

# What Physical Factors Affect Current-Voltage Characteristics of Dye Solar Cells?

Dr Hans Desilvestro, Dyesol Ltd February 2008

### 1. Introduction

The scope of this tutorial is to provide an overview of purely physical parameters affecting current-voltage characteristics of Dye Solar Cells (DSCs), mainly from a device engineering rather than a materials and chemical point of view. Factors such as chemical composition of the dye with its absorption spectrum of the adsorbed species, correct HOMO/LUMO matching with the titania conduction band and the redox couple respectively, effective electronic coupling between dye and titania surface, correct surface pH, titania particle size, morphology and chemistry as well as electrolyte additives have obviously a very direct impact on DSC performance. Such aspects and their complexity will however be treated in separate Dyesol tutorials.

Current-voltage (IV) curves represent the most important and most direct characterisation method for DSCs and for solar cells in general. The open circuit voltage (V<sub>oc</sub>), short circuit current (I<sub>sc</sub>) and the shape of the IV curve determine the efficiency  $\eta$  of DSCs under any given light condition. There are three additional important descriptors for IV curves of solar cells:

- >  $V_{mpp}$  = voltage at the maximum power point ( $P_{max}$ )
- >  $I_{mpp}$  = current at the maximum power point ( $P_{max}$ )
- > ff = fill factor: describes how well the area under the IV curve "fills in" the maximum possible rectangle defined by  $I_{sc} \times V_{oc}$  (i.e. the rectangle in light blue in Fig. 1). The fill factor can most easily be visualised by the ratio of the areas of the dark blue rectangle to the light blue one.



Figure 1: IV curve of a solar cell, along with the main descriptors and their relationship with efficiency  $\eta$  = electrical power(out)/light power(in).



In order to optimise DSC performance it is important to fully understand the factors which affect the key features of DSC IV characteristics. The scope of this DSC tutorial is to discuss the main physical design parameters which determine  $I_{sc}$ ,  $V_{oc}$  and ff.

### 2. The ideal photodiode

Any photodiode can be described by the following equivalent circuit:



**Figure 2:** Equivalent circuit of a photodiode,  $I_{gen}$  = photo generated current (corresponding to  $I_{sc}$ ,),  $I_{sat}$  = reverse saturation current, Faraday constant = 96,485 s mol<sup>-1</sup>, n = diode ideality factor, R = universal gas constant = 8.314 J K<sup>-1</sup> mol<sup>-1</sup>, T = absolute temperature, R<sub>sh</sub> = shunt resistance, R<sub>s</sub> = series resistance

While shunt resistance  $R_{sh}$  can generally be neglected for properly designed DSCs (not for silicon cells though) the series resistance  $R_s$  has a major impact on their IV curves.  $R_s$  stems from a number of limiting materials and electrochemical processes within the solar cell which will be discussed in more detail in the following sections. The total observable photocurrent  $I_{ph}$  for a photodiode with  $R_{sh} \rightarrow \infty$  and  $R_s = 0$  is thus given by:

$$I_{ph} = I_{gen} - I_{sat} \left( e^{\frac{FV}{nRT}} - 1 \right)$$
[1]

The open circuit voltage can then easily be calculated for  $I_{ph} = 0$ :

$$V_{OC} = \frac{nRT}{F} \ln \left( \frac{I_{ph}}{I_{sat}} \right)$$
[2]

The ideal solid-state photodiode has very low defect levels and thus low recombination, resulting in n being close to unity. n varies for different types of photodiodes or solar cells between 1 and  $\sim 2^{(1)}$ , depending on their defect levels.

#### 3. Influence of the diode ideality factor on IV characteristics

Equation [2] allows for an easy estimation of the diode ideality factor n. For a given photodiode and its characteristic  $I_{sat}$  value,  $I_{ph}$  is generally proportional to light intensity I. RT/F×In10 equals 0.059 mV at 25°C, therefore:

$$V_{oc}(1) - V_{oc}(2) = 0.059n \log\left(\frac{I(1)}{I(2)}\right)$$
[3]

This means that for an ideal photodiode  $V_{oc}$  decreases by 59 mV only when the light level is lowered by a factor of 10. For n = 2,  $V_{oc}$  decreases by close to 120 mV under the same



conditions. While n is close to 1 for high-quality DSCs over many orders of magnitude of light intensity  $^{2,3)}$  other solar cells such as commercial c-Si display n values between 1.26 and 1.5 <sup>1)</sup>. n values of 1.4-1.45 were reported for CdS/CdTe and CdS/CuInSe<sub>2</sub> cells by the same authors <sup>1)</sup>.

