency is thus given by the slope of recombination current density versus extracted current density at the given steady state. The dependence of the minority carrier concentration $\bar{n}$ and recombination $\bar{U}$ on $\bar{j}_e$ is achieved through the series resistance R_s as

$$\bar{n} = n_0 \exp\left[\frac{q(\bar{V} + R_s \bar{J}_e)}{k_B T}\right] \quad (20)$$

$$\bar{U} = B_{rec}(\bar{n} - n_0) \quad (21)$$

We define¹⁶ the chemical capacitance and recombination resistance from differentiating Equations 20 and 21 with respect to voltage as

$$C_\mu = \frac{q^2 L \bar{n}}{k_B T} \quad (22)$$

$$R_{rec} = \frac{k_B T}{q^2 L \bar{n} B_{rec}} \quad (23)$$

Combining Equations 20, 21, 22, 23 and substituting in Equation 19, we get

$$EQE_{PV-DIFF} = \left(1 + \frac{R_s}{R_{rec}}\right)^{-1} \quad (24)$$

Therefore, the $EQE_{PV-DIFF}$ is controlled by the ratio of the series and recombination resistances. Larger recombination (smaller recombination resistance) and large series resistances reduce the $EQE_{PV-DIFF}$. To obtain the IMPS transfer function, we apply a small perturbation to the variables in Equation 16 from a given steady state as

$$\frac{d(\bar{n} + \tilde{n})}{dt} = -\frac{\bar{J}_e + \tilde{J}_e}{qL} + \frac{\bar{J}_\phi + \tilde{J}_\phi}{qL} - (\bar{U} + \tilde{U}) \quad (25)$$

Combining Equations 17 and 25, we get

$$\frac{d\tilde{n}}{dt} = -\frac{\tilde{J}_e}{qL} + \frac{\tilde{J}_\phi}{qL} - \tilde{U} \quad (26)$$

We can express the perturbed quantities of Equations 20, 21 in terms of the modulated quantities in an IMPS measurement as

$$\tilde{n} = \left(\frac{d\bar{n}}{d\bar{J}_e}\right) \tilde{J}_e \quad (27)$$

$$\tilde{U} = \left(\frac{d\bar{U}}{d\bar{n}}\right) \left(\frac{d\bar{n}}{d\bar{J}_e}\right) \tilde{J}_e \quad (28)$$

From differentiating Equations 20, 21 and substituting in Equations 27 and 28, we have

$$\tilde{n} = \left(\frac{q R_s \bar{n}}{k_B T}\right) \tilde{J}_e \quad (29)$$

$$\tilde{U} = \left(\frac{B_{rec} q R_s \bar{n}}{k_B T}\right) \tilde{J}_e \quad (30)$$

Substituting Equations 29 and 30 in Equation 26, taking the Laplace transform and rearranging terms, we have

$$\left(\frac{i\omega q^2 L R_s \bar{n}}{k_B T} + \frac{B_{rec} q^2 L R_s \bar{n}}{k_B T} + 1\right) \hat{J}_e = \hat{J}_\phi \quad (31)$$

Using Equations 22 and 23 in 31 and rearranging terms, we have

$$Q(\omega) = \left(1 + \frac{R_s}{R_{rec}} + i\omega R_s C_\mu\right)^{-1} \quad (32)$$

where $\omega_\tau = (R_s C_\mu)^{-1}$ and the low frequency intercept, the $EQE_{PV-DIFF}$, identical to

Equation 24, is given by

$$Q'(0) = \left(1 + \frac{R_s}{R_{rec}}\right)^{-1} \quad (33)$$

The calculated IMPS transfer function in Equation 32 (see Figure 3(c)) forms an arc in the upper quadrant of a Q -plane plot, with the maxima of the arc corresponding to the characteristic frequency ω_τ , formed by the inverse product of the series resistance and chemical capacitance. The IMPS spectra can be intuitively understood as the frequency-dependent attenuation of the photocurrent through the lines of the circuit, where at high frequencies, the capacitor acts as a short circuit and prevents the extraction of current through the series resistance and outer circuit, while at low frequencies, the current is driven through either the series resistance or through the recombination resistance depending upon their magnitudes. In addition, we note that the location of the current source that represents photogeneration plays a crucial role in the form and interpretation of the spectra, which is discussed in detail in Section 6.3.

Figure 4 Scheme of a planar semiconductor electrode indicating the Fermi level of electrons (green) majority carriers (E_{Fn}), holes (white) minority carriers in the semiconductor (E_{Fp}), and holes in an intermediate state level such as a passivation layer, or a surface state (E_{FL}). Absorbed photons generate a hole flux towards the interface, which either recombine with the rate constant k_{rec} with electrons in the conduction band at the interface or are extracted into the electrolyte with characteristic rate constant k_{ct} . Also indicated is the applied voltage V_r and the bandbending voltage V_{sc} , in units of energy. (b) IMPS spectrum of the processes considered in (a). τ_s is the time constant formed by the product of the series resistance and net capacitance C_{tot} associated to the series connection of the space charge layer capacitance and the Helmholtz layer capacitance in the electrolyte. τ_t is the inverse of the sum of the rate constants of charge

transfer and recombination. ω_{st} and γ_c are the frequency and value of the intercept on the real axis. γ_c corresponds to the ratio between C_{tot} and the space charge layer capacitance.

3.2. Semiconductor/electrolyte junction

A fundamental model for understanding the IMPS response of the semiconductor/electrolyte junction was provided by Ponomarev and Peter (Ref. 11) based on a two-capacitor approach by Wilson et al.¹⁷ This model, shown in Figure 4(a), describes the competition between minority carrier transfer from the semiconductor to the electrolyte at their interface at a characteristic rate k_{ct} and recombination with electrons in the conduction band at the semiconductor interface at a characteristic rate k_{rec} . By considering a basic charge compensation between the space charge capacitance C_{sc} and the Helmholtz capacitance C_H on the electrolyte side at the interface, the IMPS transfer function was obtained as

$$Q(\omega) = Q_{ste} \frac{1+i\gamma_c\omega\tau_c}{(1+i\omega\tau_s)(1+i\omega\tau_t)} \quad (34)$$

where

$$\gamma_c = \frac{C_{tot}}{C_{sc}} \quad (35)$$

is a ratio of capacitances including the total series capacitance of the space charge and Helmholtz capacitances

$$C_{tot} = \frac{C_{sc}C_H}{C_{sc}+C_H} \quad (36)$$

The surface transfer efficiency Q_{ste} is a very important number, discussed in subsequent sections:

