Dye Solar Cells –
Part 3: IMPS and IMVS measurements

Purpose of This Note

This application note is part of a series of notes concerning dye solar cells. Theory and various types of experiments are discussed which are helpful for characterizing solar cells.

Part 1 of this series discusses basic principles of dye solar cells, their setup, and underlying electrochemical mechanisms. Part 2 addresses electrochemical impedance spectroscopy measurements on dye solar cells. Various models are discussed for analyzing impedance spectra.

This application note is part 3 and addresses IMPS and IMVS experiments on dye solar cells. Theory and implementation of both techniques are explained. Data evaluation is discussed based on experiments.

Introduction

Intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) can offer valuable information about dye solar cells (DSCs). IMPS and IMVS yield time constants which are related to the electron transport and electron recombination. Both parameters can be used to calculate the diffusion coefficient and the diffusion length, among others.

Basic principles

IMPS and IMVS are related to electrochemical impedance spectroscopy (EIS). In EIS, a constant potential or current signal is applied to a cell which is superimposed by an AC signal. The frequency is modulated. The measured sinusoidal signal has the same frequency as the applied signal but it is phase-shifted. The frequency-dependent impedance *Z* can be then calculated.

Both IMPS and IMVS operate in a similar way. Instead of modulating the amplitude of a current or potential signal, the intensity of a light beam focused on a DSC is modulated. Figure 1 illustrates both techniques.

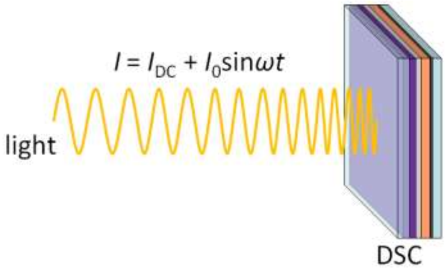

Figure 1. Sketch of the light signal focused on a DSC during IMPS and IMVS.

During IMPS and IMVS experiments, light with a base intensity I_{DC} is focused on a DSC. Upon the constant base intensity, a sinusoidal waveform with amplitude I_0 is superimposed. The frequency *f* of the sine wave is changed during an experiment. The angular frequency ω can be expressed as $\omega = 2\pi f$. The photocurrent (IMPS) or photovoltage (IMVS) respectively of a DSC is measured. Similar to EIS – but in this case light – the resultant signal has the same frequency as the applied signal, but its phase is shifted. By changing the frequency of the light signal, time-dependent information about various processes such as diffusion coefficients or reaction rates can be obtained.

EIS and IMPS/IMVS can be further differentiated by looking at the I-V curve of a DSC. Figure 2 shows stylized sketches of I-V curves with increasing light intensity. The regions covered by EIS, IMPS, and IMVS are highlighted.

The power generated by a DSC rises with increasing light intensity. As a result, the photocurrent increases leading to a higher short-circuit current I_{SC} at 0 V. In addition, the open-circuit potential E_{OC} shifts towards higher potentials, too.

Typically, experiments with DSCs are performed under constant illumination. When measuring EIS spectra, only one point of a single I-V curve can be analyzed. In contrast, the light intensity is modulated during IMPS and IMVS. This way, the cell's response within a series of I-V curves can be measured. The regions for IMPS and IMVS are highlighted in green and red in Figure 2.

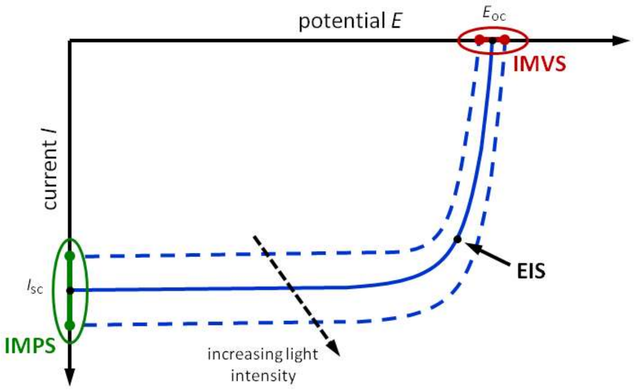

Figure 2. I-V curves of a DSC showing the regions covered by EIS, IMPS, and IMVS.

