Low-Perturbation Optoelectronic Measuring Techniques. What are they and what are they good for?

Antonio Jesús Riquelme Expósito

Abstract— In the Nanostructured Solar Cells Group at UPO we like to experiment with solar cells. We always treat them with care and delicacy, as we always use a small perturbation to analyze their response. This small perturbation can be an optical blink, of different colours or electrical, at either at a pleasant room temperature or at freezing cold conditions, in either total darkness or under extreme light soaking. Normally, all cells behave well, although perovskites ones do not appear to stand well our treatments. In any case, they always provide us with tasty information, in the form of resistances and capacitances, or kinetic constants, of different sorts. In addition, we like to run simulations and devise models of reference, to better understand their complex behavior. We do not know if we do it well or badly, but we always do it with frequency and intensity.

Key Words— Characterization, EIS, IMPS, IMVS, Spectroscopy.

◆

1. INTRODUCTION

Elucidating the behavior of the electrons inside our devices is a titanic juggling act. However, luckily for us, we have a great mix of tools at our disposal. This article will focus on low-perturbation optoelectronic measuring techniques, due to their current relevance on the field.

These techniques work by subjecting the device we want to characterize to a small electrical or optical stimulus, modulated in frequency, while keeping known conditions of voltage or steady light intensity.

It is needed to bear in mind that inside a solar device in operation many different processes take place, at different time scales and loading conditions. The idea behind small-perturbations is to separate these processes and to simplify the kinetics by assuming that small perturbation implies first order kinetics. In first order kinetics, the time evolution is described by **equation 1**.

$$n(t) = n_0 e^{-k_1 t} \quad (1)$$

where n is the electron density and k_1 is a first-order kinetic or rate constant.

There are three kinds of techniques under the low-perturbation optoelectronic measuring concept. These are Impedance Spectroscopy (EIS), Photocurrent Spectroscopy (IMPS) and Photovoltage Spectroscopy (IMVS).

2. SMALL-PERTURBATION TECHNIQUES

The three small-perturbation optoelectronic measuring techniques can be described by a universal **equation (2)**.

$$Z(\omega) = \frac{S(\omega)}{P(\omega)} \quad (2)$$

Where P represents the Perturbation, S means the signal recorded and Z is the so-called transfer function. All of them are angular frequency (ω) dependent. As we will see later, the most operative way of defining a transfer function is a complex number. The origin of the perturbation and the signal received indicated in equation (2) can vary. The full range of combinations is shown in **Table 1**.

TABLE 1

TRANSFER FUNCTIONS DEPENDING ON PERTURBATION AND RESPONSE

Transfer Function	Perturbation	Response	What we expect to find
EIS	Voltage	Current	Transport and Recombination
IMPS	Light (optical)	Short-circuit Current	Transport and Transfer
IMVS	Light (optical)	Open-circuit Voltage	Recombination

2.1. Electrical Impedance (EIS)

This technique measures the "hindrance" (resistance) presented by a circuit to a current when a voltage is applied. This useful tool allows us to understand the internal behavior of a solar device, elucidating the processes that take place inside of it.

This technique consists in applying a small perturbation of the voltage that is applied by a sinusoidal perturbation of low amplitude. The current response is also sinusoidal that depends on the frequency of the modulation. Both, response and perturbation show the same frequency in their sinusoidal behavior. However, as shown in **Figure 1**, the response can have a phase shift due (φ) to internal electric process that are taking place in the material that we are studying [1].

Antonio Jesús Riquelme Expósito. Facultad de Ciencias Experimentales, Universidad Pablo de Olavide. ajriqexp@upo.es.

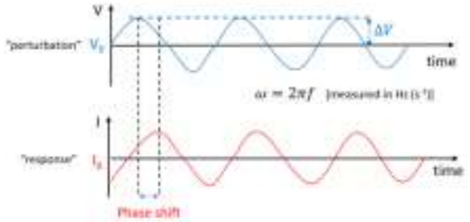

Fig 1. Impedance response in a linear system.

If we consider **Equation 2**, and **Table 1**, the perturbation for EIS is a voltage, and the response is received as current density. This is the definition of electric resistance of a simple circuit, given by Ohm's Law.

Applying a generalization of Ohm's Law and the phase shift described in **Figure 1**, we can assume **Equation 3** to describe the electrical impedance of an electrical device.

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{\Delta V sin(\omega t)}{\Delta I sin(\omega t+\varphi)} = |Z|\frac{\sin(\omega t)}{\sin(\omega t+\varphi)} \tag{3}$$

where we have two terms, ∣Z∣ is the impedance magnitude, and the other measures the phase shift between perturbation and response.