Figure 3 shows that an increase in n significantly lowers cell fill factors and efficiencies, particularly at the lower light levels because of the markedly lower open circuit voltages and hence makes those cells less effective at low light as  $V_{mpp}$  may fall below a useful level for conversion.



**Figure 3:** Calculated IV curves according to Eq. [1] and efficiency vs light level output, assuming I<sub>gen</sub> (@1 sun) = 18 mA/cm<sup>2</sup>, V<sub>oc</sub> (@1 sun) = 0.79 V and I<sub>gen</sub> linearity as a function of light intensity.

#### 4. Influence of temperature

Figure 4 shows IV curves for a typical commercial DSC design at temperatures varying from -10°C to 70°C. The effects of temperature on the key characteristics are summarised in Fig. 5. While the open circuit voltage decreases linearly by ~2 mV/decade, which is similar to Si photovoltaic cells, the maximum power point voltage of DSCs remains, in contrast to silicon, remarkably constant and only decreases slightly at temperatures above 45°C. Fill factors of DSCs increase with temperature and only start to level off and then decrease above 50-60°C. The ff maximum as a function of temperature depends on the light level. on the electrolyte composition. specifically  $|_3$ the concentration, the electrolyte viscosity and other cell design parameters such as anode-to-cathode distance.









Figure 5: Influence of cell temperature on key IV characteristics of metal-based flexible Dyesol DSC at 1 sun illumination.

 $V_{mpp}$  of Dyesol DSCs is remarkably constant and varies by only  $\pm 20$  mV over the temperature range from -10°C to 70°C (Fig. 6). The exact voltage variation can be adjusted through a number of design parameters. Lowered  $V_{oc}$  at higher temperatures is largely compensated by a corresponding increase in ff. Since  $I_{sc}$  does not vary significantly with temperature the power  $P_{mpp}$  at the maximum power point is rather constant and varies at worst by only  $\pm 12\%$  over the entire temperature range from -10°C to 70°C. Such a small influence of temperature on power output from DSCs is in sharp contrast to Si solar cells, which show a much more pronounced decrease in performance <sup>4)</sup> at higher temperatures, i.e under real life sun light illumination and a much more pronounced drop in maximum power voltage (Fig. 6).



Figure 6: Left: power-voltages curves of metal-based flexible Dyesol DSC at 1 sun illumination for various temperatures. Right: power-voltages curves of a single crystalline solar cell for various temperatures.

A power loss coefficient of  $0.65\%/K^{4}$  at  $P_{mpp}$  has been reported for Si-based solar cells. Table 1 shows a comparison between DSC and Si for 2 temperature ranges.



#### Table 1

Temperature increase	P <sub>mpp</sub> drop for DSC	P <sub>mpp</sub> drop for c-Si		
From 20° to 50°C	5%	19.5%		
From 20° to 70°C	15%	32.5%		

### **5. Influence of electrolyte conductivity**

The electrolyte resistance  $R_e$  which represents part of the series resistance  $R_s$  depends, according to Equation [4], on the electrolyte layer thickness, i.e. the distance d between the two electrodes, the electrolyte conductivity  $\sigma$  and the electrode cross section A.

$$R_e = \frac{d}{\sigma A}$$
[4]

As explained in the previous Dyesol tutorial "Ionic Liquids - The Panacea for Dye Solar Cells?" <sup>5)</sup>, in typical DSCs with an electrode-to-electrode distance of 40  $\mu$ m and a conductivity of around 0.01 S/cm at 20°C for a solvent-based electrolyte system, results in R<sub>e</sub>  $\approx$  0.4 Ohm for each cm<sup>2</sup> of cell area. This produces a voltage drop of 7 mV only at a photocurrent of 18 mA/cm<sup>2</sup>. As will be shown in Section 6 below, this is insignificant compared to the series resistance of the typical transparent conductive oxide (TCO) substrate. For solvent-free electrolyte systems such as ionic liquids the electrolyte conductivity may be lower and R<sub>e</sub> correspondingly higher.

