Application NOTE

GAMRY INSTRUMENTS

Dye Solar Cells – Part 1: Basic principles and measurements

Purpose of This Note

This application note is part of a series concerning dye solar cells. Theory and various types of experiments are discussed that are needed for characterization of solar cells.

Part 1 of this series discusses basic principles of dye solar cells, their setup, and underlying electrochemical mechanisms.

In addition, characterization of dye solar cells is demonstrated by means of basic electrochemical experiments.

Introduction

In times of fossil fuel shortage, increasing crude-oil prices, as well as rejection of conventional energy sources (e.g. coal or nuclear power plants), sustainable energy forms become more and more the focus of attentions. Hydropower, wind power, geothermal power, or biomass processing are but a few of these sustainable resources.

Another important source for renewable energy is solar power. Photovoltaics and solar thermal collectors are most widely used.

Dye solar cells (DSCs) which are discussed in this application note are thin-film cells. They are also called dye-sensitized solar cells (DSSC) or Grätzel cells named after the Swiss chemist Michael Grätzel who was greatly involved in the development of new cell types.

Manufacturing of DSCs is simple, mostly low-cost, and incorporate environmentally friendly materials. They have a good efficiency (about 10-14 %) even under low flux of sunlight.

However, a major drawback is the temperature sensitivity of the liquid electrolyte. Hence a lot of research is going on to improve the electrolyte's performance and cell stability.

Theory

Setup of a Dye Solar Cell

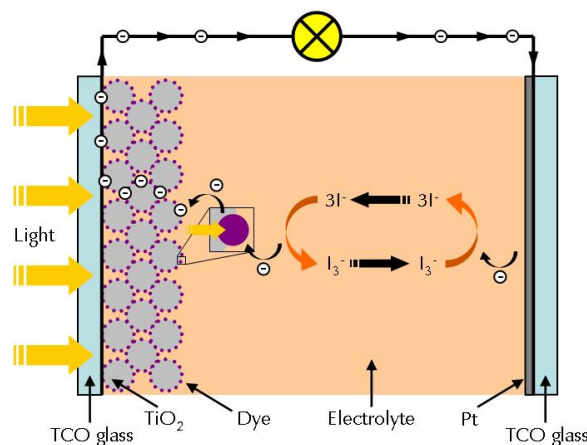Figure 1 shows a simplified diagram of a dye solar cell.

Figure 1 – Simplified setup of a dye solar cell. For details, see text.

The anode of a DSC consists of a glass plate which is coated with a transparent conductive oxide (TCO) film. Indium tin oxide (ITO) or fluorine-doped tin oxide are most widely used. A thin layer of titanium dioxide (TiO$_2$) is applied on the film. The semiconductor exhibits a high surface area because of its high porosity.

The anode is soaked with a dye solution which bonds to the TiO$_2$. The dye – also called photosensitizers – is mostly a ruthenium complex or varius organic metal-free compounds. For demonstration purposes, also plain fruit juice (such as from blackberries or pomegranates) can be used. They contain pigments which are also able to convert light energy into electrical energy.

The cathode of a DSC is a glass plate with a thin Pt film which serves as a catalyst. An iodide/triiodide solution is used as the electrolyte.

Both electrodes are pressed together and sealed so that the cell does not leak. An external load can be powered when light shines on the anode of the dye solar cell.

Principle of a Dye Solar Cell

As the name implies, the mechanism of dye solar cells is based on the photo-electrochemical processes. Figure 2 depicts an energy diagram of a dye solar cell. The following section describes all relevant electrochemical processes.
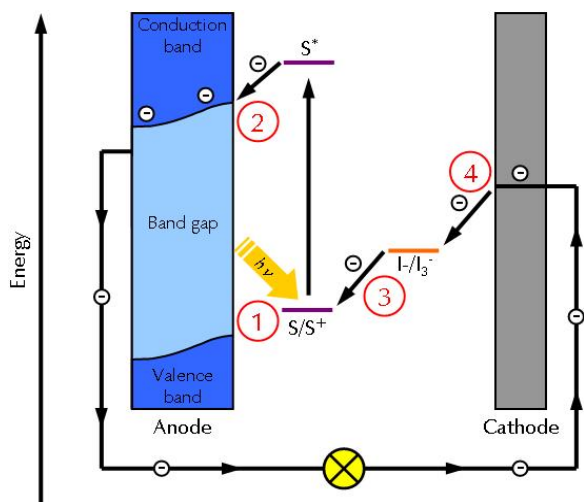

Figure 2 – Energy diagram of a dye solar cell. Highlighted in red are all single steps which are explained in the text.