$$Q_{ste} = \frac{k_{ct}}{k_{ct}+k_{rec}} \quad (37)$$

It is the low frequency intercept on the real axis, as indicated in Figure 4b. τ_s in Eq. 34 is defined as

$$\tau_s = R_s C_{tot} \quad (38)$$

in terms of the series resistance R_s and furthermore we introduce the time constants

$$\tau_c = \frac{1}{k_{ct}} \quad (39)$$

$$\tau_{rec} = \frac{1}{k_{rec}} \quad (40)$$

$$\tau_t = \frac{1}{k_{ct}+k_{rec}} \quad (41)$$

The transfer function of Equation 34 (see Figure 4(b)) yields an arc each in the upper and lower quadrants of the Q -plane plot. The arc at high frequencies is formed by the product of the series resistance and total capacitance C_{tot} while the LF arc is formed by a ratio of the rates of recombination and charge transfer. The frequency of the apex of

the low frequency semicircle is

$$\omega_{LF} = \tau_t^{-1} \quad (42)$$

If $\tau_s \ll \tau_t$, then the frequency of the intercept with the real axis at intermediate frequency can be approximated as

$$\omega_{st} = \sqrt{\frac{1 - \frac{Q_{ste}}{\gamma_c}}{\tau_s \tau_t}} \quad (43)$$

And the value of the intercept is

$$Q'(\omega_{st}) = \gamma_c \quad (44)$$

Note that this intermediate intercept is a ratio of capacitances unrelated to surface transfer efficiency, contrary to a widespread belief in the literature. A general solution for this intercept and its frequency in addition to limiting cases of the transfer function of Equation 34 are presented in appendix A.

4. A review of the applications of IMPS

4.1. IMPS in semiconductor electrodes

The starting application of IMPS occurs in the 1980s in relation to semiconductor photoelectrochemistry. The problem of an operation of a semiconductor electrode as shown in Figure 4(a) can be formulated as one of charge collection. From a number of available incident photons, one needs to determine which fraction contributes to realize the desired electrochemical reaction such as, for example, water oxidation. A number of steps intervene in the conversion of the incident photon to the reaction product, namely, the effective absorption of a photon, then successful separation of electrons and holes, the effective charge transfer across the semiconductor/electrolyte interface, and the avoidance of deleterious reactions such as corrosion of the solid surface. The dominant step is that absorbed photon flux is converted to a minority carrier flux, that is the one that is directed towards the solution, however a part of it is lost by recombination, giving an internal quantum efficiency less than unit that is the main quantity of interest.

Besides the relation of the output current to the incident light flux, another important quantity is the applied voltage. A reverse voltage facilitates charge separation and the flow of minorities to the solution. In the example of Figure 4(a), the reverse voltage increases the size of the depletion region, facilitating the flow of holes towards the electrode surface.¹⁸ On the other hand, the forward voltage can invert the sign of the current (beyond the open-circuit voltage), turning EQE negative. Therefore the experiments usually consider variations of both photon flux and applied voltage, and the influence of these variables on the conversion efficiency is analyzed.

Figure 5 Scheme of semiconductor electrodes. (a) Compact planar thin electrode. (b) Thick compact electrode. (c) Nanocrystalline porous electrode. J_{gen} is the photogenerated internal flux of minority carrier holes. J_{ct} is the charge transfer flux leading to the electrochemical reaction at the solid/liquid electrolyte interface. J_{rec} is the internal flux of recombination of minority carriers. $J_{transport}$ is the flux of transport of holes.

4.1.1. Determining the surface transfer efficiency

The early method of Salvador¹⁸⁻¹⁹ analyzes charge collection in the time domain, by comparing the starting current upon illumination and the final steady state current. The reduction of current is associated to the onset of recombination, often mediated via surface states. These models and the associated experimental tools have been nicely summarized recently by Klotz and coworkers.²⁰ The essential aspect of the method of measurement for a planar thin photoelectrode is indicated in Figure 5(a). Considering the generation of minority carrier holes in this example, the illumination creates an internal flux (by excitation of electrons) of J_{gen} towards the valence band. Then a flux J_{ct} effectively realizes the required oxidation in solution by interfacial charge transfer. The quantum efficiency of the charge extraction process is given by the quotient

$$\eta_{QE} = \frac{J_{ct}}{J_{gen}} \quad (45)$$

and it is determined by the extent of recombination of holes to electrons according to the conservation equation

$$J_{gen} = J_{ct} + J_{rec} \quad (46)$$

In the mid 1980s, the same problem²¹ was addressed using light modulated

techniques and IMPS was developed as described in Section 3.2.^{11, 22-23} The frequency resolved method has the advantage over the time transient of better experimental resolution and full spectral information, which enables the discussion of more complex mechanistic phenomena. By 1990, Laurie Peter in the landmark review paper¹⁰ provides a clear conclusion about identifying the quotient of Equation 45, based on the low frequency intercept $Q'(0)$ of the IMPS spectrum with the real axis: the more the LF intercept approaches the origin, the higher is the relative impact of recombination, see the Appendix for details. This IMPS-based method to determine a “surface transfer efficiency” became a standard and it has been used for decades,²³⁻²⁴ most often expressed in the form of a ratio between kinetic time constants for charge transfer and recombination, the value of Q_{ste} as described in Equation 37.

This type of analysis has established the focus of researchers on the value of kinetic time constants and their values, that are obtained experimentally from the determination of Q_{ste} and ω_{LF} , and their evolution with electrode potential, while other aspects of the spectral information and the variation across the change of steady state conditions have often not been considered in detail. We will address these aspects below.

4.2. Transport rates, EQE and diffusion length

In addition to the surface transfer efficiency, another important problem that has been intensely investigated in the past few decades is that of the transport and collection of charges that are generated far from the electrode surface, as indicated in Figure 5(b). Thus a flux of minorities towards the surface is established, that competes with recombination. The characteristic frequency

$$\omega_d = \frac{D_n}{d^2} \quad (47)$$

is associated with diffusive transport with chemical diffusion coefficient of electrons D_n over a distance d . As the transport is coupled with recombination of the electrons with a lifetime τ_n , the diffusion length

$$L_n = \sqrt{D_n \tau_n} \quad (48)$$

establishes the distance that photogenerated carriers may travel before disappearing. The determination of the diffusion length in connection to the photogenerated current is well described in the literature.¹⁸ The connection of diffusion length and EQE is given by elaborated techniques in inorganic solar cells.²⁵