While the electrolyte resistance has normally only a very slight direct impact on the IV characteristics the situation is complicated by concentration polarisation. Often electrolyte systems with relatively low ionic conductivity display relatively low  $I_3^-$  diffusion coefficients as well, which can have a noticeable limiting effect on photocurrents. Diffusion limitation will be discussed in more detail in Sections 8 and 9 below.

#### 6. Influence of substrate conductivity, cell width and cell contacts

In contrast to standard photovoltaic cells which are based on solid-state p-n junctions and light absorption by bulk semiconductor materials, thin-layer DSCs require at least one transparent conductive substrate. Since electronically highly conductive substrates generally display low light transmittance the substrate sheet conductivity needs to be compromised for:

- the best performance in a given application,
- ➤ cost and
- availability of transparent conductive oxide (TCO) on a substrate such as glass or plastic.

Typical sheet resistances  $\gamma$  of commercially available affordable TCO layers are in the order of 8-15 Ohm per square (Ohm/ $\Box$ ). This means that a 1 cm x 1 cm cell contacted on both sides by a bus bar displays a series resistance of 8-15 Ohm. This value is much higher than the resistance of the typical electrolyte layer ( $R_e \approx 0.4$  Ohm per cm<sup>2</sup> unit area, see Section 5 above).

For cells where the anode and cathode substrate sheet resistances are equal ( $\gamma_a = \gamma_c$ ) and where the cell electrical contacts are provided through two lateral bus bars just outside the seal structure (one on anode and one on cathode side), the current lines are particularly uniform (Fig. 7) and the current density is the same over the entire cell area. In addition such a geometry represents a good model for larger devices such as Z-interconnected DSC panels.





**Figure 7:** Top: schematic cross section through DSC along with current paths, w = width of active area (TiO<sub>2</sub>),  $w_s =$  width of cell seal structure. Bottom: schematic for Z-interconnected cells.

For a cell of length, L, the voltage, V, at any current, I, can be expressed in relation to  $V_o$ , which is the cell voltage for zero sheet resistance <sup>i)</sup>:

$$V = V_0 - IR_s = V_0 - \frac{I\gamma(w + 2w_s)}{L}$$
[5]

substituting  $I = j \times w \times L$  (where j = current density):

$$V = V_0 - j\gamma \left(w^2 + 2ww_s\right)$$
<sup>[6]</sup>

The characteristic voltage drop,  $j\gamma$ , provides the resistive voltage drop over the active surface area for any size DSC which is electrically contacted according to Fig. 7.



Figure 8: Characteristic voltage drop as a function of current density and sheet resistance

 $<sup>^{</sup>i)}~$  It is assumed that  $R_s\approx R_{substrate},~i.e.~R_e\approx 0$ 



Figure 8 shows that for high performance cells delivering maximum power point photocurrents of 15 mA/cm<sup>2</sup> or more in full sun and for a sheet resistance of 15 Ohm/ $\Box$  the characteristic voltage drop is >0.2V, which starts to seriously limit cell efficiency. Thus lower width cells are required for maximum performance in full sun.

Figure 9 graphically illustrates the resistive voltage loss according to Eq. [6] with its quadratic dependence on cell width. Thus cell geometry needs to be optimised depending on the light conditions in the application. For cells operating under lower average light, larger cell widths can be adopted than for cells where highest output under direct sun light is required.



**Figure 9:** Resistive voltage drop as a function of cell and seal width for  $j\gamma = 0.225$  V, e.g. for 15 mA/cm<sup>2</sup> and 15 Ohm/ $\Box$  anode and cathode substrate.

Figure 10 shows calculated IV curves for DSCs of different widths based on resistance-corrected  $V_o$  curves according to Eq. [5].



**Figure 10:** IV curves at full (left) and 0.33 sun (right) as a function of active area width, calculated from I vs V<sub>o</sub> curves.  $\gamma = 12 \text{ Ohm/}\Box$ , w<sub>s</sub> = 2.5 mm. The I vs V<sub>o</sub> curves were obtained from a typical Dyesol DSC from V<sub>o</sub> = V + IR<sub>s</sub>, where R<sub>s</sub> was determined through electrochemical impedance spectroscopy (EIS).



If anode and cathode substrate sheet resistances are not equal and/or if other bus bar geometries are used the current density is no longer homogeneous over the cell area and calculations become more involved. Figure 11 shows calculated voltage and current distribution maps for a 10 cm × 1 cm cell with one electrode substrate being a metal sheet and the other being contacted by bus bars around its entire perimeter.



