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Investigating Dye-Sensitised Solar Cells

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ABSTRACT

At present there is a global concern of environmental issues and future energy supplies, for instance global warming and the rapid depletion of fossil fuels. This trepidation has initiated a more critical investigation into alternative and renewable sources of power such as geothermal, biomass, hydropower, wind and solar energy. The immense dependence on electrical power in today's society has prompted the manufacturing of devices such as photovoltaic (PV) cells to help alleviate and replace current electrical demands of the power grid. The most popular and commercially available PV cells are silicon solar cells which have to date the greatest efficiencies for PV cells. The drawback however is that the manufacturing of these cells is complex and costly due to the expense and difficulty of producing and processing pure silicon. One relatively inexpensive alternative to silicon PV cells that we are currently studying are dye-sensitised solar cells (DSSCs or Grätzel Cells). DSSCs are biomimetic solar cells which are based on the process of photosynthesis. The SFI Strategic Research Centre for Solar Energy Conversion is a research cluster based in Ireland formed with the express intention of bringing together industry and academia to produce renewable energy solutions. Our specific research area is in DSSC and their opto-electrical properties. We are currently developing testing equipment for multiple DSSC and optoelectronic models which will describe the performance and behaviour of DSSCs.

1. INTRODUCTION

The commercial market for solar energy production is currently dominated by conventional silicon based solar cells. Silicon solar cells prospered primarily due to the developments within the semiconductor industry¹. PV cells with efficiencies of up to ~40% have been reported^{2,3}.

The drawback with silicon solar cells is that the associated manufacturing process is quite costly and complex⁴. Silicon is the second most abundant element and comprises of 25.7% of the Earth's crust however it is not found free in nature but in oxides (e.g. flint, sand, quartz) and as silicates (clay, asbestos, granite). The use of expensive clean room fabrication conditions and energy intensive material processing are necessary when working with this material⁵.

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One flexible and cost effective alternative to the traditional $p - n$ junction PV device is thin film organic material devices such as DSSCs. In silicon systems the semiconductor takes on the dual role of charge carrier transport and light absorption, whereas in the DSSC these two operations are separated⁶.

The appealing factor of DSSCs is that their concept derives from the area of biomimetics. These DSSC devices are assembled so that they are made to imitate or mimic nature in some way. Here there are analogies to the process of photosynthesis. In photosynthesis and DSSCs, incoming light is absorbed by an organic dye and electrons are produced which results in the production of both positive and negative charge carriers.

A schematic of the cross-section of a typical DSSC can be seen in Figure 1. A monolayer of an organic dye is attached to a mesoscopic film of a wide bandgap oxide semiconductor. The dye absorbs incident light and produces electrons, which are then injected into the conduction band of the semiconductor oxide. The electrons are transported across the nanocrystalline TiO_2 layer to the current collector (anode). From here the electrons pass through the external circuit and subsequently to the counter electrode (cathode). The sensitizer is regenerated by the organic hole conductor which transports the positive charges to the counter electrode where recombination occurs. Under solar exposure there is no net chemical change and light absorbed is in part converted to electrical power.