In the early 1990s, a substantial innovation introduced the nanocrystalline semiconductor electrodes in electrochemistry and solar energy conversion with dye-sensitized solar cells.²⁶⁻²⁷ The essential new aspect of nanoparticulate electrodes is indicated schematically in Figure 5(c): the charge transfer flux across the semiconductor/electrolyte interface is spatially coupled with the transport in the direction normal to the macroscopic contact. These electrodes, therefore, generated a new set of questions concerning charge separation and transport,²⁸ especially concerning a significance of diffusive transport, in opposition to the predominance of the depletion

layer in traditional electrodes as shown in Figure 4(a). In a few years, the frequency resolved techniques and especially IMPS were applied to these types of systems, mainly to nanostructured TiO_2 electrodes used in dye-sensitized solar cells, especially by Laurie Peter, Daniel Vanmaekelbergh, and their respective coworkers.²⁹⁻³¹ In particular, IMPS became a well-established method to determine the diffusion coefficient in dye-sensitized solar cells, based on the identification of the frequency of Equation 47.^{9, 32-33}

The focus on the evolution of kinetic time constants that correspond to the maxima in the arcs observed in a Q -plane plot has traditionally neglected the analysis of the absolute value of the *real part* of the IMPS transfer function, in contrast with the technique of IS, where the resistance is a preferred quantity for analysis and reporting. We now argue that the absolute value of Q' contains significant physical information, which only has meaning when the IMPS transfer function is of the normalized form shown in Equation 3.

As discussed previously in Equation 7, the real part of the normalized IMPS transfer function at some frequency is a derivative of the steady-state EQE, just as the resistance is a derivative of the $j - V$ curve. In fact, there is a long tradition of reporting the variation of electrical current with respect to light intensity, in order to establish mechanistic models for the charge separation process, for example in the work of Salvador.³⁴⁻³⁵ This approach to steady state analysis was not generally transposed to the IMPS treatment. An exception is the result shown in Figure 6, where the low frequency limit of Q is reported versus a function of the light flux.³⁶

Figure 6 The low frequency limit of the IMPS transfer function of a nanoparticulate TiO_2 electrode as a function of $\phi^{-0.5}$. (a) $d = 0.9 \mu\text{m}$, (b) $d = 4.0 \mu\text{m}$. Reproduced with permission from Ref. 36, Copyright 1996, American Physical Society.

Taking Figure 6 as a reference, we can explore in more detail the connection between

steady state EQE and the real part of Q . In many experimental instances, a power law is a good description of the relation of photocurrent to light flux,¹⁴ as follows

$$\bar{J}_e = k\bar{J}_\phi^n \quad (49)$$

Here, n is an exponent that accounts for measurements over several orders of light intensity and k is a proportionality constant. Using Equation 8, we have the steady state EQE_{PV} as

$$EQE_{PV-SS} = k\bar{J}_\phi^{n-1} \quad (50)$$

and the corresponding differential quantity, corresponding to $Q'(0)$, is

$$EQE_{PV-DIFF} = nk\bar{J}_\phi^{n-1} \quad (51)$$

It follows that $EQE_{PV-SS} = EQE_{PV-DIFF}$ only when the extracted current density has a linear dependence on the input photon current density ($n = 1$). However, in many types of experiments, the dependence of photocurrent on photon flux is far from linear. For example, the result of Figure 6 indicates that the current depends on incident illumination with exponent $n = 0.5$. In general, a typical behaviour is that $n = 1$ for systems with highly effective charge extraction, while $n = 0.5$ occurs under charge extraction controlled by intense recombination.³⁴ Therefore, a simple analysis of the LF limit of the normalized IMPS transfer function can yield information regarding absolute charge collection values and recombination.

Even though IMPS was not generally applied to obtain absolute values of charge collection efficiency, the analysis of nanocrystalline electrodes gave rise to several influential analyses for dynamic characterization related to obtaining the diffusion length L_n from the measurement of quantum efficiency. The first method generally applied is due to Södergren et al.¹² It is based on the measurement of the action spectra (ie $EQE_{PV-SS}(\lambda)$) by illumination of the film electrode from either of both sides, the substrate and the electrolyte. Using some theoretical expressions derived from a diffusion-recombination model, it is possible to determine L_n , however, only in the case that it is shorter than the active film thickness, otherwise the collection efficiency is the same by illumination from both sides.

Another approach to determine L_n is a separate determination of the two quantities in Equation 48, the diffusion coefficient and electron lifetime, by different modulated techniques, to take their product to form L_n . An example is the combination of IMPS and IMVS to obtain the diffusion length for both dye-sensitized solar cells³⁷ and photoanodes.³⁸ However, a number of investigations by IS and IMPS established that both D_n and τ_n are strong functions of illumination (or steady state) rather than material constants.^{7, 9} A compensation of both dynamic coefficients giving a nearly constant diffusion length was often observed, and it was explained in terms of the effect of carrier trapping on the measurement by small perturbation modulated techniques.³⁹⁻⁴⁰ Meanwhile, the method based on the spectral analysis of charge collection was systematically applied to dye-sensitized solar cells in which the low quality of TiO_2

films produced short diffusion length.⁴¹ Some authors noted the disparity between values of diffusion length obtained from the action spectra and from small perturbation transient methods.⁴² The difference was explained by Mora-Seró and Bisquert in terms of the variable diffusion length due to nonlinear recombination.⁴³ The detailed connection between alternative approaches of measurement was clarified⁴⁴⁻⁴⁵ and the control of the different methods provided the ability to distinguish internal and external quantum efficiency in situations of strong dependence of the diffusion length with the background illumination.⁴⁶

4.3. Capacitances and equivalent circuits

Now we revise the spectral analysis of IMPS concerning the imaginary part of the spectra, which unavoidably leads one to consider the interpretation of the capacitances in the system and their variation as one changes the steady-state conditions of voltage or illumination. In electrochemical systems and solar cell devices, there are a number of candidate capacitances to appear in any system, namely:

C_H , the Helmholtz capacitance at the electrode surface.

C_{sc} , the surface depletion capacitance associated to the space charge layer in Figure 4(a).

C_{cell} , the overall setup or “cell” capacitance of an electrochemical cell.

C_μ , the chemical capacitance associated to charging a semiconductor state such as the conduction band. It emerges in a basic solar cell model as shown in Equation 22, and it becomes very large in the case of TiO_2 nanocrystalline electrodes, for example.

C_{ss} , the surface state capacitance (a particular type of chemical capacitance⁴⁷), associated to charging and discharging the surface states or traps. The formation of a detailed kinetic model allows to establish an equivalent circuit model that distributes the chemical capacitances for conduction band, valence band and surface states.⁴⁸

In traditional photoelectrochemistry, the question of the capacitances of a typical system as that of Figure 4(a) was considered well established. This is why in the early papers of IMPS, some equivalent circuits include the C_H and the C_{sc} , and eventually the significance of the cell capacitance dominating high frequency features was determined. However in practice, establishing the capacitances of a typical specific system, such as a metal-oxide semiconductor, a nanocrystalline semiconductor electrode, or a solar cell, is far from trivial. This is one question that has not been analyzed in general in the IMPS method, due to the focus on time constants obtained from characteristic frequencies.