Figure 11: (Anode-cathode) potential (top, V) and current (bottom, A/cm<sup>2</sup>) distribution maps for a DSC operating at the maximum power point based on a 10 cm x 1 cm active area electrode of 15 Ohm/□ substrate sheet resistance, contacted at both sides and both ends by conductive bus bars. The second (metallic) electrode is assumed to have zero sheet resistance.

#### 7. Influence of the counter electrode

In order to understand the influence of the counter electrode on DSC IV characteristics, some fundamental electrochemistry needs to be introduced. Electrochemical reactions are generally described by the Butler-Vollmer equation [7], which relates current and voltage through the "overpotential"  $\eta = E - E_o$ , defined as the potential difference between the applied electrode potential and the electrode equilibrium potential  $E_o$ .  $E_o$  is the  $I_3^-/I^-$  redox potential in the case of DSCs.  $k_o$  is the electron transfer constant at zero overpotential, which characterises the electrocatalytic activity of an electrode,  $\alpha$  is a symmetry factor which is normally close to 0.5, n the number of exchanged electrons in the rate-determining step and  $c_{red}$  and  $c_{ox}$  represent  $I^-$  and  $I_3^-$  concentrations.

$$j = k_0 \left[ c_{red} e^{\frac{(1-\alpha)n\eta F}{RT}} - c_{ox} e^{\frac{-\alpha n\eta F}{RT}} \right]$$
[7]

Counter electrodes (CEs) of DSCs can effectively be evaluated independently in symmetrical CE-CE cells through IV curves and/or EIS. Figure 12 shows IV curves for symmetrical cells of 3 different internal cell thicknesses. In order to extract electrokinetically useful information from such curves they need to be corrected for the cell series resistance according to Eq. [8] (see the thin dark blue curve in Fig. 12).

$$V_{corr} = V - IR_s$$
[8]

With the internal cell thicknesses employed, diffusion limitation occurs at  $j_{lim} = 22 \text{ mA/cm}^2$  for the thickest cell and at >50 mA/cm<sup>2</sup> for the thinnest. Such information is very important in order to understand the limits for various electrolyte systems, also as a function of



temperature in order to establish if DSC performance may become limited by mass transport within the thin layer cell ( $I_3^-$  mainly). Mass transport (diffusion) polarisation ( $R_{diff}$ ) can be corrected through Eq. [9] which then provides the electron transfer current density,  $j_{ET}$ , of the symmetrical cell (see the blue curve in Fig. 12). For cell B, losses due to diffusion polarisation, amount to ~90 mV <sup>iii</sup>) at 20 mA/cm<sup>2</sup>, which starts to have a serious impact on fill factor and thus cell efficiency. As a rule of thumb,  $j_{lim}$  should be at least twice as high as the targeted photocurrent in a given application. In cases where  $j_{lim}$  is smaller than 20 mA/cm<sup>2</sup>, the DSC short circuit current may be purely limited by mass transport (see also Section 9).

 $j_{ET} = \frac{j}{\left(1 - \frac{j}{j_{\rm lim}}\right)}$ 

[9]

For  $\alpha$  =0.5, anodic and cathodic overpotentials at a given absolute current are equal. For any cathodic  $\alpha$ -value, 100×(1-  $\alpha$ )% of the polarisation occurs at the cathode (see light blue curve in Fig. 12) and 100  $\alpha$ % at the anode. The experimental data can best be fitted by a cathodic  $\alpha$ -value of 0.45 (open circles in Fig. 12). Since the counter electrode in a DSC operates as a cathode, i.e. it electrochemically reduces I<sub>3</sub><sup>-</sup> to 3I<sup>-</sup>, it can be estimated that a DSC "sees", at a given current density, around 50-55% of the R<sub>s</sub> and R<sub>diff</sub> corrected polarisation determined from symmetrical cells as shown by the light blue curve in Fig. 12. This curve is very useful to estimate the influence of the counter electrode on the IV characteristics. It can be seen that the electrokinetic voltage loss at 20 mA/cm<sup>2</sup> amounts to ~80 mV which is substantial and will significantly lower ff. Such a j<sub>ET</sub> curve is an indication that the counter electrode characteristics should be improved through optimisation of the Pt deposition method and/or through increasing the I<sub>3</sub><sup>-</sup> concentration (see also next Section). Ideally the charge transfer resistance R<sub>ct</sub> at 0 V (in CE-CE cells) should be below 4-6 Ohm cm<sup>2</sup>, which corresponds to 2-3 Ohm cm<sup>2</sup> for each electrode. R<sub>ct</sub> can be determined by EIS or from the slope at 0 V of the j<sub>ET</sub>(cathode) curve.