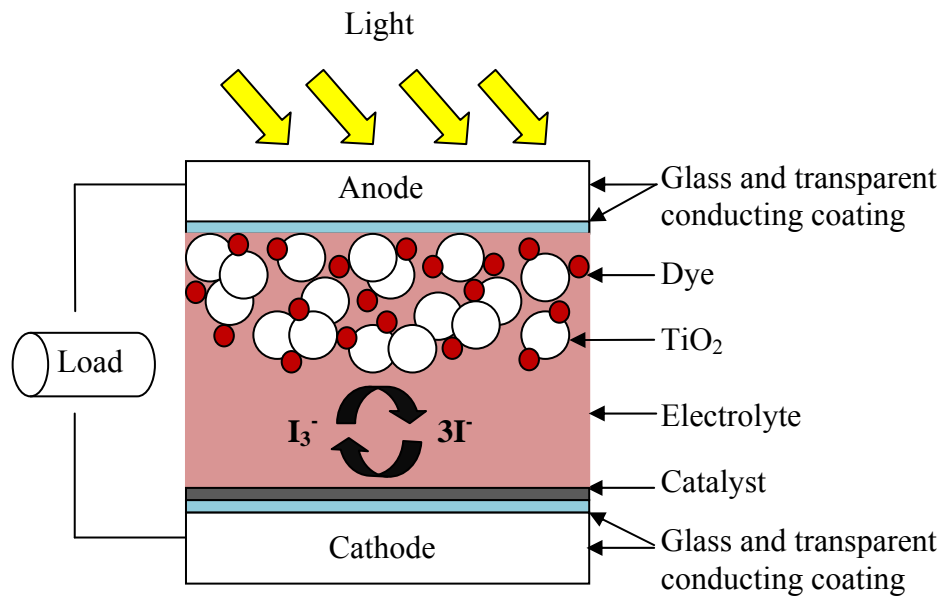


Figure 1. Schematic of the energy flow in a dye sensitised solar cell.

Both natural photosynthesis and DSSCs use organic dyes such as anthocyanins. In DSSCs a mesoscopic film of titanium dioxide replaces nicotinamide adenine dinucleotide phosphate ($NADP^+$), and carbon dioxide replaces the electron acceptor. Iodide and triiodide (I, I_3) replace the water and oxygen in photosynthesis as the electron donor and oxidation product⁷.

DSSCs do not require-clean room conditions for fabrication and they can be made reasonably robust to environmental conditions, unlike silicon solar cells.

2. METHODOLOGY

We constructed rudimentary DSSCs and obtained current-voltage (I-V) values. These simple DSSCs consist of two glass microscope slides (4 cm x 2 cm) where each face of the slides are coated with a layer of transparent conducting coating as shown in Figure 1. Suitable transparent conducting coatings include ZnO and SnO₂ however our choice of coating was fluorine doped SnO₂⁷. By measuring the electrical conductivity to find the resistance of the microscope glass slides it becomes apparent which face contains the transparent conducting coating.

Doctor-blading is a simple and effective technique which can be used to produce a thin and uniform layer of TiO₂ on the glass slide. This involves masking three edges on one side of the conductive face of the glass slide with Scotch tape. This allows a mould or channel to form in which the TiO₂ solution can flow or drop-cast. Also by preventing the TiO₂ solution over the entire face of the glass slide it allows for the introduction of electrical contacts. The commercial colloidal TiO₂ can be deposited using a pipette and spread over the unmasked area to produce an even layer of approximately 10 μm depth.

The mask is removed with care once the TiO₂ layer has dried. Sintering is required in order to ensure that the layer of TiO₂ adheres onto the glass slide. This process takes approximately 5 – 10 minutes in a pre-heated furnace at 450°C. The TiO₂ layer changes from a white colour to a brownish colour. This is due to the natural organic matter in the layer. The TiO₂ layer reverts back to its original white colour once it has been successfully sintered onto the glass slide. After the sintering process the glass slide has to be cooled to prevent excessive thermal stress as this can lead to cracking or detachment (flaking) of the layer. This glass slide is the negative (the anode) of the DSSC.

The negative electrode can be dyed with a suitable dye. The dye used in this experiment was an anthocyanin Hibiscus. The Hibiscus was extracted from dried Hibiscus flowers which were soaked in a petri-dish filled with boiling water i.e. 100°C. The glass slide was submerged face up in this solution for approximately 10 minutes to ensure that the dye had completely diffused into the TiO₂ layer. The glass slide was removed from the petri-dish using tweezers and distilled water was used to rinse off any excess dye. The glass slide was left face up to air dry.

The counter electrode (the cathode) was produced by coating the transparent conducting layer on the second glass slide with a light carbon layer. The simplest method and most cost effective material is to apply a HB pencil directly to the glass slide and apply a graphite coating to the transparent conducting surface. Excess or loose graphite particles can be removed by gently blowing or brushing them away. This layer acts as the catalyst for the triiodide – iodide (I₃⁻, I⁻) regeneration reaction.

The two electrodes were placed on top of each other with the catalyst-coated electrode on top of the TiO₂ layered electrode. These two glass slides were offset with respect to one another. This displacement provides two exposed conducting inner cell surface areas. To hold the glass slides in place mechanical clips were used. The cell was activated by placing several drops of the electrolyte solution (triiodide – iodide) at the edge of the glass slides and allowing capillary action to draw the solution down between the anode and cathode. The inner exposed surfaces provided the cell electrode contact points⁸.