As mentioned above, using complex numbers enables a more simply representation of the magnitude being used and input and output phases. To accomplish this, we use Euler's relation to determine a mathematical expression in terms of Z_0, which represents the impedance magnitude, and the phase shift φ, that can also be separated in two components, one real and another imaginary, as shown in **Equation 4**.

$$Z = |Z|e^{-j\varphi} = |Z|\cos(\varphi) - |Z|sen(\varphi) \tag{4}$$

2.2. IMPS and IMVS

IMPS and IMVS are two closely related techniques. In both of themthe intensity of a light source is modulated, and its response in the device is measured as a function of modulation frequency. IMPS is normally performed under short circuit conditions, and gives us information about carrier transport. On the other hand, IMVS is normally performed at open circuit and gives us information about recombination [2].

The way of performing these experiment is to set a base intensity of light focused on the device, and superimpose a light perturbation with sinusoidal waveform. During the experiment the frequency of this perturbation changes, giving us time-dependent information about several processes like diffusion coefficients and lenghts or reaction rates[3]. This information is contained in a certain set of rate or *time constants*.

As done before with Electrical Impedance, we can relate **Equation 2** and **Table 1**, and assuming the mathematical logical process, concerning Euler's relation, we can describe the transfer functions for IMPS (Y) and IMVS (Z_{PV}) with **Equation 5** and **Equation 6**.

$$Y(\omega) = \frac{J(\omega)}{I(\omega)} = \frac{\Delta J sin(\omega t)}{\Delta I sin(\omega t+\varphi)} = |Y|e^{i\varphi} = |Y|\cos(\varphi) - |Y|sen(\varphi) \tag{5}$$

$$Z_{PV}(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{\Delta V sin(\omega t)}{\Delta I sin(\omega t+\varphi)} = |Z_{PV}|e^{i\varphi} = |Y|\cos(\varphi) - |Y|sen(\varphi) \tag{6}$$

2.3. Connection between the techniques

It is easy to demonstrate that the three small-perturbation techniques (EIS, IMPS and IMVS) are related by definition by equation **7**:

$$Z(\omega) = \frac{Z_{PV}(\omega)}{Y(\omega)} \tag{7}$$

where Z(ω) is the solar cell impedance, Z_{PV} (ω) is the solar cell IMVS and Y(ω) is the IMPS [4].

The parallel combination of these three techniques provides a very useful tool for a direct analytical description by identifying charge storage modes via system capacitances in addition to charge transfer by resistance components.

2.4. Good practices for the measurements

All these techniques need to fulfill three golden rules in order to the data collected to be reliable: linearity, causality and stability [5].

In order to meet these three conditions, we need to ensure that the applied perturbation amplitude is small enough to assume that the response of the cell is linear (which implies that **Equation 1** holds). We also need to be sure that the measured response of the device is directly correlated to the applied stimulus, and it does not come from an outside noise or any other source, which means that there is causal connection between stimulus and response. Finally, yet importantly, if we want the stability principle to be met we need to make sure that the overall state of the system does not change during the acquisition of the data (stability).

One of the ways of checking stability is performing a j-V curve or cyclic voltagram before and after the measurement, checking if any change is observed [2].

As for the linearity condition, we can use a Lissajous plot as the one in **Figure 2** that represents perturbation vs response. If the plot shows an elliptical shape with a central symmetry with respect to its origin, or a straight line, we have met linearity condition [6].

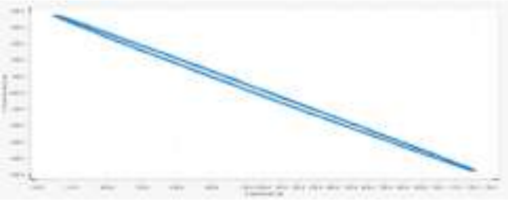

Fig 2. Example of Lissajous Plot, obtained from an IMPS experiment using a 465nm wavelength LED.

Regarding causality, we need to ensure that the measurements are performed under dark conditions, where the only illumination source is controlled by us.

3. UNDERSTANDING THE SPECTRA

The frequency analysis of the response to the perturbations enables us to gather very valuable information about transport kinetics, recombination and collection of charge, along with internal resistances and capacitances. As mentioned before, transfer functions of these three techniques have two separated components, a real and an imaginary, which also represents the relation between the magnitude of the measured property and the phase shift between the perturbation and the device's response. These two elements are represented by Nyquist plot and Bode plot.