**Figure 12:** IV curves of symmetrical CE-CE cells for 3 different cell internal thicknesses A>B>C, adjusted by suitably chosen seal gaskets. R<sub>S</sub>-correction of the B-cell through Eq. [8] with R<sub>s</sub> determined from EIS. R<sub>diff</sub> correction through Eq. [9]. The cathodic IV curve (light blue) is based on 55% polarisation from the (R<sub>S</sub>+R<sub>diff</sub>) corrected curve (blue). (O): calculated from Eq. [7] with n = 1 and  $\alpha$  = 0.45.

<sup>&</sup>lt;sup>ii)</sup> See the voltage difference between the curves "R<sub>s</sub> correction cell B" and "j<sub>ET</sub>(CE-CE cell)" in Fig. 12



Figure 13 shows IV curves for two cells with two counter electrodes prepared under different conditions. Clearly, fill factors and thus efficiencies are lower for cell E compared to D. jET vs V curves were calculated based on R<sub>ct</sub> values and Eq. [10] derived from Eq. [7]. Within the DSC community IV curves are generally plotted to show anodic currents in the +I/+V guadrant. Thus cathodic currents on the counter electrodes are in the -I/+V guadrant, i.e. pointing downwards and towards the right with increasing polarisation. For the sake of convenience these cathodic CE currents are mirrored in Fig. 13 along the x-axis thus showing at a glance the voltage losses at the counter electrode as a function of DSC photocurrent. Through correction of the DSC IV curves for the case of an "infinitely" fast counter electrode ( $R_{ct}$ =0), fill factors were improved from 0.57 to 0.60 (+5% relative) for cell D and from 0.51 to 0.59 (+15% relative) from E. While the two corrected curves iii) (dashed curves in Fig. 13) do not entirely coincide this analysis showed that the difference in ff values and thus efficiencies between the two cells is largely due to the counter electrode. This type of analysis represents a valuable development tool in order to weigh up anticipated increases in device efficiency against factors such as raw materials and production costs or allocation of R&D effort.



**Figure 13:** IV curves of cells D and E at full sun along with  $-j_{ET}$  and corrected IV curves for  $R_{ct} = 0$ . The  $-j_{ET}$  curves were calculated from Eq. [10] with  $R_{ct}$  determined by EIS: 3.1 Ohm cm<sup>2</sup> (D), 8.2 Ohm cm<sup>2</sup> (E).

Apart from its electrocatalytic features influencing DSC IV characteristics, the counter electrode can impact DSC photocurrents through its optical properties as well, particularly for devices where the light enters the cells through the counter electrode (reverse illumination). For such devices catalytic activity and optical transmittance of the electrocatalyst layer (mainly Pt) need to be carefully balanced. The method of Pt deposition can have a significant impact on the optical transmittance, while not necessarily affecting catalytic activity.

<sup>&</sup>lt;sup>iii)</sup> Possible reasons may be the somewhat simplistic assumptions, uncertainties in the symmetry factor  $\alpha$  and possibly subtle differences at the dye/TiO<sub>2</sub> interface or between other cell parameters.



#### 8. Influence of iodine concentration

The influence of the iodine  $(I_3)$  concentration on DSC IV curves is a very complex one, including physical and chemical factors:

- Iodine absorbs violet and blue light and thus may significantly limit photocurrents with increasing concentration, particularly for reverse illuminated cells and for cells with relatively thick electrolyte layers (>40 micron).
- Low I<sub>3</sub><sup>-</sup> concentration can lead to mass transport limitations. In a thin layer cell of internal thickness d, the mass transport (diffusion) limited current density is given by Eq. [11]:

$$j_{\rm lim} = \frac{2nFD[I_3^-]}{d}$$
[11]

n represents the number of transferred electrons (n=2 for the  $I_3^-/I^-$  redox couple <sup>iv)</sup>) and D the diffusion coefficient of the limiting species ( $I_3^-$ ). For [ $I_3^-$ ]  $\approx 0.1$  M, D is in the range  $3-5\times10^{-6}$  cm<sup>2</sup>/s, and for an internal cell thickness of 40 microns diffusion limited currents of 30-50 mA/cm<sup>2</sup> can be achieved. Diffusion coefficients increase with increasing temperature according to the Stokes-Einstein equation [12] where  $\eta_k$  is the kinematic viscosity and r the hydrodynamic radius, i.e. the radius of the solvated ionic species. Thus D increases proportionally to the absolute temperature T and also because viscosity generally decreases with temperature.