3. RESULTS

For our solar cell Hibiscus dye extracted from cell dried Hibiscus flowers was used for the dye and a carbon coating of graphite from a HB pencil was used for the counter electrode. Other cyanin dyes commonly found in biological systems (plants) were explored such as raspberry and blackberry juice. However the observed current values were considerably lower than those measured using the Hibiscus dye employed in our cell. Using a 20 W 12 V halogen lamp as a light source, positioned 20 cm from the solar cell and using the electronic circuit described in Figure 2.

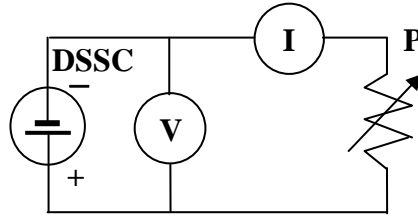


Figure 2. Circuit schematic for measuring the current-voltage characteristics of the (DSSC) solar cell. P: 10k Ω Potentiometer. V: Voltmeter. I: Ammeter.

The current and voltage were measured and an I-V curve was obtained as in Figure 3.

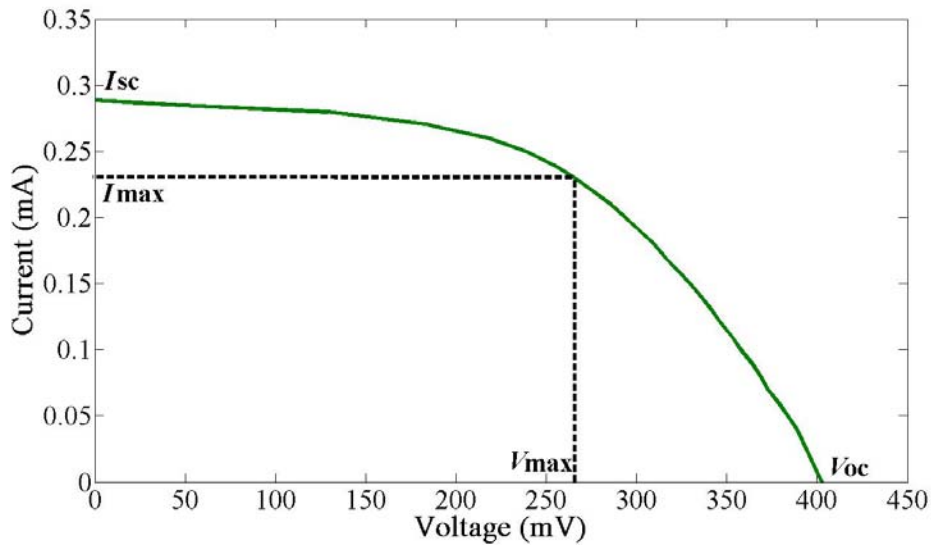


Figure 3. Typical current voltage (I-V) curve for a solar cell stained with Hibiscus dye.

In standard semiconductor diode theory^{9,10} the forward biased diode current, i_D , is commonly approximated as a function of the voltage V across the diode using the following expression

$$i_D = I_s \left[\exp\left(\frac{qV}{kT}\right) - 1 \right]. \quad (1)$$

I_s is commonly referred as the *saturation* or *scale current*. $q = 1.6 \times 10^{-19}$ C is the charge on the electron, $k = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant and T is the temperature in degrees Kelvin (0 K = 273.15 °C). These terms can be bundled together into a single variable V_T called the *thermal voltage*

$$V_T = \frac{kT}{q}, \quad (2)$$

which at room temperature has the value $V_T \sim 25$ mV.

In our case we propose to model our DSSC using the schematic representation shown in Figure 4.

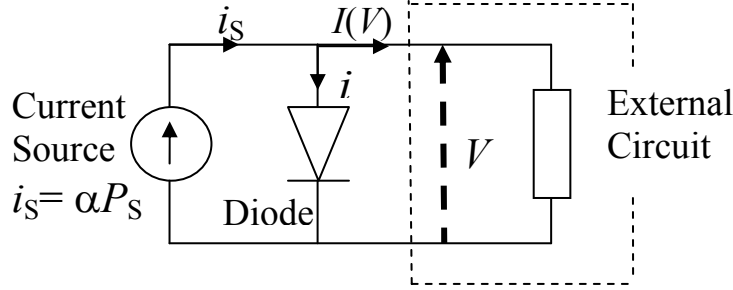


Figure 4. Schematic diagram of illustrating our proposed model of the operation of a DSSC.