For example, in the IS analysis of hematite electrodes for water splitting, the appearance of two arcs has been interpreted in terms of a model that contains the capacitances C_{sc} and the C_{ss} .⁴⁹ The capacitances have been established by analysis of their dependence with bias voltage, and it is even possible to identify the existence of band pinning by the charging of the surface state. This type of analysis validating the capacitances that lies at the heart of interpretation of IS results has not yet been realized in the IMPS analysis of semiconductor electrodes, where the focus continues on the

evolution of time constants and the relative charge transfer efficiency,^{20, 23-24} following the tendency established at the historical origin of the method.

Since the early stages of the application of IMPS, it became important to correlate the results of the different frequency resolved methods, especially IS with IMPS,^{11, 50} and later the method of Intensity Modulated Phovoltage Spectroscopy IMVS (with transfer function W_Φ).⁵¹ In recent years, since 2010, the connection between the three measurements, IS, IMPS and IMVS has been analysed from a more general point of view. Halme⁵² considered the transport models such as in dye-sensitized solar cells and other works described the results from combined measurements of photoelectrochemical responses of hematite film electrodes.⁵³⁻⁵⁴ A relationship between the different transfer functions has been established in these works:

$$Z(\omega) = \frac{W_\Phi(\omega)}{Q_\Phi(\omega)} \quad (52)$$

However, the relation of the different techniques to an underlying physical model has been often hesitant, since it appears that different techniques may excite alternative physical processes and provide substantially different information. A general study by Bertoluzzi and Bisquert¹³ established a principal solution for a semiconductor system dominated by one type of electronic carrier. In such systems, chemical capacitances will transform carriers to voltage by the variation of Fermi levels, and excitation by light or voltage must produce commensurate results. The physical model describing the results of the different techniques as IS and IMPS is the same and is unique, and such conclusion implies that a single, unified equivalent circuit (EC) describes the results of the different transfer functions. This means that the passive elements as resistances and capacitances that represent the fundamental physicochemical response are the same for any excitation procedure. However, the application of current and voltage sources associated to the perturbation depends on the particular method, so that spectral shapes are rather different in the separated techniques. It turns out that in the case of complicated spectra composed of many internal contributions, the different methods are able to convey complementary pieces of information.

As an example, the actuation of different modulated techniques on a system is shown in Figure 3(a) for the most basic solar cell, consisting of the parallel combination of a chemical capacitance C_μ related to filling the density of states (DOS) of the semiconductor and the recombination resistance R_{rec} , as described in Section 3.1. The response in both IS and IMPS measurements is an arc in the upper quadrant. For the Z-plane plot of IS shown in Figure 3(b), the arc is displaced from the origin by an amount equal to the series resistance R_s . The characteristic angular frequency of the arc at the maxima is given by inverse of the time constant formed by C_μ and R_{rec} (the electron lifetime).⁴⁰ The width of the arc is given by the value of R_{rec} . In an IMPS Q-plane plot shown in Figure 3(c), the arc begins at the origin and its width is determined by the ratio of R_s and R_{rec} , with its characteristic angular frequency at the maxima given by inverse of the time constant formed by C_μ and R_s . The difference in the nature of the time

constants occurs due to the differences in the perturbing quantities in either measurement. In an IMPS measurement, the modulation of the carrier concentration n is achieved through the potential drop across the series resistance due to the modulated extracted current while in IS, it is modulated from the external contacts by the modulated voltage. Therefore, while the EC is the same, the nature of the coupling of elements that produce spectral features are very different for either technique.

It is obviously of great interest to identify the unique equivalent circuit for an advanced system such as a perovskite solar cell. This requires that the different modulated methods must be operated at the same steady state condition. We will describe this approach below, but first we summarize a number of important properties of perovskite solar cells.⁵⁵

Figure 7 (a) CPD distribution of a MAPI cell under open-circuit conditions obtained Kelvin probe force microscopy (KPFM) measurements. Whereas the black profile shows the initial CPD profile for dark conditions, the red and blue profiles are the illuminated case, leaving one electrode floating directly after switching on the illumination, as shown in the legend. The white arrows show the buildup of V_{oc} . (b) Calculated charge densities (y axis) from the potential distribution. Reproduced with permission from Ref. 60, Copyright 2016, American Chemical Society.

5. General properties of perovskite solar cells

State-of-the-art PSCs are generally synthesized by a mixture of cations and anions, incorporating Methylammonium (MA), Formamidinium (FA), Cesium (Cs) and sometimes Rubidium (Rb) in the ‘A’ position of the structure, Lead (Pb) in the ‘B’ position and Iodide, Bromide and Chloride in the ‘X’ position. The idea behind the combination of these materials was to nullify the drawbacks of these elements when used individually in a PSC, such as large bandgaps, low tolerance to moisture and structural and thermal instability.

Consequently, these mixed-cation PSCs have shown efficiencies⁵⁶ in excess of 21% and long-term stability (500 hours) under operating conditions.⁵⁷ However, it is interesting to note that these stable, high efficiency PSCs also show⁵⁸⁻⁵⁹ a large low frequency (LF) capacitance, a characteristic feature of the ordinary MAPI configuration. This LF capacitance is directly or indirectly related to a range of steady state and dynamic effects in the PSC.

At steady-state conditions, the mobile ions in the PSC accumulate at the interface of the perovskite with the electron selective contact (ETL) or hole selective contact (HTL), depending upon the external bias voltage or illumination conditions as seen from the sharp potential drops near the contacts in Figure 7(a).⁶⁰ This can be accompanied by the accumulation of electronic carriers also, creating a large density of charge in a small layer at these interfaces (see Figure 7(b)).⁶¹ It is this charge accumulation at the PSC/selective contact interfaces that generates the large LF capacitance. These regions can serve as preferential regions of recombination and can also have a significant effect on charge extraction into the selective contacts due to the sharp potential drops that are encountered here.

Figure 8 (a) Equivalent circuit of the PSC using insights from IS. C_g is the geometric capacitance, R_s , R_{HF} and R_{LF} are the series, high frequency and low frequency resistances. C_{LF} is the low frequency capacitance. Evolution of (b) capacitances and (c) resistances at OC conditions for MAPI cells of different thicknesses as shown. Adapted with permission from Ref. 67, Copyright 2016, American Chemical Society.