- **Nyquist Plot:** It represents the real component in the X-axis, and the imaginary component as Y-axis, as shown in **Figure 3**.

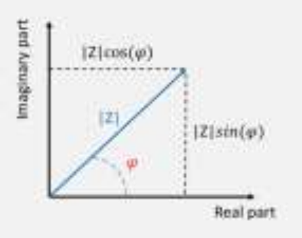

Fig 3. Representation of Nyquist plot building.

- **Bode Plot:** It represents in a double Y plot, where X-axis is the frequency and there are two Y-axis. One of them represents the magnitude of the transfer function, and the other the shift phase, as shown in **Figure 4** and **Figure 5**.

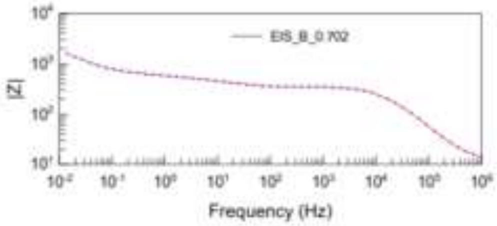

Fig 4. Representation of Y-axis referring to the Magnitude of a Bode Plot.

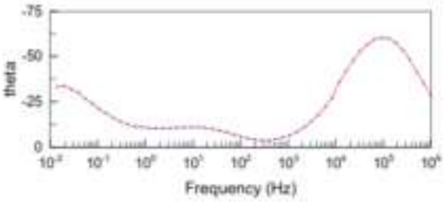

Fig 5. Representation of Y-axis referring to shift phase of a Bode Plot.

Since in the Bode Plot the frequency is represented, we can distinguish between high frequencies, medium frequencies and low frequencies phenomena, and, from the position of the peaks, we can determine the time constant of each process that we can find in our experiments and that happen in differents time scales [2].

4. PRACTICAL IMPLEMENTATION: PEROVSKITE SOLAR CELLS EIS ANALYSIS

First off, we need to know that a metalorganic perovskite solar cell is a type of device with perovskite **ABX_3** structure where A is a cation, normally organic, B is a metallic cation and X a halide like Br or Cl. Most common structure used is the Methylammonium lead halide, also known by its chemical formula as $MAPbX_3$) [7]. A typical crystalline perovskite structure can also be seen in **Figure 6**. These devices are very promising, having grown its record efficiencies from 3,8% to 22,7% in less than 10 years [8].

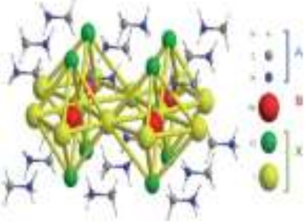

Figure 6: Methylammonium lead halide solar cell structure [9].

As we have discused in the previous section, an EIS experiment results in a Nyquist plot and a Bode plot. In **Figure 7** and **Figure 8** appear the EIS spectra of a same device measured under different light intensities from a 630 nm wavelength LED as illumination source.

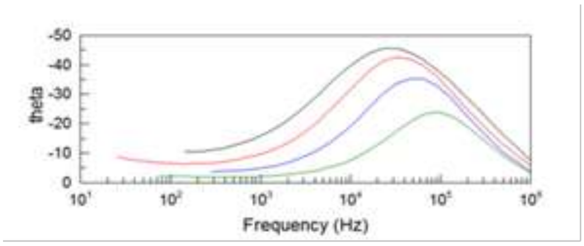

Fig 7. Example of Nyquist plot of an EIS experiment of a Perovskite solar cell.

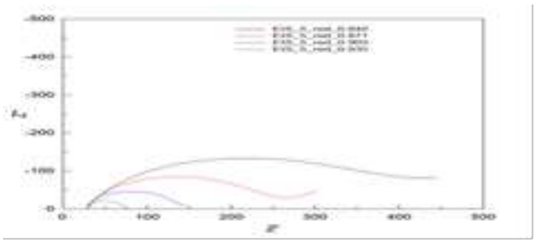

Fig 8. Example of shift phase Y-axis of a Bode plot of an EIS experiment of a Perovskite solar cell.

We can assume that every semicircle of the Nyquist Plot represents a different process taking place inside the solar device. The equivalence in the Bode plot to each semicircle that we can see in the Nyquist plot as a peak in the shift phase Y-axis of the Bode plot.

In order to give a real meaning to these figures so we can extract valuable information about the physical process behind these plots, we need to adjust the spectra to an equivalent circuit that simulates the internal electrical process in our device.

These equivalent circuits can include three elements: resistors, capacitors and inductors [2].