We assume that the current source output, i_s , is linearly proportional to the illuminating solar light intensity (power) P_s ,

$$i_s = \alpha P_s. \quad (3)$$

Applying Kirchhoff's law (current conservation at a node) in the forward biased case, (i.e., $V > 0$), it can be shown that

$$I(V) = i_s - i_D = \alpha P_s - i_D. \quad (4)$$

Assuming our DSSC exhibits a diode like behaviour, then using Equation (1) and (2) gives

$$I(V) = \alpha P_s - I_s \left[\exp\left(\frac{V}{V_T}\right) - 1 \right]. \quad (5)$$

Clearly the relationship between output voltage and output current is nonlinear, $I = f(V)$, and Ohms Law will at best be obeyed in a piece-wise fashion. We note that we do not require either i_s or V_T to be governed by the same relationship (arise due to the same physical effects) as the variables in Equation (1).

An important point on the I - V curve, will be the point at which maximum power is supplied which is sometimes referred to as the 'knee of the curve'. An example of an experimental curve is given in Figure 5.

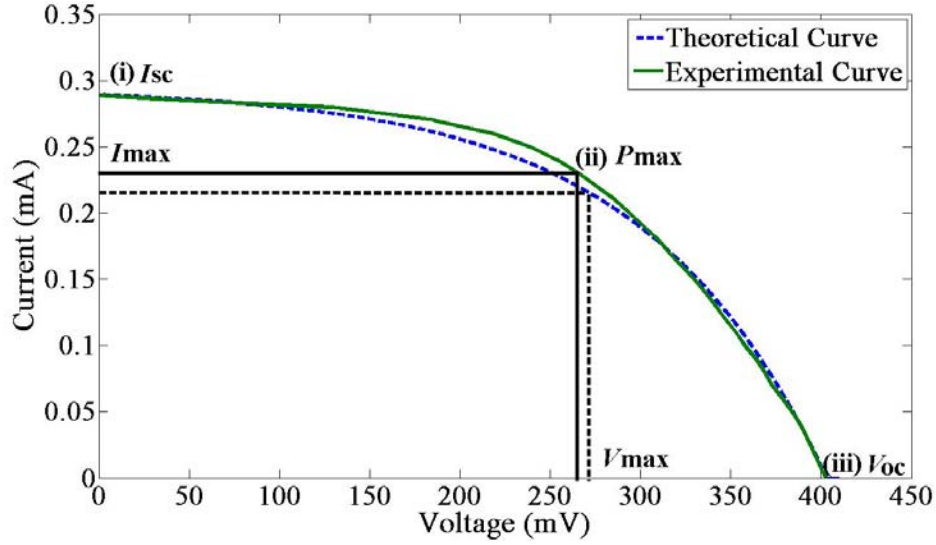


Figure 5. Theoretically predicted and experimentally obtained I-V curves for a DSSC.

Three points of significance are labelled on this graph. Point (i) $I = I_{SC}$ the short circuit current when $V = 0$; Point (ii) the knee point $\{I_{MAX}, V_{MAX}\}$ which is the point of maximum power, $P_{MAX} = I_{MAX}V_{MAX}$, output, and Point (iii) $V = V_{OC}$ the open circuit voltage when $I = 0$.

We wish to use these values at these points in our experimental curves in order to reduce the number of independent variables appearing in our proposed model. In this way the appropriateness of the model can be tested.

For Point (i) it is clear that

$$I = I_{SC} = i_s = \alpha P_s \quad (6)$$

For Point (iii) Equation (5) can be re-written as

$$0 = i_s - I_s \left[\exp\left(\frac{V_{oc}}{V_T}\right) - 1 \right]. \quad (7)$$

This equation can re-written as

$$I_s \left[\exp\left(\frac{V_{oc}}{V_T}\right) - 1 \right] = i_s. \quad (8)$$

In order to examine Point (ii) we must now define an expression for our output power P

$$P(V) = I(V)V = \left\{ \alpha P_s - I_s \left[\exp\left(\frac{V}{V_T}\right) - 1 \right] \right\} V. \quad (9)$$