In addition to affecting steady-state characteristics, the kinetics of the PSC electrical response are also strongly governed by the slow charging and discharging of the LF capacitor in the order of milliseconds-seconds, observed in various experiments such as V_{oc} decay,⁶² luminescence measurements⁶³ and also from capacitance measurements in the form of a singular negative capacitance at low frequencies.⁶⁴⁻⁶⁵ This also manifests in the well-studied effect of dynamic hysteresis, which is a variation in the j-V response of the PSC depending upon experimental parameters such as biasing voltage, light intensity and scan rate and direction.⁶⁶ These insights into the PSC operation yielded the reliable EC of Figure 8(a).⁶⁷ This consists of a resistance R_{HF} in series with a $R_{LF}||C_{LF}$ pair that is related to interfacial charging and its corresponding resistance. These elements are shunted by a HF capacitance, now accepted as the geometric capacitance C_g of the device. The evolution of these elements are shown in Figure 8(b). The LF capacitance reaches very high values in the order of milliFarads (mF), while the resistances show an exponential evolution in a coupled fashion, typical of recombination resistances, though the LF resistance shows unrealistic ideality factors in several cases. This charge accumulation was further observed to be strongly dependent on the material used for the selective contact⁶⁸ and also connected to the mechanism of degradation in performance of PSCs, where the ions are not blocked at the selective contacts but can enter them, creating irreversible chemical reactions that alter energy levels and transport properties of the selective contacts.⁶⁹⁻⁷¹ These observations indicate that the resistance to charge the interfaces of the PSC (discussed in subsequent sections) and the reactivity of these charges to create chemical reactions are important factors that govern the stability and operation of the PSC.

Figure 9 Commonly observed IMPS Q -plane responses for PSCs at SC conditions.

6. The IMPS response of the PSC

6.1. A summary of literature results

Figure 9 summarises the set of Q -plane plots generally observed when measuring a PSC. Usually, only one or two arcs are observed in the upper quadrant (high frequency (HF) region), though in certain cases, three arcs have been observed.⁷²⁻⁷⁴ At low frequencies, an arc is observed in the lower quadrant. The general method of interpretation of the IMPS spectra of the PSC in the community so far is the association of characteristic time constants (obtained from the peaks in a $-Q''$ versus frequency plot) to transport signals, as discussed in Section 4. Therefore, the arcs in the upper quadrant have been generally attributed to transport processes of either electronic carriers within the perovskite or selective contacts, or related to ionic movement within the perovskite.^{73, 75-76} However, Pockett et al.⁷⁷ have correctly attributed the formation of the HF arc to the time constant formed by the series resistance and the geometric capacitance of the cell. In the case of the LF arc in the lower quadrant, there is not a clear understanding, with explanations related to slow recombination and charge transfer in the PSC based on the photoelectrochemical model developed by Peter et al.,¹¹ discussed in Section 3.2. In fact, charge transfer efficiencies for the PSC using this model have been calculated.⁷⁷⁻⁷⁸

The existing interpretations of the IMPS spectra of the PSC are questionable, particularly with respect to the transport of photogenerated carriers. It is well established that the PSC is a fast transporter of electronic carriers, with reported diffusion coefficients D of the order of $0.1 \text{ cm}^2\text{s}^{-1}$, which yields the characteristic frequency of diffusion from Equation 47 for a sample with thickness $L = 300 \text{ nm}$ as $\sim 1 \times 10^8 \text{ Hz}$.

This frequency is beyond the range of frequencies used and hence, electronic transport in the perovskite is too fast to be observed in an IMPS measurement. A similar argument can be made regarding electronic transport in the selective contacts as well. However, the observation of ionic transport cannot be ruled out, though it has not yet been observed in a direct fashion for standard PSCs, which is the observation of a straight line sloped at 45 degrees to the real axis characteristic of semi-infinite diffusion.^{9, 79}

Figure 10 (a) Evolution of steady state extracted current density versus input photon current density and (b) Q -plane plot for a regular configuration MAPI cell (14.79% efficiency) measured at SC conditions for DC photon current density as shown in legend. (c) Evolution of the different types of $EQEPV$ versus DC photon current density. $EQEPV-DIFF$ values obtained by differentiating the values in (a). (d) log-log plot of steady state extracted current density versus input photon current density that yields the exponential dependence of extracted current on input photon current density. IMPS measurements were made using 470 nm blue LED in the frequency range 10 mHz -20 kHz. Adapted with permission from Ref. 14. Copyright 2018, American Chemical Society.

6.2. The connection of EQE and IMPS in the PSC

Based on the definitions of the IMPS transfer function and the EQE_{PV} , a useful strategy is to identify the evolution of the three quantities defined in Equations 6, 7 and 8 for PSCs in order to confirm that they indeed represent similar quantities. This was experimentally demonstrated by Ravishankar et al.¹⁴

The evolution of the steady state and differential EQE_{PV} of a regular configuration (compact-TiO₂ (c-TiO₂) + mesoporous TiO₂ (m-TiO₂)/Perovskite/2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene(Spiro-OmeTAD)) MAPI cell is shown in Figure 10(c). The $EQE_{PV-DIFF}$ obtained from the LF limit of the IMPS Q -plane response and from differentiating the steady state values match quite nicely and do not show much evolution over the range of light intensities used. However, EQE_{PV-SS} rises sharply at low light intensities and saturates at high light intensities to a similar value of $EQE_{PV-DIFF}$. Based on the discussion in Section 4.2, it can be concluded that the photocurrent response in the MAPI PSC is non-linear at low light intensities, as observed from the divergence in values of EQE_{PV-SS} and $EQE_{PV-DIFF}$ in Figure 10(c) and the exponent obtained from the log-log plot in Figure 10(d). This is likely related to the poor conductivity of MAPI PSCs at low light intensities, which can cause poor charge collection.⁸⁰⁻⁸¹

Figure 11 Evolution of $EQE_{PV-DIFF}$ of a regular configuration MAPI cell measured by the differential spectral response method for different chopper frequencies (500 Hz reference) under a) 0 DC white light bias and (b) $10 \text{ mW} \cdot \text{cm}^{-2}$ DC white light bias. (c) Q -plane plot of a MAPI PSC measured at $90 \text{ mW} \cdot \text{cm}^{-2}$ DC blue (470 nm) light bias and (d) corresponding evolution of real part of Q versus frequency. Adapted with permission from Ref. 14. Copyright 2018, American Chemical Society.

