Application Area: Energy

Dye sensitized solar cells, IMVS and IMPS measurements

Keywords

Photovoltaic devices, dye sensitized solar cells (DSC), impedance spectroscopy, intensity-modulated photovoltage spectroscopy (IMVS), intensity-modulated photocurrent spectroscopy (IMPS)

Summary

A solar cell or photovoltaic cell is a device that converts light energy into electrical energy. Dye-sensitized solar cells (DSC) are currently subject of intense research in the framework of renewable energies as a low-cost photovoltaic (PV) device. Electricity generated from a PV produces zero emissions, and can produce energy anywhere the sun shines.

The standard characterization technique of a PV device consists of the determination of the DC Current-Voltage curves under different incident light intensities. Alongside DC characterization methods, it is also possible to analyze the behavior of these devices using electrochemical impedance spectroscopy (EIS).

To characterize photovoltaic devices, two additional frequency domain methods can be used. These methods are based on the modulation of the light intensity. The response from the cell is measured as a voltage or a current depending on the experimental conditions. Therefore two different measurements can be performed:

- *Intensity modulated photovoltage spectroscopy* (IMVS): measurement of the transfer function between the modulated light intensity $\varphi\ (mw\ cm^{-2})$ and the generated AC voltage $V\ (V)$
- *Intensity modulated photocurrent spectroscopy* (IMPS): measurement of the transfer function between the modulated light intensity $\varphi\ (mw\ cm^{-2})$ and the generated AC current $I\ (A)$.

This application note illustrates the use of the Metrohm Autolab PGSTAT302N equipped with a FRA32M module, in combination with the Autolab Optical Bench kit to perform IMVS and IMPS characterization of photovoltaic devices.

Experimental conditions

All the measurements were performed on a dye-sensitized solar cell, using the N719 dye, supplied by Solaronix. The light source was equipped with a 627 nm (red) LED light.

Three IMVS and IMPS measurements were performed at light intensities of 5 mW/cm^2, 10 mW/cm^2 and 50 mW/cm^2.

The AC amplitude was set to 10% of the light intensity value.

The measurements were performed between 10 kHz and 100 mHz, ten data points per decade.

IMVS measurements

The intensity-modulated photovoltage spectroscopy measurements provide additional information on the internal dynamics of the cell. The IMVS data corresponds to the values of the transfer function, $Z(IMVS)$, between the modulated light intensity and the measured AC potential of the cell, at open-circuit. The transfer function follows the below Equation below:

$$Z(IMVS) = \frac{\Delta V}{\Delta \varphi^{LED}} e^{j\varphi} \qquad 1$$

Where $Z(IMVS)$ is the transfer function, $\Delta V\ (V)$is the variation of the photo-generated solar cell voltage, $\Delta \varphi^{LED} (mW/cm^2)$ is the variation of the light intensity, $j = \sqrt{-1}$ and φ is the phase shift between the two modulated signals. As so defined, the transfer function $Z(IMVS)$ gives a value in voltage versus light intensity, V/(mW/cm^2).

IMVS measurements provide information about the electron lifetime and electron-hole recombination dynamics under open-circuit conditions. Figure 1 shows a schematic overview of the IMVS measurements.

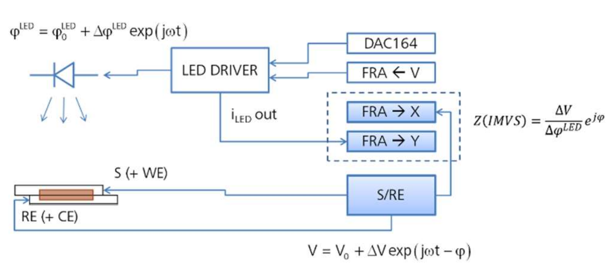

Figure 1 – Overview of the experimental setup for the IMVS measurements.

Here, the modulated voltage signal is generated as sum of the DC voltage offset given by the DAC164 and the AC voltage modulation given by the FRA ←V. The generated signal is converted into current by the LED driver. The current signal $i_{LED}\ out$ is sent to the LED driver and to the FRA →Y input of the FRA32M module.