The following sections describe both techniques and various parameters more detailed.

Intensity-modulated photocurrent spectroscopy – IMPS

During IMPS, the potential of a DSC is potentiostatically controlled and set to 0 V (short-circuit conditions). The generated photocurrent is measured. The green line-segment in Figure 2 indicates the range measured during IMPS.

Electron transport time τ_{tr}

At short-circuit conditions, the band gap between non-conductive valence band and conduction band of the semiconductor is maximum. As a result, nearly no electrons are injected into the conduction band. Most reactions occur on the back layer of the anode and electrons are migrating from the location where they are generated to the electrode's back layer.

The corresponding electron transport time constant τ_{tr} can be evaluated by IMPS. The technique exhibits a specific frequency f_{IMPS} which is inversely proportional to τ_{tr} according to Equation 1.

$$\tau_{tr} = \frac{1}{2\pi \cdot f_{IMPS}} \qquad \text{Eq. 1}$$

A more detailed data analysis of IMPS measurements is discussed in the Experiments section.

Intensity-modulated photovoltage spectroscopy – IMVS

IMVS experiments are performed under open-circuit conditions. The photovoltage of a DSC is measured during IMVS. The cell is galvanostatically controlled and the current is set to 0 A. The red line-segment in Figure 2 indicates the measured range during an IMVS experiment.

Electron recombination time τ_{rec}

The open-circuit potential is the maximum potential of a DSC before power is dissipated instead of being generated. The band gap between valence band and conduction band is small at this potential. Hence reactions on the back layer of the anode are less likely. Most generated photoelectrons are injected into the semiconductor's conduction band. In addition, the DSC reaches steady-state at the open-circuit potential. This means that the rate of electron injection into the conduction band is equal to the electron recombination rate.

IMVS can be used to evaluate the rate of electron recombination or the electron lifetime. The technique yields a frequency f_{IMVS} which is inversely proportional to the electron recombination time constant τ_{rec}, see Equation 2.

$$\tau_{rec} = \frac{1}{2\pi \cdot f_{IMVS}} \qquad \text{Eq. 2}$$

A more detailed data analysis of IMVS measurements is discussed in the Experiments section.

Additional parameters

Both time constants can be further used to estimate the charge-collection efficiency η_{cc} (see Equation 3). It is a crucial factor for characterizing the overall performance of dye solar cells. The higher η_{cc} is, the more efficient is a cell.

$$\eta_{cc} = 1 - \frac{\tau_{tr}}{\tau_{rec}} \qquad \text{Eq. 3}$$

High charge-collection efficiencies can be achieved by increasing the time for electron recombination or decreasing the electron transport time.

In addition, the electron diffusion coefficient D can be calculated. At low potentials, electron transport is mainly restricted by diffusion through the electrode's active film with thickness L. Electron recombination can be nearly completely ignored at such low potentials and only the electron transport time constant τ_{tr} matters. Equation 4 can be used to calculate the electron diffusion coefficient.

$$D = \frac{L^2}{2.35 \cdot \tau_{tr}} \qquad \text{Eq. 4}$$

At higher potentials or when using less-efficient cells, electron recombination plays a more important role. Electron transport and recombination are competing with each other. Hence the effective electron diffusion length L_D becomes smaller. It can be calculated by Equation 5.

$$L_D = \sqrt{D \cdot \tau_{\text{rec}}} \qquad \text{Eq. 5}$$

For good efficiencies, the effective diffusion length L_D should be greater than the film thickness L. This means that electrons can be efficiently collected at the electrode before they recombine.

Experiments

The following sections describe IMPS and IMVS experiments on a DSC, including data analysis. For all experiments, a red LED (λ_{em} = 625 nm) was focused on a DSC. The base intensity of the light source was varied between 5.1 mW and 34.7 mW. The AC amplitude was set to 10 % of the applied base intensity. Frequency modulation was applied between 10 kHz and 10 mHz.

