Unravelling the meaning of negative values of Intensity Modulated Photocurrent Spectroscopy in solar energy conversion devices

Drialys Cardenas-Morcoso[a1]

[1]Institute of Advanced Materials, Universitat Jaume I, Castelló, Spain

The meaning of negative IMPS transfer function values was experimentally demonstrated, providing a powerful opto-electronic method toward specific operational mechanisms insights in photoelectrochemical systems.[b]

The detailed understanding of the optoelectronic properties of semiconductor materials used in photo-electrochemical (PEC) systems for solar-assisted fuel production, is key to further establish adequate strategies to overcome its limitations. Usually, this is a complex task, which involves the use of characterization methods delivering a set of results, which must be interpreted based on theoretical models. Small perturbation techniques are particularly useful to disentangle carrier dynamics in complex systems. Nevertheless, the interpretation of the obtained results can be challenging, and many controls and iterative validations are needed for a sound mechanistic description. In addition, the presence of "atypical" spectroscopic features makes interpretation even more complex. However, these anomalous features constitute a valuable source of information, which remains ignored in many occasions.

The Incident Modulated Photocurrent Spectroscopy (IMPS) technique has an important advantage for the study of PEC devices, by providing a small modulation of the minority carrier —playing the dominant role in the PEC performance—, with a modulated incident photon flux. An anomalous feature has been observed during IMPS measurements in $BiVO_4$ photoelectrodes, by a change of quadrant from positive to the negative real part of the complex plane representation at low frequency, usually at the region closer to the open circuit potential (OCP) (See Figure 1). In previous reports, this feature has been assigned to the switch of the photocurrent sign at this region. [1]. However, we have experimentally demonstrated that this feature is not related to the photocurrent sign, but it is directly connected to the variation of the steady-state extracted photocurrent j_e with the incident illumination intensity j_ϕ, *i.e.* the differential external quantum efficiency (EQE_{diff}) [2].

Note that, the connection between the EQE_{diff} and the low frequency value of IMPS ($Q(0)$) has been previously described in perovskite solar cells [3], finding that both values are directly linked to the dc component of the slope of $\overline{j_e}$ with $\overline{j_\phi}$, as depicted in Eq. 1. The bar over the symbols denotes the steady-state condition.

$$Q(0) = \frac{\widehat{j_e}(0)}{\widehat{j_\phi}(0)} = \frac{\partial \overline{j_e}}{\partial \overline{j_\phi}} = EQE_{\text{diff}} \qquad (1)$$
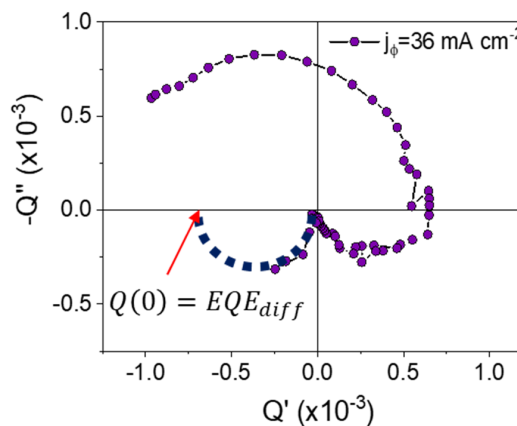

Figure 1: Complex representation of the IMPS transfer function on $BiVO_4$ photoanodes, measured at $-0.05\,V_{\text{RHE}}$, showing the low frequency value, $Q(0)$. Figure adapted with permission from the American Chemical Society [2].

However, such a connection had not been established to explain the change of sign of the low-frequency IMPS value observed in photoelectrodes used for PEC water splitting. Usually, the treatment of IMPS measurements in PEC systems is carried out by using a rate constants model, which focuses on the evaluation of the competition of charge transfer and recombination process at the electrode surface [4, 5]. However, the analysis of kinetic constants, which corresponds to the maximum ω of each arc observed in the Q complex plane, usually neglects the analysis of the value of the real part of Q. In order to clearly show this relation, the $j_e - j_\phi$ steady-state curve of the $BiVO_4$ photoanode at an applied potential near to the OCP was recorded. Each point was measured during a sufficiently long time to reliably capture the steady-state condition of $j_e - j_\phi$, and to be compatible with the low-frequency domain of the IMPS measurements (100 s). As shown in Figure 2, at lower j_ϕ values there is a region where the extracted photocurrent is positive and its value decreases when increasing the light intensity, leading to a negative slope and, consequently to a negative EQE_{diff}. This observation was in good agreement with the measured negative Q transfer function at low frequency. Analogously, at higher j_ϕ, the negative EQE_{diff} is related to the decreasing $j_e - j_\phi$ slope, independently of the negative sign of the photocurrent.