STEP 1: The dye molecule is initially in its ground state (S). The semiconductor material of the anode is at this energy level (near the valence band) non-conductive.

When light shines on the cell, dye molecules get excited from their ground state to a higher energy state (S^*), see equation 1.

$$S \xrightarrow{h\nu} S^*$$
Eq. 1

The excited dye molecule has now a higher energy content and overcomes the band gap of the semiconductor.

STEP 2: The excited dye molecule (S^*) is oxidized (see equation 2) and an electron is injected into the conduction band of the semiconductor. Electrons can now move freely as the semiconductor is conductive at this energy level.

$$S^* \longrightarrow S^+ + e^-$$
Eq. 2

Electrons are then transported to the current collector of the anode via diffusion processes. An electrical load can be powered if connected.

STEP 3: The oxidized dye molecule (S^+) is reduced by the electrolyte's redox couple (see equation 3).

$$S^+ + 3I^- \longrightarrow S + I_3^- + 2e^-$$
Eq. 3
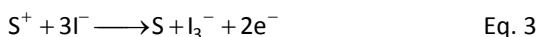
STEP 4: The iodide/triiodide redox couple is regenerated on the cathode. Triiodide is reduced to iodide (see equation 4).

$$I_3^- + 2e^- \longrightarrow 3I^-$$
Eq. 4

Important parameters

A solar cell generates current when light shines on it. The output current depends strongly on the potential of the cell as well as intensity of the incident light. Current-potential curves (also called I-V curves) illustrate the relationship.

Similar to standard cyclic-voltammetry experiments, a potential E is applied and swept between an initial and final potential. The current I of the cell is measured. In addition, a light source with a constant intensity is focused on the solar cell to generate power.

Figure 3 shows a typical I-V curve of a solar cell for increasing light intensities and when no light is present.
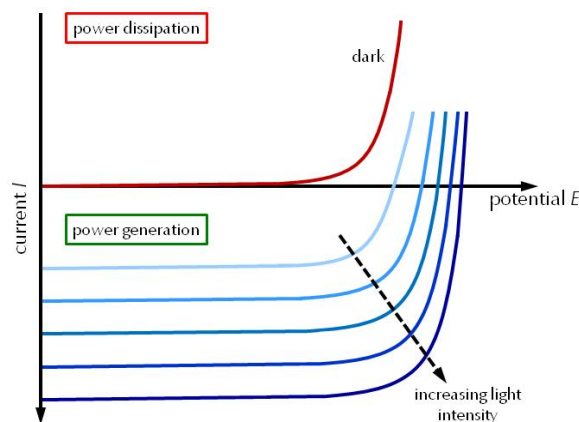

Figure 3 – Schematic diagram of I-V curves with and without light. For details, see text.

A dye solar cell behaves like a diode when no light is present. No current is generated and energy is needed to power the cell.

The I-V curves shift further down when light is focused on a DSC. The solar cell generates now current which increases with increasing light intensities.

Current flux is nearly constant at lower potentials. It reaches its maximum when the potential is zero. The generated current decreases with increasing potential. It is zero at the open-circuit potential. Above this potential, an external bias voltage is needed to power the cell. The cell can get damaged at excessively high values.