The LED driver turns the current into light φ^{LED}, composed of an offset $\varphi_0^{LED}$and a modulation $\Delta\varphi^{LED}\exp(j\omega t)$. The modulation contains the phase $\omega\ (Hz)$ and time $t\ (s)$ information, and $j = \sqrt{-1}$.

The light shines on the solar cell, which generates a photovoltage signal V, recorded by the PGSTAT from the S (+ WE) and RE (+ CE) leads.

The photo-generated voltage V is composed of an offset V_0 and a modulation $\Delta V\exp(j\omega t - \varphi)$. The modulation contains the phase $\omega\ (Hz)$ and time $t\ (s)$ information, $j = \sqrt{-1}$, and the phase φ angle, which describes the time difference between the LED light and the photovoltage signals.

The photovoltage signal is sent to the FRA →X input of the FRA32M module.

Finally, the software calculates the transfer function $Z(IMVS)$ as ratio between the modulation of the photovoltage $\Delta V\exp(j\omega t - \varphi)$ and the modulation of the light intensity $\Delta\varphi^{LED}\exp(j\omega t)$.

Figure 2 shows the IMVS Nyquist plot recorded under constant illumination of 5 mW/cm^2 (blue dots), 10 mW/cm^2 (red dots), and 50 mW/cm^2 (green dots).

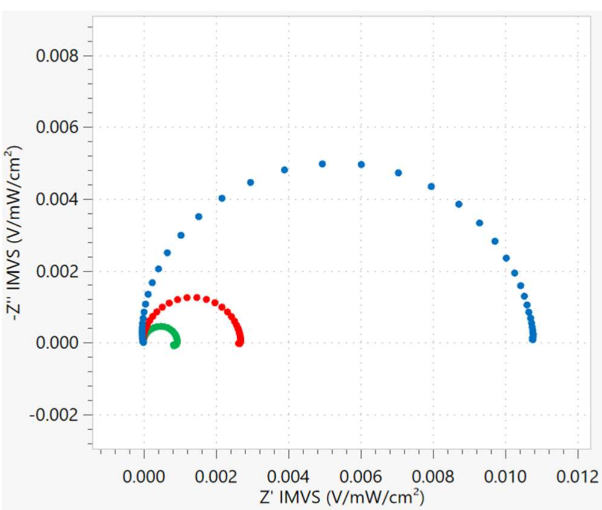

Figure 2 – IMVS measurement obtained at 5 mW/cm^2 (blue dots), 10 mW/cm^2 (red dots), and 50 mW/cm^2 (green dots).

As light intensity increases, the semi-circle radius decreases.

In Figure 3, the plot of the imaginary component of the IMVS transfer function versus the frequency is shown.

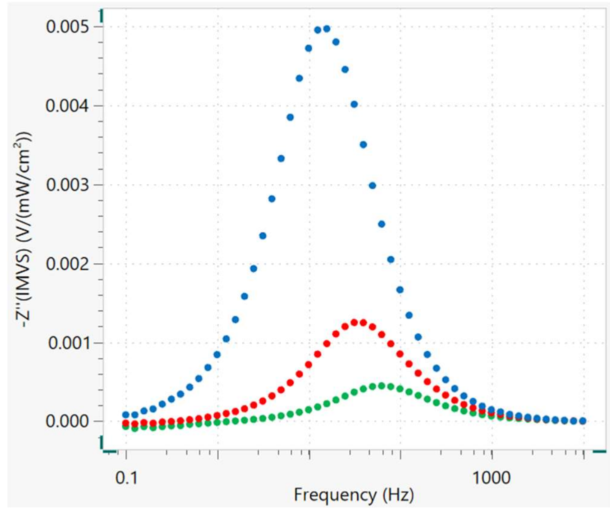

Figure 3 – Imaginary component -Z"(IMVS) of the IMVS transfer function plotted versus the frequency at 5 mW/cm^2 (blue dots), 10 mW/cm^2 (red dots), and 50 mW/cm^2 (green dots).