An interesting point to be considered is the frequency-dependent evolution of the $EQE_{PV-DIFF IMPS}$ of the PSC, shown in Figure 11(d). Moving from high to low frequencies, the $EQE_{PV-DIFF}$ is increased and reaches a maximum value by the formation of an arc or multiple arcs in the upper quadrant. However, this is followed by a transition to the lower quadrant and a concomitant reduction in the $EQE_{PV-DIFF}$ at very low frequencies. The nature and width of this LF arc is also dependent upon the DC photon current density. This observation indicates that the PSC is limited from achieving its maximum $EQE_{PV-DIFF}$ due to a LF mechanism that reduces the extracted photocurrent density at the contacts. This effect has significant ramifications on the validity of the $EQE_{PV-DIFF}$ measured for a PSC using the differential spectral response method. This is shown in Figures 11(a) and (b), where different chopper frequencies

yield almost a 10% variation in the $EQE_{PV-DIFF}$. Therefore, it becomes imperative to explicitly report the chopper frequency used to obtain a set of $EQE_{PV-DIFF}$ data of a PSC in order to avoid inaccurate estimation of the PSC performance parameters.

Figure 12 (a) EC of a PSC during an IMPS measurement. (b) Simulated Q -plane response of the EC of (a). Adapted with permission from Ref. 14. Copyright 2018, American Chemical Society.

6.3. The Perovskite Solar Cell Model

An important pathway to understand the IMPS response of the PSC is to establish a suitable EC that reproduces the spectra to subsequently extract mechanistic information. A first attempt to this approach was carried out¹⁴ using an EC well established from IS measurements, shown in Figure 8(a) and discussed in Section 5.

Based on this EC, the singular transition of the Q -plane response to the lower quadrant at low frequencies was explained by placing the current sources for steady state and modulated photogeneration across only the HF resistance, as seen in Figure 12(a). This generates the Q -plane response (see Ref. 82 for derivation) shown in Figure 12(b). The arc in the upper quadrant corresponds to a time constant formed by the series resistance and the bulk dielectric capacitance. The corresponding HF intercept on the real axis is given by

$$Q'_{HF} = \left(1 + \frac{R_s}{R_{HF}}\right)^{-1} \quad (53)$$

This is identical to the behaviour of the basic solar cell model described in Section 3.1. At low frequencies, C_g behaves as a blocking element and the $R_{LF}||C_{LF}$ pair that forms the LF time constant introduces a frequency dependence to the extracted photocurrent that creates a delay and moves the response to the lower quadrant. At the LF limit, the LF capacitor is blocked and the LF resistor acts like an extra series resistor, giving the LF intercept on the real axis as

$$Q'(0) = \left(1 + \frac{R_s + R_{LF}}{R_{HF}}\right)^{-1} \quad (54)$$

This causes the $EQE_{PV-DIFF}$ of the PSC to be reduced at low frequencies. This effect indicates that there are electrical limitations to the $EQE_{PV-DIFF}$ of the PSC which are easily quantified through the above description, making IMPS a very powerful tool in the development of PSCs. Achieving high efficiency PSCs will involve reducing or eliminating this LF arc, which appears to be related to unique charge recombination and discharge mechanisms at the PSC interfaces involving interactions between both electronic and ionic carriers.

6.4. IMPS at open-circuit conditions

Due to the inherent variability in the nature of the PSC depending upon materials and experimental conditions, obtaining reproducible and representative response from measurements is critical in order to correctly identify directions of improvement. In this context, combining the inferences and results obtained from both IS and IMPS measurements appears an excellent strategy to cross-check and confirm the validity of ECs used and the evolution of their parameters. This is aided by the fact that the results of both IS and IMPS measurements should provide the same parameters, since the underlying EC of the PSC is the same, as established in previous sections. Therefore, we now discuss the results of IMPS measurements carried out at open-circuit (OC) conditions by Ravishankar et al.⁸² to supplement and confirm the well-established results of IS at OC conditions for PSCs.

The structure of the different samples used for the measurements consisted of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite absorber with different ETL layers, namely c- TiO_2 + m- TiO_2 , [6,6] -phenyl-C61-butyric acid methyl ester (PCBM) and c- TiO_2 prepared using flash infra-red annealing (FIRA). The HTL used was Spiro-OmeTAD. These samples are hereafter referred to as Meso, PCBM and Flat cells respectively.

Figure 13 IMPS spectra (frequency range 10 mHz -20 kHz) of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ cells with Spiro – OmeTAD as the HTL measured at OC conditions under DC $90 \text{ mW}\cdot\text{cm}^{-2}$ blue (470 nm) illumination and different ETLs - (a) Meso – (m-TiO_2) (b) PCBM – ([6,6] - phenyl-C61-butyric acid methyl ester) and (c) Flat (no ETL) samples. The efficiencies of the Meso, PCBM and Flat cells were 4.99%, 7.18% and 2.74% respectively. Inset shows intermediate frequency arc. (d) IS spectra at OC conditions of the same samples measured under DC $90 \text{ mW}\cdot\text{cm}^{-2}$ white light illumination and (e) corresponding evolution of capacitance versus frequency. Adapted with permission from Ref. 82. Copyright 2019, American Chemical Society.

Figure 13(a), (b) and (c) shows the IMPS spectra at OC conditions of the measured samples and the corresponding IS spectra at OC conditions are shown in Figure 13(d). It can be seen that the IMPS spectra show the existence of an extra characteristic process (second arc in upper quadrant) at intermediate frequencies in PSCs that is not observable from IS spectra. In order to account for this extra IF process, the EC in Figure 12(a) was

modified to include an extra IF capacitor C_{IF} charged through a resistor R_{IF} , shown in Figure 14(a).

Figure 14 (a) Modified PSC EC during an IMPS measurement that includes an IF resistance and capacitance. (b) Simulated IMPS Q -plane plot and (c) IS Z -plane plot and their corresponding time constants at OC conditions using the EC in (a). Note that the generalized HF time constant for IS is given in Table 1. Parameters used were $R_s = 120$ and $20 \, \Omega \cdot \text{cm}^2$ for (b) and (c) respectively, $R_{HF} = 30 \, \Omega \cdot \text{cm}^2$, $R_{LF} = 20 \, \Omega \cdot \text{cm}^2$, $R_{IF} = 300 \, \Omega \cdot \text{cm}^2$, $C_g = 10^{-7} \, \text{F} \cdot \text{cm}^{-2}$, $C_{IF} = 10^{-4} \, \text{F} \cdot \text{cm}^{-2}$, $C_{LF} = 10^{-2} \, \text{F} \cdot \text{cm}^{-2}$. Reproduced with permission from Ref. 82. Copyright 2019, American Chemical Society.

The corresponding time constants of these 3 processes are shown in Figure 14(b), where the additional IF time constant is formed by the product of the series resistance and the IF capacitance. IMPS measurements are able to resolve these features unlike IS because of the transition of the LF phenomena to the lower quadrant of the Q -plane plot and also due to the different nature of time constants formed in either measurement, as shown in Figures 14(b) and 14(c) and summarised in Table 1.