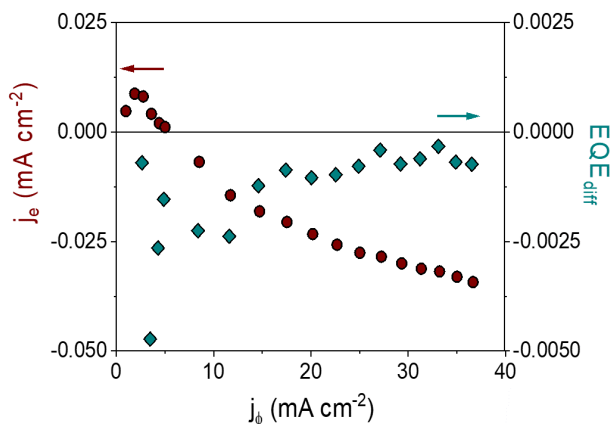This experimental proof of a particular operational

Figure 2: $j_e - j_\phi$ steady-state curve recorded for a BiVO$_4$ photoanode, and the calculated EQE_{diff} from its slope. Figure adapted with permission from the American Chemical Society [2].

point, where both the IMPS response and the EQE_{diff} are negative, while the photocurrent remains positive was critical for demonstrating that the negative value of the real part of the Q transfer function is associated with the derivative of the photocurrent with the light intensity, independently of the sign of the photocurrent. Moreover, this interpretation further establishes the measurement of the $j_e - j_\phi$ curves as a powerful optoelectronic method containing valuable information on specific recombination and trapping mechanisms during the operation of photoelectrodes.

In BiVO$_4$ photoanodes, $EQE_{\text{diff}} = 0$ at voltages close to OCP indicates an invariant value of $\overline{j_e}$ with $\overline{j_\phi}$, indicating that $j - V$ plots at different light intensities will converge to the same OCP value. This can be indicative of Fermi level pinning on BiVO$_4$. On the other hand, the observations of a negative EQE_{diff} at voltages close to or beyond the OCP, suggest that incident light intensity promotes the filling of a local density of shallow traps around the electron Fermi level, promoting the recombination of photogenerated holes with the trapped electrons. This leads to a decrease

in j_e. At larger applied anodic bias, the shallow traps are filled with holes, allowing the photogenerated holes to be efficiently extracted and causing an increase of photocurrent with light intensity, and hence, a positive EQE_{diff}, as usually observed in water oxidation conditions.

Summary

It was demonstrated that the negative values of the real part of Q is not related to the photocurrent sign, but it is directly connected to the variation of the steady state extracted photocurrent with the incident light intensity. Moreover, it was shown that the real part of Q contains significant physical information, allowing further understanding of operational mechanisms of photoelectrodes and hence, paving the way in searching for successful strategies to improve the current efficiencies of PEC systems for solar-assisted fuel production.

Notes

a. Email: drialys.cardenas@list.lu. Current author's affiliation: Luxembourg Institute of Science and Technology, Belvaux, Luxembourg

b. Original version of this article is Ref. [2]

References

[1] Antuch, M.; Millet, P.; Iwase, A.; Kudo, A. *Applied Catalysis B: Environmental,* 237 (2018) 401-408

[2] Cardenas-Morcoso, D.; Bou, A.; Ravishankar, S.; García-Tecedor, M.; Gimenez, S.; Bisquert, J. *ACS Energy Letters,* 5 (2020) 187-191

[3] Ravishankar, S.; Aranda, C.; Boix, P. P.; Anta, J. A.; Bisquert, J.; Garcia-Belmonte, G., *The Journal of Physical Chemistry Letters,* 11 (2018) 3099-3104

[4] Peter, L. M., *Chemical Reviews,* 90 (1990) 753-769

[5] Ponomarev, E. A.; Peter, L. M. *Journal of Electroanalytical Chemistry,* 396 (1995) 219-226