Several parameters can be derived from I-V curves which are discussed in the following sections. Figure 4 shows a schematic overview of an I-V curve including parameters.
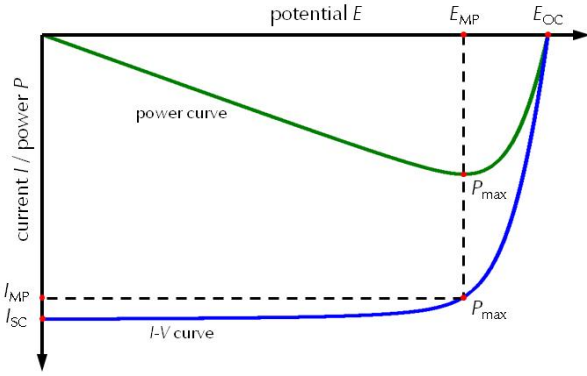
Figure 4 – Schematic I-V curve and power curve of a solar cell. Several important parameters are shown. For details, see text.

Short-circuit Current

The short-circuit current I_{SC} is the highest current that can be drawn from a solar cell. The cell voltage is at this point zero. Hence the generated power is also zero.

$$I_{SC} = I_{max} = I(E = 0) \qquad \text{Eq. 5}$$

The short-circuit current increases with increasing light intensity.

Open-circuit Potential

The open-circuit potential E_{OC} is the highest voltage of a solar cell at a given light intensity. It is also the potential where current flow through a solar cell is zero.

$$E_{OC} = E_{max} = E(I = 0) \qquad \text{Eq. 6}$$

E_{OC} is increasing with increasing light intensity.

Power

The generated power P of a solar cell can be calculated by the following formula:

$$P = E \cdot I \qquad \text{Eq. 7}$$

The calculated power can be also plotted versus the applied potential (see Figure 4). The resulting power curve exhibits a power maximum P_{max}.

Fill Factor

The Fill factor (FF) is an important parameter to specify the overall capabilities of a cell. It describes the quality and idealness of a solar cell.

The Fill factor is the ratio of maximum generated power P_{max} to theoretical power maximum P_{theo} of a solar cell. The general formula for the Fill Factor is:

$$FF = \frac{P_{max}}{P_{theo}} = \frac{E_{MP} \cdot I_{MP}}{E_{OC} \cdot I_{SC}} \qquad \text{Eq. 8}$$

E_{MP} and I_{MP} are potential and current of the I-V curve where the generated power is at the maximum.

The Fill factor can be also represented by rectangles in an I-V curve. Figure 5 shows a schematic illustration.
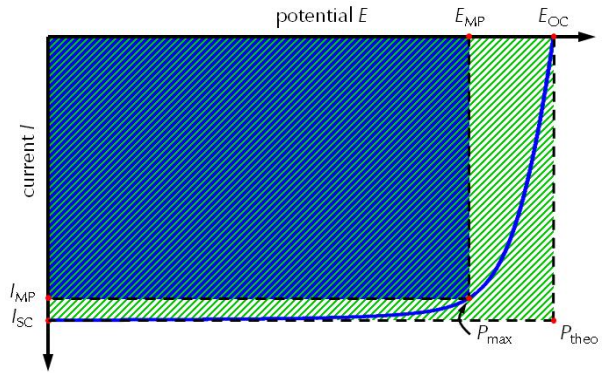

Figure 5 – Graphical illustration of the Fill factor. For details, see text.

In the ideal case, an I-V curve is a rectangle (green area). The power maximum is at E_{OC} and I_{SC} and the Fill factor is one.

However, non-ideal conditions caused by parasitic effects decrease the power maximum and the I-V curve rounds off. The resulting true area which represents the power maximum (blue rectangle) is smaller. It is covered by the potential E_{MP} and current I_{MP}.

Note that the Fill Factor is not equal to the efficiency of a solar cell.

Series and Shunt Resistance

As mentioned before, parasitic effects caused by internal resistances lead to power loss in a solar cell. These resistances can be described by a series resistance (R_S) and shunt resistance (R_{SH}).

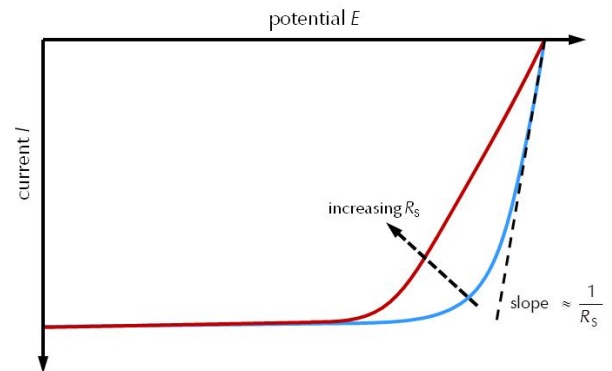Figure 6 and Figure 7 show how both resistances affect the shape of an I-V curve.