- Resistors introduce resitance in the circuit, which are elements that opposes to the charge flux, and their representation is the R symbol of **Figure 9.**

- Capacitors work by accumulating the electrical charge that is flowing in the circuit. The capacitance is different at each voltage applied and their representation is the C symbol of **Figure 9**.

- Inductors represent processes that introduces new electric charge into the circuit, and they are represented by the L symbol of **Figure 9**.

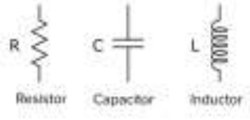

Fig 9. Symbols of Resistors, Capacitors and Inductors used in electric circuits.

We can adjust the spectra obtained in **Figure 7** and **Figure 8** using an equivalent circuit that consists on a serie resistor, normally related to the contacts of the devices and a set of a resistor and a capacitor in parallel that represents the behavior of the solar device, as shown in **Figure 10**.

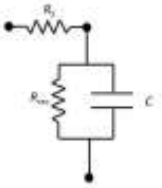

Figure 10: Example of equivalent circuit adapted to the results shown in **Figure 7** and **Figure 8**.

Using appropriate software, as ZView (Scribner), we can run automatic simulations in order to find the values of resistances and capacitances that best fits our results. By checking the Bode plot, we can determine the time scale where our process are taking place. High frequencies process are normally related to electron transport and recombination, while low frequencies are more likely to refer to ionic diffusion and interfacial charge accumulation [2].

5. CONCLUSIONS

Small-Perturbation Optoelectronic Measuring Techniques provide us with tons of information that help us to better understand the performance of solar cells and to detect internal process. In this way, we can determine the electrochemical behavior of these devices, so we can gain further understanding of charge transport and transfer efficiency to the contacts in operation conditions. These techniques have multiple applications and variants. We can collect very meaningful data not only by the techniques itself, but also by combining them with changes in the wavelength of the illumination, temperature condition or voltage level, among many others.

However, there are certain aspects and warnings that must be held into account when working with these tools. Although they are very promising and provide us with tons of data, we can be tempted to expect from the experiment more information than what it can actually give. Secondly, even though models are useful for simplifying and understanding reality, we must avoid using a model without physical significance. This means that a good fitting to a model does not necessarily mean a correct interpretation of the impedance response.

Despite these aspects, the advantages of the Small-Perturbation Optoelectronic techniques outweigh the difficulties so we refuse to be discouraged, but we keep working trying to get the most from these techniques, among many others in the long way of elucidating the photovoltaic devices behavior.

ACKNOWLEDGEMENTS

I wish to thank Professor Juan Antonio Anta and his whole team (Nanostructured Solar Cells Group) for providing me with the opportunity of specializing in the techniques mentioned in this article, by conducting a pHD research in the field.

BIBLIOGRAPHIC REFERENCES

[1] Lasia, A., *Electrochemical Impedance Spectroscopy and its Applications*, DOI 10.1007/978-1-4614-8933-7_2, Springer Science+Business Media New York, 2014, pp 7 – 20, 48 – 62.

[2] Guillén, E., Ramos, F.J., Anta, J.A., Ahmad, S., *Elucidating Transport-Recombination Mechanisms in Perovskite Solar Cells by Small-Perturbation Techniques*, J. Phys. Chem. C 2014, 118, 22913-22922.

[3] Bertoluzzi, L.; Bisquert J., *Investigating the Consistency of Models for Water Splitting System by Light and Voltage Modulated Techniques*, J. Phys. Chem. Lett., 2017, 8, 172-180.

[4] Halme, J., *Linking optical and electrical small amplitude perturbation techniques for dynamic performance characterization of dye solar cells,* Phys. Chem. Phys., 2011, 13, 12435-12446.

[5] Lvovich, V. F., *Impedance Spectroscopy: Applications to Electrochemical and Dielectric Phenomena;*Wiley: Somerset, USA, 2012.

[6] Orazem, M.E.; Tribollet, B. *Electrochemical Impedance Spectroscopy;* 2011th ed.; Joh Wiley & Sons.

[7] Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. *Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells.* J. Am. Chem. Soc. 2009, 131 (17), 6050-6051.

[8] NREL. NREL: National Center for Photovoltaics Home Page https://www.nrel.gov/pv/ (accessed Apr 8, 2018).

[9] Antonietta, L. M. et al, Nature Materials 12, 2013, 1087-1089.

Antonio Jesús Riquelme Expósito graduated in Environmental Sciences at Pablo de Olavide University in 2014. He is currently conducting his pHD research on Fundamental Studies of Electronic Dynamics in Solar Cells based on hybrid perovskite.