	IMPS	IS
HF time constant	$R_s C_g$	$[\frac{1}{R_{HF}} + \frac{1}{R_{IF}}]^{-1} C_g$
IF time constant	$R_s C_{IF}$	$R_{IF} C_{IF}$
LF time constant	$R_{LF} C_{LF}$	$R_{LF} C_{LF}$
HF intercept	$(1 + R_s [\frac{1}{R_{HF}} + \frac{1}{R_{IF}}])^{-1}$	$R_s + [\frac{1}{R_{HF}} + \frac{1}{R_{IF}}]^{-1}$
IF intercept	$(1 + \frac{R_s}{R_{HF}})^{-1}$	$R_s + R_{HF}$
LF intercept	$(1 + \frac{R_s + R_{LF}}{R_{HF}})^{-1}$	$R_s + R_{HF} + R_{LF}$

Table 1 Time constants and intercepts on the real axis obtained in a Q -plane plot and Z -plane plot for the EC of Figure 14(a).

We note that the IS HF time constant in Table 1 breaks down to the formula shown in Figure 14(c) at OC conditions where R_{HF} dominates the parallel combination between itself and R_{IF} . In the more general case, far from OC conditions, the EC of Figure 14(a) can yield three arcs in the upper quadrant of the Z -plane plot, as has been observed previously,⁸³ with the IF and LF arcs merging into each other to yield two arcs upon moving towards OC conditions.

From fitting of the experimental data, the values of the elements of the EC could be obtained. The new feature, C_{IF} , was seen to be two orders smaller than the LF capacitance. The new IF resistor R_{IF} was observed to be of a few hundreds of Ohms, varying strongly depending upon the sample. We also note that large series resistance values ($\sim 100 \Omega \cdot \text{cm}^2$) were obtained, whose resolution requires a further extension to the model as discussed in Ref. 82.

Based on the large value of the IF capacitance, similar to the LF capacitance, it was attributed to the accumulation of anions and electrons at the HTL/perovskite interface. The IF resistance is then responsible for the charging/discharging of this interface. From the EC of Figure 14(a), it can be seen that the IF resistance cannot contribute to the steady state operation of the device as it is in series with the IF capacitance. However, it can contribute in a kinetic measurement, such as a j -V curve. The total impedance of the EC of Figure 14(a) for $\omega_{HF} \gg \omega \gg \omega_{IF}, \omega_{LF}$ is

$$Z_{net} = R_s + [\frac{1}{R_{HF}} + \frac{1}{R_{IF}}]^{-1} \quad (55)$$

For scan rates that satisfy this condition, the less resistant pathway between the recombination resistance R_{HF} and the interface charging resistance R_{IF} will dominate

the device impedance as shown in Equation 55. Therefore, at low or intermediate forward biases, where R_{HF} is very large, R_{IF} and its evolution will control the net device impedance. This is shown in the simulations of Figure 15, with the net device resistance varying strongly for standard scan rates of a j-V measurement depending upon the magnitudes of R_{HF} and R_{IF} . Therefore, the charging/discharging of the perovskite/selective contact interfaces can play a key role in controlling the device resistance at low to intermediate forward biases, which can explain the large reduction in FF upon scanning from reverse to forward bias, which is yet to be explained clearly.⁸⁴

Figure 15 Simulated real part of resistance values versus frequency using the equivalent circuit of Figure 14(a), for different values of R_{HF} and R_{IF} as shown in the legend. The dotted lines indicate the frequencies corresponding to scan rates of $100 \text{ mV}\cdot\text{s}^{-1}$ (blue) and $300 \text{ mV}\cdot\text{s}^{-1}$ (red) respectively. Parameters used were $R_s = 20 \text{ }\Omega\cdot\text{cm}^2$, $R_{LF} = 2000 \text{ }\Omega\cdot\text{cm}^2$, $C_s = 10^{-7} \text{ F}\cdot\text{cm}^{-2}$, $C_{IF} = 5\cdot 10^{-4} \text{ F}\cdot\text{cm}^{-2}$, $C_{LF} = 5\cdot 10^{-2} \text{ F}\cdot\text{cm}^{-2}$. Reproduced with permission from Ref. 82. Copyright 2019, American Chemical Society.

Figure 16 (a) j-V curves of $(FA_{0.83}MA_{0.17})_{0.95}Cs_{0.05}Pb(I_{0.83}Br_{0.17})_3$ triple cation high efficiency PSC and a low efficiency MAPI PSC (b) IMPS Q -plane plots at OC conditions of a high efficiency (16.87%) triple cation PSC (triangles) and low efficiency (10.6%) MAPI PSC (circles) for DC blue (470 nm) light intensities as shown in the legend. (c) Extracted resistances and (d) capacitances at OC conditions for the triple cation PSC (triangles) and MAPI PSC (circles) obtained from the equivalent circuit of Figure 14(a). Colours corresponding to different resistances and capacitances shown in legend.

6.5. IMPS Characteristics of Low and High Efficiency Perovskite Solar Cells

Based on the analysis carried out so far, a fruitful strategy to understand the mechanisms driving high efficiency PSCs is to compare them with low efficiency cells and identify any significant variation in capacitances or resistances that can be pinpointed as the limiting factor. To this end, we carry out a detailed IMPS analysis at OC conditions of a high efficiency triple cation $(FA_{0.83}MA_{0.17})_{0.95}Cs_{0.05}Pb(I_{0.83}Br_{0.17})_3$ cell and a low efficiency MAPI cell, whose j-V curves are shown in Figure 16(a). A strong reduction is seen in the j_{sc} of the MAPI cell, while the V_{oc} is reduced by ~100 mV

compared to the triple cation cell. However, it is interesting to note that both the cells show the same limitation at low frequencies, where the Q -plane response shifts to the lower quadrant and is reduced, similar to that observed in Figure 10(b), indicating similar mechanisms at both SC and OC conditions that affect the LF response for both high and low efficiency PSCs. The calculated resistances and capacitances for both the cells using the model of Figure 14(a) are shown in Figures 16(c) and 16(d). While the resistances are very similar, the most interesting aspect is the capacitances, where both the IF and LF capacitances, associated to charging of the perovskite/selective contact interfaces, are larger in the case of the high efficiency triple cation cell. Similar large capacitances for high efficiency triple cation PSCs have also been reported.⁵⁸⁻⁵⁹

This indicates that the accumulation of charge at the interfaces is a common feature of both low and high efficiency PSCs and is hence not a deleterious effect by itself. However, this charge accumulation is also related to the reduction in the $EQE_{PV-DIFF}$ at low frequencies, whose resolution can allow for maximum charge extraction and higher efficiencies. We conclude that it is the interactions of the accumulated charges at the perovskite/selective contact interfaces that is the underlying factor governing these effects that ultimately determines its quality.