Figure 6 – Effect of the series resistance R_S on the shape of an I-V curve.

The series resistance R_S can be estimated by the inverse of the slope near the open-circuit potential (see Figure 6).

Ideally, the series resistance would be zero. However, resistances of metal contacts or bulk substrate lead to an additional voltage drop within the cell. As a result, the

slope of the curve near E_{OC} decreases with increasing R_S. Hence both the area under the curve and the power maximum decrease.

Note that the open-circuit potential E_{OC} is not affected by R_S because the current flow is zero. The short-circuit current is also unaffected by R_S. Only very large values can lead to a reduction of I_{SC}.
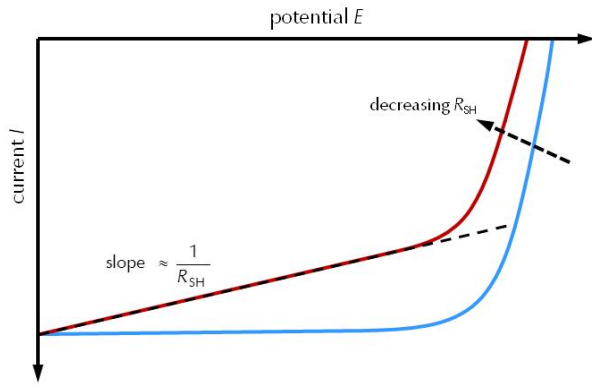

Figure 7 – Effect of the shunt resistance R_{SH} on the shape of an I-V curve.

R_{SH} can be estimated by the inverse slope near the short-circuit current I_{SC} (see Figure 7). In the ideal case, this resistance is infinite so that no additional current path exists. The lower R_{SH} the more the slope of the I-V curve increases near the short-circuit current. This leads also to a smaller open-circuit potential E_{OC}.

The shunt resistance R_{SH} can be modeled by a parallel resistor. It is mainly caused by leakage current through the cell caused by impurities or defects in the manufacturing process.

Power maximum, Fill factor, and efficiency are negatively affected by small shunt resistances.

> **Note:** Both calculations of R_S and R_{SH} should be only used as estimations near the open-circuit potential and short-circuit current respectively.

Efficiency

The efficiency η is the ratio between maximum generated power P_{max} and electrical input power P_{in} from the light source.

$$\eta = \frac{P_{max}}{P_{in}} \cdot 100\% \qquad \text{Eq. 9}$$

In order to calculate the efficiency, the power of the incident light P_{in} has to be known.

> **Note**: For more information on calculating the light power, see Gamry's technical note at www.gamry.com:
>
> **Measuring the Optical Power of your LED**

Experiments

The following sections describe various experiments with dye solar cells. All DSC accessories are from Solaronix. The solar cell uses titania and platinum electrodes. The electrolyte is a 50 mM iodide/triiodide solution in acetonitrile. Ruthenizer 535-bisTBA is used as dye. The active area of the cell is 0.64 cm^2.

Figure 8 shows a series of I-V curves with increasing light intensities (from bright to dark). The potential of the solar cell was swept between 0 V and the open circuit potential for several cycles. The sweep rate was 5 mV/s to ensure a steady-state cell operation.