In order to identify our maximum output power point we recall that at the extremum value, P_{MAX} , for which $\frac{dP}{dV} = 0$. Taking the derivative of Equation (9) with respect to V gives

$$\alpha P_s - I_s \left[\exp\left(\frac{V}{V_T}\right) - 1 \right] + V \left\{ -I_s \left[\exp\left(\frac{V}{V_T}\right) - 1 \right] \left(\frac{1}{V_T} \right) \right\}. \quad (10)$$

We set this equal to zero in order to find the value of $V = V_{MAX}$ at which $P = P_{MAX}$.

$$\alpha P_s - I_s \left[\exp\left(\frac{V_{MAX}}{V_T}\right) - 1 \right] \left[1 + \left(\frac{V_{MAX}}{V_T} \right) \right] \equiv 0, \quad (11)$$

$$\Rightarrow \alpha P_s - I_s \left[\exp\left(\frac{V_{MAX}}{V_T}\right) + \frac{V_{MAX}}{V_T} \exp\left(\frac{V_{MAX}}{V_T}\right) - 1 - \frac{V_{MAX}}{V_T} \right] \equiv 0. \quad (12)$$

Therefore

$$\frac{\alpha P_s + I_s}{I_s} = \left[\exp\left(\frac{V_{MAX}}{V_T}\right) \right] \left[1 + \frac{V_{MAX}}{V_T} \right] - \frac{V_{MAX}}{V_T}. \quad (13)$$

Equation (13) can be solved numerically to find the value for V_{MAX} . Then substituting back into (5) I_{MAX} can be found and thus P_{MAX} calculated.

An important parameter used to quantify the performance of the DSSC is the Fill Factor, FF . This is defined as

$$FF = \frac{I_{MAX} V_{MAX}}{I_{SC} V_{OC}}. \quad (14)$$

This dimensionless parameter is used to define the overall DSSC efficiency η

$$\eta = \frac{FF \times I_{SC} \times V_{OC}}{P_S} = \frac{I_{MAX} V_{MAX}}{P_S}. \quad (15)$$

Clearly the quantities I_c , V_{oc} , FF and η of a solar cell defined above are crucial performance characteristics. When testing a solar cell all four quantities must be defined for a particular wavelength or spectrum. The Standard Test Conditions (STC) for solar cells are at a temperature of 25°C, at a power density 1000 W m⁻² in the Air Mass 1.5 spectrum¹. From the experimental results for our cell, see Figure 5, the fill factor was determined using Equation (14) to be $FF = 0.525$, where $I_{MAX} = 0.26$ mA, $V_{MAX} = 266$ mV, $I_{sc} = 0.289$ mA and $V_{oc} = 403$ mV¹¹.

It is clear however that this model is insufficient¹², and our aim is, starting from first principles, to provide a physical reasonable and useful model which build on those models previously developed^{13,14}. Ultimately we wish to explain and link variations in bulk physical parameter values, i.e. V_T above, with variations in the material composition (i.e., dye type and concentration), of the DSSC.

4. CONCLUSION

The manufacturing, modelling and characterisation of a simple DSSC has been described. We note that the production of very simple devices and basic measurements under non ideal conditions were reported. It was evident however that small and reproducible photocurrents were obtainable using rudimentary DSSCs. It is our intention to repeat these experiments under standard testing conditions to obtain the power conversion efficiency.

The efficiencies of these DSSCs can be improved with a suitable dye. Organic dyes like Hibiscus dye can be used as a suitable and inexpensive photosensitiser for DSSCs⁷. However as noted one of the most widely used but expensive dyes used in DSSCs with high power conversion efficiencies is the inorganic (metallic) ruthenium^{15,16}. Apart from being inexpensive Hibiscus was more easily sourced and environmentally friendly.

Organic dyes are in general preferable to inorganic dyes as they have higher molar extinction coefficients, they are more cost effective and many variations of the same class of dye can be examined. One result of the greater maximum absorption coefficients of organic dyes is the possibility of fabricating thinner porous dyed TiO₂ nanocrystalline layers¹⁷, leading to potential improvements in cross plane conductivity. One example of such an organic dye is porphyrin^{18,19}.

Future work includes improving and refining our theoretical models and comparing them to experimental results under standard testing conditions.

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