7. Conclusions

Based on the large variability in spectra observed in IS Z -plane plots and the general difficulty in characterizing the PSC, we establish IMPS as an important alternative small perturbation technique to probe the physical mechanisms governing the PSC operation. In order to provide a strong basis for understanding the technique, a detailed study of the historical application of IMPS for charge transfer in semiconductor electrodes and for transport considerations in dye-sensitized solar cells is carried out. These applications have established a focus on kinetic time constants, their evolution and their connection to characteristic transport phenomena, which has been extended to the study of the PSC. By establishing the connection of the IMPS transfer function and its relation to the measured external quantum efficiency (EQE_{PV}), we provide an argument for focussing on absolute values of the normalized IMPS transfer function that provides information on recombination and collection efficiency. Furthermore, from basic models of the solar cell, we stress the importance of developing an equivalent circuit representation that can adequately resolve the different capacitive features that are generally not straightforward from kinetic equations. Using these insights, it is identified that IMPS allows the quantification of the singular reduction in the EQE_{PV} of PSCs at low frequencies that is related to charge accumulation and their subsequent discharge kinetics at perovskite/selective contact interfaces. This is related to the low frequency elements of the EC that are outside the region of the current source that represents photogeneration for the PSC. This generates the shift in response to the lower quadrant and the concomitant reduction in the EQE_{PV} at low frequencies. Furthermore, the meaning of the time constants observed in an IMPS measurement is clarified, concluding that they

are arbitrary coupling of different elements of the equivalent circuit and not necessarily related to transport processes. Finally, the charging/discharging of the perovskite/selective contact interfaces is found to be a common and critical factor in both low and high efficiency PSCs, confirming that further development of the PSC will therefore involve gaining control over the interfacial charging process and the kinetics and reactivity of the accumulated charge at the interfaces.

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Appendix A: Exact solution and limiting cases of semiconductor/electrolyte junction model

The real and imaginary parts of Equation 34 are given by

$$Q' = \frac{Q_{ste}(1-\omega^2\tau_s\tau_t+\omega^2\tau_c\gamma_c(\tau_s+\tau_t))}{(1-\omega^2\tau_s\tau_t)^2+\omega^2(\tau_s+\tau_t)^2} \quad (\text{A.1})$$

$$Q'' = \frac{Q_{ste}(\omega\tau_c\gamma_c-\omega(\tau_s+\tau_t)-\omega^3\tau_c\tau_s\tau_t)}{(1-\omega^2\tau_s\tau_t)^2+\omega^2(\tau_s+\tau_t)^2} \quad (\text{A.2})$$

To obtain the intercept on the real axis of the Q -plane plot at intermediate frequencies, we set Equation A.2 equal to zero, which yields the frequency and value of the intercept as

$$\omega_{st} = \sqrt{\frac{\tau_c\gamma_c-(\tau_s+\tau_t)}{\gamma_c\tau_c\tau_s\tau_t}} \quad (\text{A.3})$$

$$Q'(\omega_{st}) = \frac{\alpha\gamma_c(\alpha\frac{\tau_s}{\tau_t}+\frac{1}{\alpha}-1-\frac{\tau_s}{\tau_t})}{(1+\frac{\tau_s}{\tau_t})(\alpha^2\frac{\tau_s}{\tau_t}+1-\alpha(1+\frac{\tau_s}{\tau_t}))} \quad (\text{A.4})$$

where

$$\alpha = \frac{Q_{ste}}{\gamma_c} \quad (\text{A.5})$$

Applying the condition $\tau_s \ll \tau_t$ to Equations A.3 and A.4 yield the values of Equations 43 and 44.

We now consider two limiting cases of the transfer function of Equation 34 that correspond to either fast recombination or fast charge transfer to the electrolyte.

Case 1: Fast recombination

In this case, we have the limiting condition $\tau_{rec} \ll \tau_c$. Applying this condition to the transfer function of Equation 34, we get

$$Q = \left[\frac{(1+i\omega\tau_s)(1+i\omega\tau_{rec})}{i\omega\tau_{rec}\gamma} \right]^{-1} \quad (\text{A.6})$$

This yields an arc in the upper quadrant (see Figure A1(a)) whose characteristic frequency is

$$\omega_{HF} = \frac{1}{\tau_s} \quad (\text{A.7})$$

τ_s is the time constant related to the series resistance and net capacitance C_{tot} as indicated in Equation 38. An arc in the lower quadrant is also obtained with a characteristic frequency

$$\omega_{LF} = \frac{1}{\tau_{rec}} \quad (\text{A.8})$$

The fast recombination dominates the LF response and drives the charge transfer efficiency Q_{ste} to 0.

Case 2: Fast charge transfer

The limiting condition for fast charge transfer is $\tau_c \ll \tau_{rec}$. Applying this condition to the transfer function of Equation 34, we get

$$Q = \left[\frac{(1+i\omega\tau_s)(1+i\omega\tau_c)}{1+i\omega\tau_c\gamma} \right]^{-1} \quad (\text{A.9})$$

This yields two arcs in the upper quadrant (see Figure A1(b)) with the LF intercept Q_{ste} reaching the maximum value of 1, due to the efficient transfer of charge to the electrolyte. The characteristic frequency of the HF arc is the same as that in Equation A.7, while the characteristic frequency of the LF arc is

$$\omega_{LF} = \frac{1}{\tau_c} \quad (\text{A.10})$$

Figure A1 IMPS response of the semiconductor/electrolyte junction model described in Section 3.2 for the limiting cases of (a) fast recombination and (b) fast charge transfer. τ_{rec} and τ_c are the time constants for recombination and charge transfer to the electrolyte respectively. τ_s is the time constant formed by the product of the series resistance and net capacitance C_{tot} formed by the series connection of the space charge layer capacitance and the Helmholtz layer capacitance in the electrolyte. Parameters used were $\tau_s = 0.0001\text{s}$, $\tau_t = 0.01\text{ s}$, $\tau_c = 3.33\text{s}$ and 0.01s for (a) and (b) respectively, $\tau_{rec} = 0.01\text{s}$ and 3.33s for (a) and (b) respectively, $C_{sc} = 10^{-7}\text{ F/cm}^2$, $C_h = 10^{-6}\text{ F/cm}^2$, $C_{tot} = 9.1 \times 10^{-8}\text{ F/cm}^2$.

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TOC Graphic

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