$$D = \frac{kT}{6\pi\eta_k r}$$
[12]

Increasing I<sub>3</sub><sup>-</sup> concentration leads to lower V<sub>oc</sub> because of the enhanced parasitic electron back transfer reaction [13] from TiO<sub>2</sub> conduction band (CB) electrons. It has been reported that V<sub>oc</sub> at 82 mW/cm<sup>2</sup> decreases by around 65 mV at 298 K per tenfold increase in iodine concentration <sup>2</sup>).

$$I_3^- + 2e^-(TiO_2CB) \to 3I^-$$
[13]

➢ Low I₃<sup>-</sup> concentrations result, according to Eq. [7], in lower currents at the counter electrode and consequently lead to lower DSC fill factors.

Thus the iodine concentration exerts antagonistic effects on cell performance through  $V_{oc}$ ,  $I_{sc}$  and ff and needs to be carefully tuned for a given application and as a function of the chosen cell design.

#### 9. Influence of mass transport conditions

Some of the effects of mass transport have been discussed in Section 7 in relation to symmetrical CE-CE cell characteristics and in Section 8 in regards to iodine concentration. Since the iodide [I<sup>-</sup>] concentration in a DSC is generally significantly higher than triiodide [I<sub>3</sub><sup>-</sup>], transport of the latter species from the porous  $TiO_2$  network to the counter electrode is normally the major ion transport limitation. In thin layer cells linear concentration profiles are established across the cell relatively quickly. Under diffusion limitation the triiodide concentration at the counter electrode surface drops to zero and the surface concentration at  $TiO_2$  doubles with respect to the average triiodide concentration of a cell in the dark. The increase in  $I_3^-$  concentration at the titania surface decreases its open circuit voltage (by ~20 mV). On the CE side, the low steady-state  $I_3^-$  concentration slows the electron transfer

<sup>&</sup>lt;sup>iv)</sup> Note that n in Eq. [11] designates the number of electrons transferred according to the reaction stoichiometry (n=2) while in Eq. [7] it shows the number of electrons transferred in the rate limiting step.



reaction and lowers ff and  $V_{oc}$  because of the redox potential at the CE surface becoming more negative and thus closer to the TiO<sub>2</sub> Fermi level.

Figure 14 shows IV curves for cells A',B',C' based on the same cell internal thicknesses as the symmetrical cells A,B,C discussed in Section 7 above. With standard Dyesol cells however, diffusion polarisation can only be observed under light levels corresponding to concentrated sun light. Figure 14 shows that ff values decrease with increasing cell thickness A'>B'>C' at an illumination level corresponding to 2 suns. Note that  $j_{lim}$  in the illuminated cell A' is higher than in the symmetrical cell A (see Fig. 12) due to the temperature increase under illumination.



Figure 14: IV curves at 2 suns of cells A', B', C' with 3 different internal cell thicknesses A'>B'>C'.

In order to sustain 15 mA/cm<sup>2</sup> photocurrents with acceptable voltage loss,  $j_{lim}$  should be  $\geq$  30 mA/cm<sup>2</sup> under the operating temperature conditions. For d = 25  $\mu$ m it follows from Eq. [11]:

$$D(I_3) \times [I_3] \ge 2 \times 10^{-10} \text{ mol/(cm s)} = 2 \times 10^{-8} \text{ mol/(m s)}$$
 [14]

In high-boiling solvents such as methoxypropionitrile,  $I_3^-$  diffusion coefficients of  $3-5\times10^{-6}$  cm<sup>2</sup>/s can be achieved. Thus iodine concentrations of 0.04-0.065 M would be sufficient. For cells of 40 µm internal thickness [I<sub>3</sub><sup>-</sup>] concentrations would need to be adjusted to 0.06-0.1 M. The situation is aided through the higher temperatures achieved under full sun illumination. Solvents with even higher boiling points or ionic liquids display lower diffusion coefficients, mainly due to their higher viscosity. Thus higher iodine concentrations may be required for such systems, resulting in the disadvantages discussed in Section 8 such as lower V<sub>oc</sub> due to faster electron back transfer reaction and higher light absorption by the more concentrated iodine solution.