In order to maintain pseudo-linearity, only small intensity amplitudes were applied. In addition, the cell was illuminated prior to each experiment and its open-circuit potential was measured until it was constant. This step ensured that the DSC could fully warm up and reach constant temperature.

IMPS

Figure 3 shows a series of IMPS experiments with Nyquist-type plots at different base intensities. The imaginary part of the measured photocurrent is plotted versus its real part. The intensity is increasing from bright to dark green.

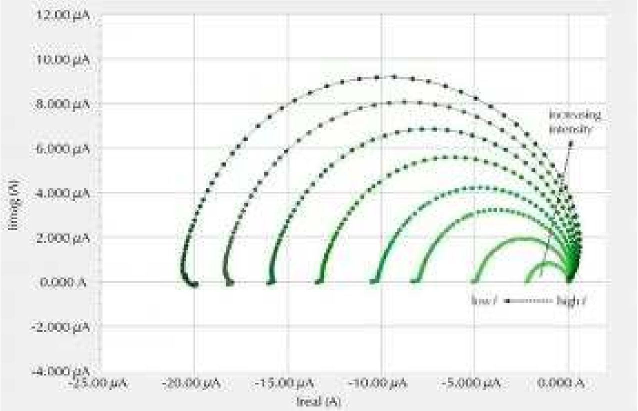

Figure 3. IMPS Nyquist-type plots at different intensities.

All curves have the shape of a single semicircle. The radii of the semicircles increase with greater light intensities. The high-frequency end is on the right side of each curve.

The curves show a maximum at intermediate frequencies. This point is characteristic for the electron transport through the pores of the anode to the back layer. The frequency at this maximum is related to τ_{tr}.

Figure 4 shows the corresponding Bode-type plots. The imaginary part of the measured photocurrent is plotted versus the frequency in a semi-logarithmic style. This graphical presentation is generally used for evaluation of data because it directly shows the frequency of each point.

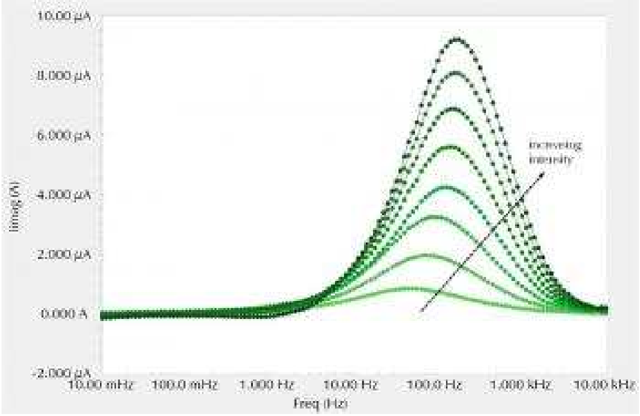

Figure 4. IMPS Bode-type plots at different intensities.

All curves exhibit a maximum which shifts to higher frequencies with increasing intensities. This means that the electron transport is faster when the light intensity is increased. The corresponding time constant τ_{tr} is decreasing and can be calculated by Equation 1. Table 1 on the next page lists all data obtained from this experiment.

IMVS

Figure 5 shows various Nyquist-type plots from IMVS experiments on the same cell at different light intensities. The intensity is increasing from bright to dark green.

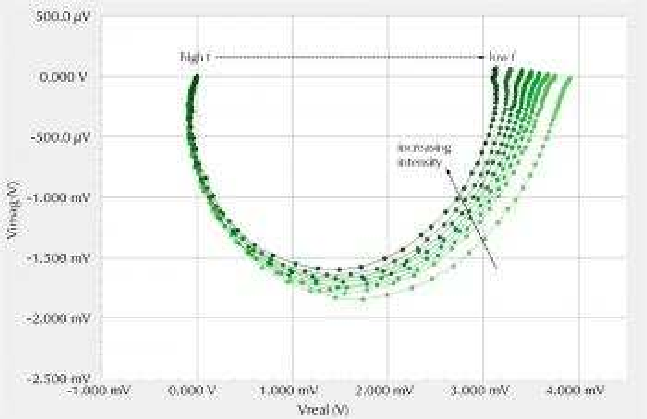

Figure 5. IMVS Nyquist-type plots at different intensities.