The light intensity of the red LED (625 nm) was stepwise increased from 5.1 mW to 37.2 mW for each curve. Only the last forward cycle for each intensity is shown. The distance between LED and dye solar cell was 3 cm.
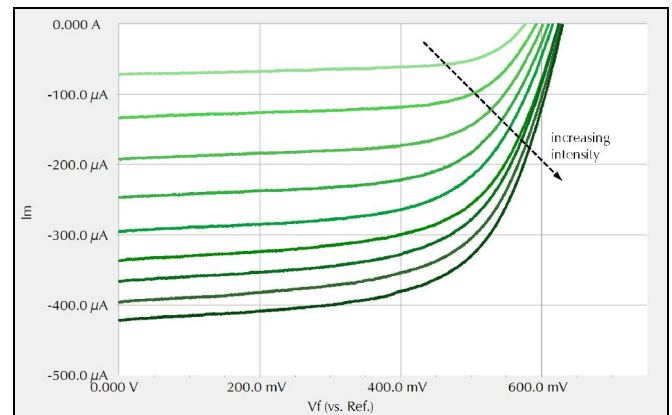

Figure 8 – Series of I-V curves with increasing light intensities (from bright to dark). For details, see text.

As expected, current increases with increasing light intensity. In addition, the open-circuit potential shifts to higher values. Hence the generated power of the solar cell is increasing. Figure 9 shows the corresponding power curves.
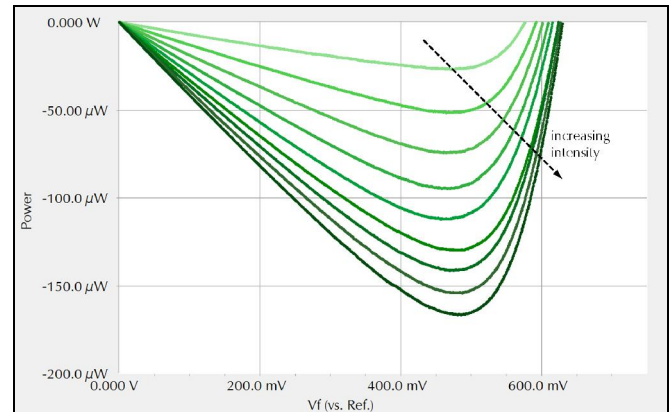

Figure 9 – Corresponding series of power curves with increasing light intensities (from bright to dark).

The power maximum P_{max} shifts slightly towards more negative currents and higher potentials.

The following table lists up several parameters that can be evaluated from the I-V curves and power curves shown in Figure 8 and Figure 9.

P_{in} [mW]	I_{SC} [µA]	E_{OC} [mV]	P_{max} [µW]	P_{theo} [µW]	FF [%]	η [%]
5.1	-72.0	576.7	-29.2	-41.5	0.70	0.58
14.9	-192.5	601.8	-89.9	-115.8	0.78	0.60
23.9	-295.5	615.8	-140.7	-182.0	0.77	0.59
31.5	-366.7	624.3	-179.0	-228.9	0.78	0.57
37.2	-422.3	629.8	-208.5	-266.0	0.78	0.56

Table 1 – Summary of parameters calculated from I-V curves and power curves.

The Fill factor stays nearly constant at about 0.78. It is smaller at low light intensities.

The efficiency is in general very low at about 0.6 %. In this regards, note that a red LED with a narrow wavelength range was used for these experiments. The efficiency slightly decreases with increasing light intensities.

In addition, R_S and R_{SH} can be estimated from the slopes of an I-V curve (see also Figure 6 and Figure 7). Table 2 sums up a list of calculated resistances for the I-V curves shown in Figure 8.

P_{in} [mW]	R_S @ E_{OC} [Ω]	R_{SH} @ I_{SC} [kΩ]
5.1	792	41.0
14.9	413	21.2
23.9	328	17.7
31.5	260	15.2
37.2	227	13.2

Table 2 – List of calculated series resistances R_S and shunt resistances R_{SH} for different light intensities.

The results show that both R_S and R_{SH} are decreasing with increasing light intensities. Lower R_S-values tend to increase Fill factor and efficiency of a DSC. However, decreasing R_{SH}–values can negatively affect the performance of a DSC.

Both trends can be explained by rising conductivities caused by higher temperatures within the cell. The following section explains the effect of temperature on a DSC. It also addresses various issues which should be taken into account of when performing experiments with DSCs.

Difficulties when measuring Solar Cells

Temperature changes

Temperature changes affect the performance of a dye solar cell. Dye solar cells do warm up when light shines on the cell. This can affect the Fill factor as well as the efficiency of a DSC.