The interrelationship between diffusion coefficients and viscosity through Eq. [12] has been discussed in more detail in the Dyesol tutorial "Ionic Liquids - The Panacea for Dye Solar Cells?" <sup>5)</sup>.



### **10. Titania layer thickness**

Optimization of titania layer thickness is very important for DSCs since insufficient  $TiO_2$  would not adsorb enough dye and thus the cell would not absorb sufficient light resulting in low photocurrents. On the other hand too thick a  $TiO_2$  layer has to be avoided as well since it will

- increase the length of the electron pathways, particularly for reverse-illuminated cells, and thus decrease ff and V<sub>oc</sub> and, in extreme cases, even I<sub>sc</sub>;
- unnecessarily increase the total TiO<sub>2</sub> surface area and therefore increase the extent of electron back transfer reaction [13] and lower V<sub>oc</sub>;
- increase the diffusion length of I<sup>-</sup>/l<sub>3</sub><sup>-</sup> species through the congested and tortuous mesoporous network, which can increase d in Eq. [11] and lower l<sub>sc</sub>;
- > waste material (TiO<sub>2</sub> and dye) which cannot be utilised to their full 'potential'.

Figure 15 shows that the amount of adsorbed dye, as assessed through dye desorption in aqueous NaOH, increases virtually linearly with TiO<sub>2</sub> film thickness. I<sub>sc</sub> increases steeply up to 6  $\mu$ m TiO<sub>2</sub> film thickness, then improves much slower towards 12  $\mu$ m before saturating beyond ~15  $\mu$ m. This result clearly shows that any TiO<sub>2</sub> and dye beyond 12  $\mu$ m cannot be utilised effectively anymore, at least for the specific dye and cell parameters in the described test. While it is known that the dye absorption spectrum is red-shifted through adsorption on titania, the absorbance of the dissolved dye can provide a first approximation on how much light can be absorbed by the dyed film. This method is particularly useful for TiO<sub>2</sub> films on non-transparent substrates and/or for opaque films and it does not require knowledge of any extinction coefficients. The absorbance A of the dye solution produced from desorbing dye from a TiO<sub>2</sub> electrode area A into a volume v of liquid and measured in a cuvette of optical path length *l* results in the absorbance Av/*Al* under the (simplistic) assumption that the extinction coefficient for the adsorbed dye is the same as for dye in solution. Thus the percentage of the absorbed light can be estimated through Eq. [15]:

$$1-T \approx 1 - 10^{(-Av/A_l)}$$
[15]

This simple analysis indicates that 97.5% of the 500 nm light is absorbed by a 12  $\mu$ m dyed titania film and that further increase in TiO<sub>2</sub> film thickness is barely justified. The validity of this analysis is supported by I<sub>sc</sub> following the same trend as the 1-T function in Fig. 15.



Figure 15: Left:  $I_{sc}$  of metal-based flexible Dyesol DSCs under reverse illumination at 0.33 sun as a function of TiO<sub>2</sub> layer thickness along with the absorbance at 500 nm of desorbed dye in aqueous NaOH. Right: same current data along with (1-T) calculated from Eq. [15].



# 11. Optical engineering

None of the known dyes today absorb the entire solar spectrum. The most stable rutheniumbased dyes do not collect and convert light at wavelengths longer than 700 nm efficiently. Light management and optical engineering optimised for a given design can significantly increase light absorption. Particularly for the standard illumination geometry, i.e. the light being directed into the cell from the TiO<sub>2</sub> side, light scattering layers on the electrolyte side or a balanced mixture of smaller and larger TiO<sub>2</sub> particles can significantly improve the light harvesting efficiency. Mirror-like <sup>6)</sup> or white light diffusers as panel background and/or frontside antireflective layers can further improve cell efficiency. Dyesol produces a range of titania pastes ranging from maximizing photon trapping to maximising transparency. Pastes are specifically designed to provide the preferred nano-morphology for each dye.