Similar to IMPS experiments, each curve shows one semicircle in the complex plane. The radius of the arc is decreasing with increasing intensities. The frequency value at the minimum of each semicircle is related to the recombination time constant τ_{rec} according to Equation 2.

Figure 6 shows the corresponding Bode-type plots. All curves show a minimum which tends to shift to higher frequencies with increasing light intensities. This means that the lifetime of the electrons or recombination time respectively is decreasing. Table 1 in the next section summarizes all data from this experiment.

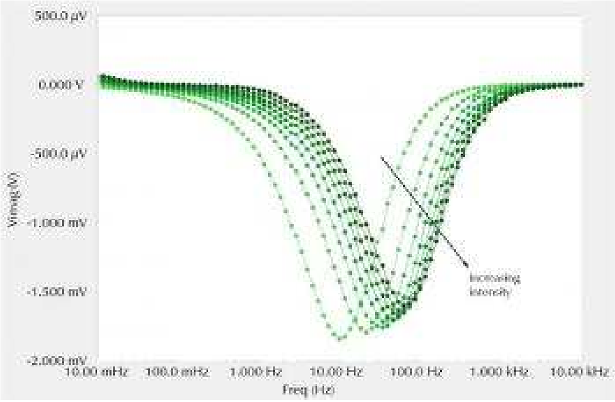

Figure 6. IMVS Bode-type plots at different intensities.

Data analysis

Table 1 lists all parameters obtained from the previous IMPS and IMVS experiments. The Bode-type plots in Figure 4 and Figure 6 yield the frequencies f_{IMPS} and f_{IMVS}. The corresponding time constants τ_{tr} and τ_{rec} are calculated using Equations 1 and 2. The charge-collection efficiency η_{cc} is calculated by Equation 3.

The measurements show that the time constant for the electron transport τ_{tr} is in general smaller than the time constant of the recombination time τ_{rec} at a given intensity. This fact is important for a good cell performance.

P [mW]	f_{IMPS} [Hz]	τ_{tr} [ms]	f_{IMVS} [Hz]	τ_{rec} [ms]	η_{cc}
5.1	44.7	3.6	10.0	15.9	0.78
10.1	70.8	2.2	21.5	7.4	0.70
14.9	89.1	1.8	34.2	4.7	0.62
19.5	125.9	1.3	39.8	4.0	0.68
24.0	141.3	1.1	46.4	3.4	0.67
28.1	149.5	1.1	54.1	2.9	0.64
31.6	158.5	1.0	59.4	2.7	0.63
34.7	177.8	0.9	63.9	2.5	0.64

Table 1. Summary of parameters obtained from IMPS and IMVS experiments at different light intensities.

In addition, both parameters are decreasing with increasing light intensities. However, the cell's performance at higher intensities is not improving. τ_{rec} decreases much faster than τ_{tr}. This can be shown by the calculated charge collection efficiency η_{cc}. It is decreasing with increasing light intensities from about 0.78 at 5.1 mW to about 0.64 at 34.7 mW. Hence electron recombination is much more affected by intensity changes than the electron transport.

Summary

This application covers the techniques IMPS and IMVS which are both related to EIS. The intensity of a light beam focused on a DSC is changed by modulating its frequency. The generated photocurrent or photovoltage respectively are measured. Both techniques allow obtaining important information about various reaction and transport parameters.

In addition, IMPS and IMVS measurements are performed on small DSCs. The light intensity is increased stepwise and the influence on the cell's performance is discussed. The time constants for the electron transport and the electron recombination are calculated. Both parameters can be further used to obtain information about the charge-collection efficiency and diffusion parameters.

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