Dye solar cells are very sensitive to temperature changes as they incorporate semiconductor materials. The semiconductor's band gap narrows with increasing temperatures (see also Figure 2).

This leads on the one hand to rising conductivities. As a results, the short-circuit current is increasing. On the other hand, the open-circuit potential is decreasing. Figure 10 illustrates this effect.

For this experiment, light was focused on a cold DSC and several consecutive I-V curves were measured (from bright to dark). The light intensity was kept constant at 37.2 mW.
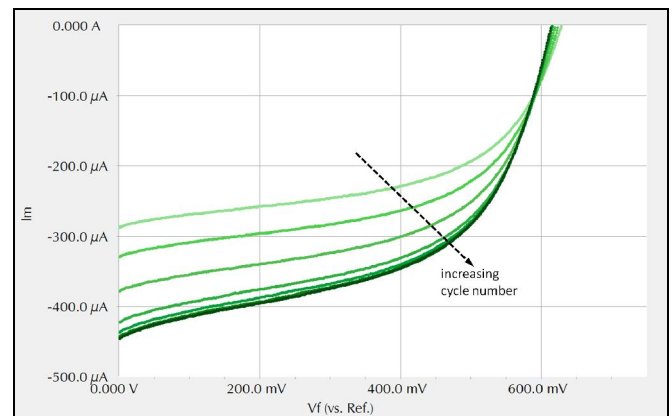

Figure 10 – I-V curves at different cycles. The 1st, 5th, 10th, 20th, 30th, 40th, 50th, 60th, and 70th cycle are shown (from bright to dark). For details, see text.

Initially, the incident light slowly warms up the solar cell . In this phase, short-circuit current and open-circuit potential are drifting significantly and slopes of the curves near I_{SC} and E_{OC} are changing.

The I-V curves begin to overlap not until after 40 cycles when the cell temperature stabilized.

> **Note:** For correct data evaluation, it is necessary to stabilize the cell temperature. Running several consecutive cycles helps to verify that the temperature is constant. Only data of overlapping I-V curves should be used for final calculations.

Scan rate

Another relevant parameter when measuring I-V curves is the scan rate. High scan rates can lead to significant hysteresis between forward and reverse cycle (see Figure 11).
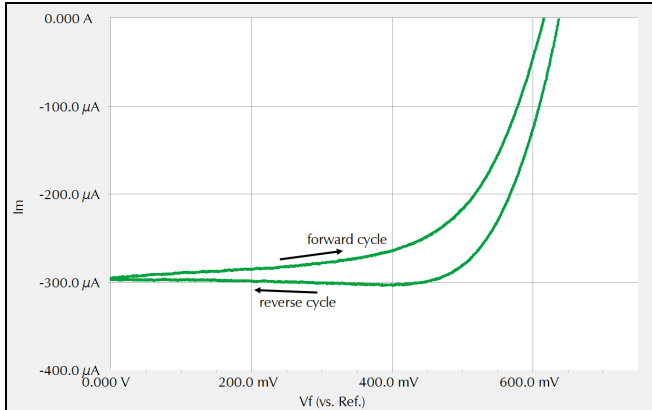

Figure 11 – Hysteresis effect between forward and reverse cycle during an IV-experiment.

Hysteresis is mainly caused by polarization effects as well as light-induced changes in the cell's chemistry. Differences between forward and reverse cycle make data evaluation more difficult and can lead to wrong results. In order to find a suitable scan rate we recommend that you perform several cycles while adjusting the scan rate.

Low scan rates increase the measurement time but they reduce the hysteresis effect. In addition, low scan rates allow steady-state cell operation. If I-V curves show only minor hysteresis, data of forward and reverse cycle can be averaged together.

Summary

This application note relates to measurements with dye solar cells (DSCs). Basic principles and the setup of DSCs are discussed. In addition, several important parameters are explained and calculated.

Experiments with real DSCs are performed using a red LED. I-V curves are measured and converted into power curves. Both curves are used to calculate different important parameters to characterize the DSC.

Finally, helpful advice is provided for better, more reliable measurements and results.

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