Figure 16 shows results by Sharp <sup>7)</sup> with the "black dye" and how the haze factor (i.e. light scattering property) can significantly increase the current output of a DSC.





### **12. Additional physical factors influencing IV characteristics**

There are quite a number of additional factors which influence DSC output and which need to be considered in order to obtain meaningful and reliable IV data:

- Nature of the electrical contact: providing a low electrical resistance contact to the measuring leads is particularly important for larger area/high current devices. Good electrical contacts can be obtained through bus bars applied by screen printing or ultrasonic welding, followed by soldering the test leads to the bus bars.
- Lighting conditions: care needs to be taken to avoid any diffuse or stray light hitting the device under test, which may artificially increase device output. IV curves are best measured in black box on a matt black background.
- Masking: cell masking can be used to accurately define the illuminated cell area in the case of a well collimated light beam. With a more diffuse light source, on the other hand, masking can be used to artificially boost measured currents due to internal light reflection and indirect illumination of the masked area. Fill factor increases through masking due to lower absolute current resulting in less resistive losses (see also Section 6). Used correctly though, masking can provide more accurate cell performance data<sup>8)</sup>.



## **13. Summary and conclusions**

The key physical factors which determine DSC IV characteristics have been discussed in detail. Table 2 summarises the various parameters and how they affect DSC output.

#### Table 2

Parameter	Target values	Influence on			
	Comments				
	Underperformance for	ff	V <sub>oc</sub>	I <sub>sc</sub>	Eff
Diode ideality factor	Ideally n = 1				
	For 2 > n >> 1	R	л И	-	Y
Temperature	Ideally 20-50°C				
	< 0°C	Y	7	Ы	Ы
	> 50°C	~ -	Ы	~ -	Ы
Electrolyte conductivity	Ideally not much lower than 0.01 S/cm,				
	mainly to maintain high enough $D(I_3^-)$ , see				
	sections 7-9				
TCO conductivity	Needs compromising for performance				
	and cost				
	< 10 Ohm/□	7	Ы	Ы	7
	> 15 Ohm/□, low light levels	-/ש	7	~ -	~ -
	> 15 Ohm/ $\Box$ , at higher light levels	7	7	-/ש	Ľ
Cell width	Needs optimisation for the application				
	>> 10 mm, at higher light levels	<b>N</b>	-	ב/-	Ľ
Cell contacts	Bus bars with sufficient cross section				
	and conductivity. Soldered leads				
	Otherwise:	N	-	-	N
Counter electrode	Rct < 3 Ohm cm <sup>2</sup>				
	Rct >> 3 Ohm cm <sup>2</sup> , at higher light levels	Ľ	~ -	-	Y
	Too much electrocatalyst	~ -	~ -	Ы	Ы
Iodine concentration	To be optimised depending on the application,				
	design and the solvent used				
	>> 0.1 M	7	L N	Ľ	Y
	<<0.02 M, at higher light levels	7	7	<b>(≌)</b> * <sup>)</sup>	Y
Mass transport	$D(I_3) \times [I_3] / d \ge 7.5 \times 10^{-8} \text{ mol/(cm}^2 \text{ s})$				
	= 7.5×10 <sup>-4</sup> mol/(m <sup>2</sup> s)				
	[I <sub>3</sub> ] too low	<b>N</b>	7	<b>(≌)</b> * <sup>)</sup>	N
	$D(I_3)$ too low (electrolyte too viscous)	<b>N</b>	-	<b>(≌)</b> * <sup>)</sup>	<b>N</b>
	d too thick	<b>N</b>	Ы	<b>(≌)</b> * <sup>)</sup>	Ľ
TiO <sub>2</sub> layer thickness	To be optimised for each dye				
	Too thin	-/7	7	R	Ľ
	Too thick	Ы	Ы	-/7	Ы
Optical engineering	Light scattering particles, back reflectors				
	or diffusers, antireflection layer				
	If inadequate:	<b>-/</b> ч	-/u	Ľ	N

 $^{^{\ast)}}$  Only for  $j_{\text{photo}}$  being close to  $j_{\text{lim}}$  according to Eq. [11]



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**About the author:** Dr Hans Desilvestro is Chief Scientist for the Dyesol Group. Since completing his PhD under Prof Michael Graetzel at EPFL in 1985, he has been involved for more than 20 years in electrochemical R&D and manufacture of electrochemical devices, particularly DSC and advanced rechargeable batteries.