Here, it can be noticed that the frequency corresponding to the minimum of the imaginary part of the IMPS transfer function, -Z"(IMVS), increases as the light intensity increases, which indicates that the electron lifetime decreases. Therefore, the electron recombination is more pronounced at high illumination intensities.

IMPS measurements

The intensity-modulated photocurrent spectroscopy measurements provide complementary information on the internal dynamics of the cell. The IMPS data corresponds to the values of the transfer function, H_{IMPS}, between the modulated light intensity and the measured AC current of the cell, at short-circuit. The transfer function follows the Equation below:

$$Z(IMPS) = \frac{\Delta i}{\Delta\varphi^{LED}} e^{(j\varphi)} \qquad 2$$

Where $Z(IMPS)$ is the transfer function, $\Delta i\ (A)$ is the variation of the photo-generated solar cell current, $\Delta\varphi^{LED}\ (mW/cm^2)$ is the variation of the photon flux, $j = \sqrt{-1}$ and φ is the phase shift between the two signal. As so defined, the transfer function $Z(IMPS)$ gives value in current versus a light intensity, A/(mW/cm^2).

IMPS measurements provide information about the electron lifetime and electron-hole recombination dynamics as well as the equivalent mass transport of the charge carriers.

Figure 4 shows a schematic overview of the IMPS measurements.

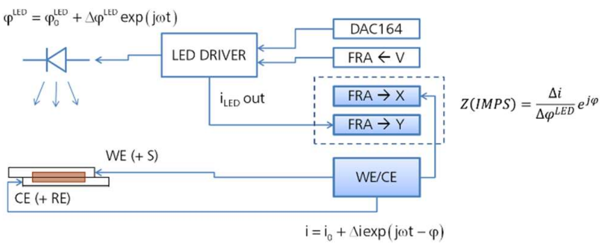

Figure 4 – Overview of the experimental setup of the IMPS measurements

Here, the modulated voltage signal is generated as sum of the DC voltage offset given by the DAC164 and the AC voltage modulation given by the FRA ←V. The generated signal is converted into current by the LED driver. The current signal $i_{LED}\ out$ is sent to the LED driver and to the FRA →Y input of the FRA32M module.

The LED driver turns the current into light φ^{LED}, composed of an offset φ_0^{LED} and a modulation $\Delta\varphi^{LED}\exp(j\omega t)$. The modulation contains the phase $\omega\ (Hz)$ and time $t\ (s)$ information, and $j = \sqrt{-1}$.

The light shines on the solar cell, which generates a photocurrent signal i, recorded by the PGSTAT from the S (+ WE) and RE (+ CE) leads.

The photo-generated current *i* is composed of an offset i_0 and a modulation $\Delta i\exp(j\omega t - \varphi)$. The modulation contains the phase $\omega\ (Hz)$ and time $t\ (s)$ information, $j = \sqrt{-1}$, and the phase φ angle, which describes the time difference between the LED light and the photocurrent signals.

The photovoltage signal is sent to the FRA →X input of the FRA32M module.

Finally, the software calculates the transfer function $Z(IMVS)$ as ratio between the modulation of the photocurrent $\Delta i\exp(j\omega t - \varphi)$ and the modulation of the light intensity $\Delta\varphi^{LED}\exp(j\omega t)$.

Figure 5 shows the IMPS Nyquist plot recorded under constant illumination of 5 mW/cm^2 (blue dots), 10 mW/cm^2 (red dots), and 50 mW/cm^2 (green dots).

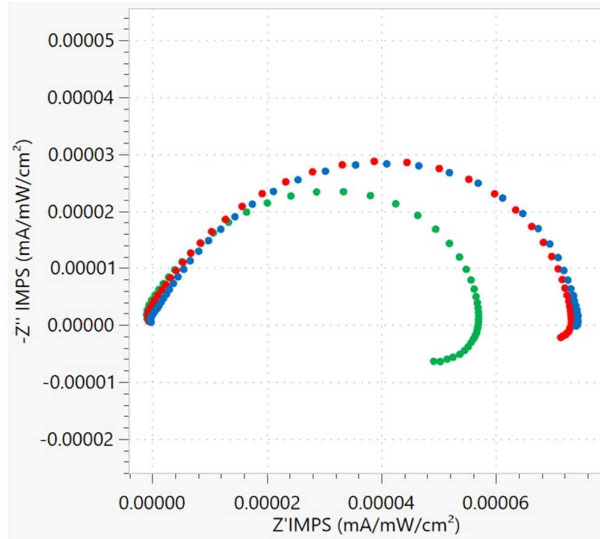

Figure 5 – IMPS measurement obtained at 5 mW/cm^2 (blue dots), 10 mW/cm^2 (red dots), and 50 mW/cm^2 (green dots).

The IMPS data is similar to the data obtained in the IMVS measurements. At high frequencies the modulated photocurrent approaches zero. This indicates that the modulation frequency is faster than the relaxation of the charge carrier density. This is due to transport to the contacts and back reaction.

The same conclusion can be inferred from the plot of the imaginary component versus the frequency (see Figure 6).

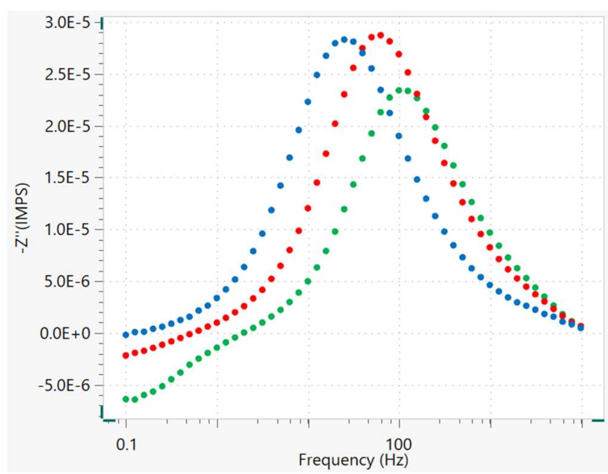

Figure 6 – Imaginary component -Z''(IMPS) of the IMPS transfer function plotted versus the frequency at 5 mW/cm^2 (blue dots), 10 mW/cm^2 (red dots), and 50 mW/cm^2 (green dots)..

Also in the case of IMPS, the frequency corresponding to the minimum of the imaginary part of the IMPS transfer function –Z''(IMPS) increases as the light intensity increases, which indicates that the electron lifetime decreases.

Comparison of the characteristic frequencies obtained with IMPS and IMVS data indicates that the electron lifetime is longer at open-circuit conditions. This can be seen when comparing the IMVS data with IMPS data which is done at short circuit condition. See Figure 7.

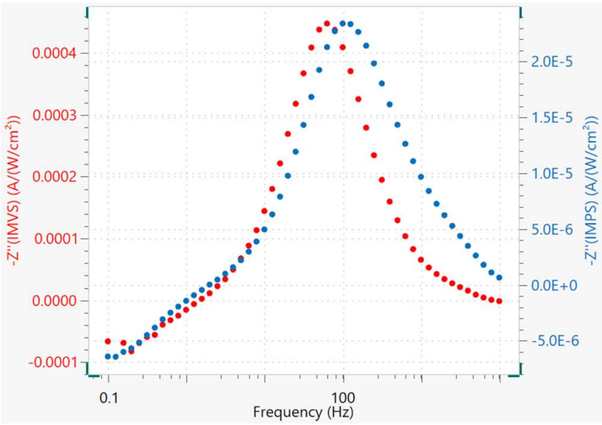

Figure 7 – Comparison of the -Z” versus frequency plots for IMPS (blue dots) and IMVS data (red dots), obtained at 50 mW/cm²

Conclusions

This application note illustrated the use of the Autolab Optical Bench kit to perform IMPS and IMVS measurements, in combination with Metrohm Autolab PGSTAT.

The cell can be studied at different experimental conditions and under different light intensities. The IMPS and IMVS data provide additional information related to the electron lifetime.

Acknowledgments

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/en/products/electrochemistry**.