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Characterising Dye-Sensitized Solar Cells

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ABSTRACT

With growing energy and environmental concerns due to fossil fuel depletion and global warming there is an increasing attention being attracted by alternative and/or renewable sources of power such as biomass, hydropower, geothermal, wind and solar energy. In today's society there is a vast and in many cases not fully appreciated dependence on electrical power for everyday life and therefore devices such as PV cells are of enormous importance. The more widely used and commercially available silicon (semiconductor) based cells currently have the greatest efficiencies, however the manufacturing of these cells is complex and costly due to the cost and difficulty of producing and processing pure silicon. One new direction being explored is the development of dye-sensitised solar cells (DSSC). The SFI Strategic Research Centre for Solar Energy Conversion is a new research cluster based in Ireland, formed with the express intention of bringing together industry and academia to produce renewable energy solutions. Our specific area of research is in biomimetic dye sensitised solar cells and their electrical properties. We are currently working to develop test equipment, and optoelectronic models describing the performance and behaviors of dye-sensitised solar cells (Grätzel Cells). In this paper we describe some of the background to our work and also some of our initial experimental results. Based on these results we intend to characterise the opto-electrical properties and bulk characteristics of simple dye-sensitised solar cells and then to proceed to test new cell compositions.

Keywords: Solar, dye-sensitised, biomimetic, Grätzel Cells

1. INTRODUCTION

Conventional silicon and more exotic quantum based solar cells continue to drive the solar energy production and dominate the commercial market. However over the last decade momentum has grown in support of organic solar cell technology. Silicon solar cells flourished over the years due to the knowledge and material obtained from the semiconductor industry because of the technical expertise and financial investment in fabrication plants in these areas, conventional PV cells have acquired respectable efficiencies¹.

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The disadvantage of silicon solar cells is that the associated manufacturing process is complex and costly². While it would seem that there is a plentiful supply of the required raw material, since after oxygen, silicon is the second most abundant element and comprises of 25.7% of the Earth's crust. The disadvantage of working with silicon is that it is not found free in nature but is found as oxides (e.g. sand, quartz, flint) and as silicates (e.g. granite, asbestos, clay). Energy intensive processing and clean room fabrication condition are essential when working with this material³.

One economically viable and flexible alternative to the $p - n$ junction photovoltaic (PV) devices is to look at thin film organic-material devices, specifically dye-sensitised solar cells DSSC. In silicon systems the semiconductor takes on the dual role of charge carrier transport and light absorption, whereas in DSSC these two operations are separated⁴.

An attractive feature of these dye-sensitised solar cells is that the concept derives from the area of biomimetics, that is that DSSC devices are made so as to imitate or mimic nature in some way. In this case there are analogies to the process of photosynthesis. In both cases incoming light is absorbed by an organic dye and electrons are produced, resulting in the production of positive and negative charge carriers.

A schematic of a DSSC can be seen in Figure 1 where a monolayer of an organic dye which is attached to a mesoscopic film of a wide bandgap oxide semiconductor. The dye absorbs incident light and produces electrons, which are injected into the conduction band of the semiconductor oxide. The electrons are transported across the nanoparticle layer to the current collector (anode). From here the electron passes through the external circuit and subsequently to the counter electrode (cathode). The sensitizer is regenerated by the organic hole conductor and transports the positive charges to the counter electrode where recombination occurs. Under solar exposure there is no net chemical change; light is 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⁻, I₃⁻) replaces water and oxygen as the electron donor and oxidation product⁵.

Operational devices can be made in non-clean room conditions and can be made reasonably robust to environmental conditions unlike silicon solar cells.

2. HISTORICAL OVERVIEW

Edmund Becquerel is credited with being the first person to have reported the photoelectric effect in 1839. He noted that a photocurrent was produced when silver coated platinum electrodes were immersed in electrolyte^{6,7}.

The next significant development came from Willoughby Smith's experiments in 1873 on electrical currents passing through a bar of crystalline selenium, which found that its resistance was reduced when the bar of crystalline selenium was exposed to light rather than been kept in the dark. Following on from this in 1897 William Adams and Richard Day reported that a current was produced when light fell upon selenium, which had two heated platinum contacts and no external power supply⁸.

In 1894 Charles Fritts constructed the first large area solar cell by using plates made from two different metals and compressing molten selenium between them. Fritts was able to adhere a thin semi-transparent layer of gold leaf onto a thin film of selenium to produce the first thin film photovoltaic. The results of this experiment paved the way for the study of solar cells in the 19th century^{9,10}.

The photoelectric effect was also detected in copper-cuprous oxide thin film structures, in lead sulphide and thallium sulphide. In these cells there was a layer of semitransparent metal deposited onto the semiconductor, which provided the asymmetric electronic junction¹¹. It was Goldman and Brodsky in 1914 that associated the photoelectric effect to the existence of a barrier to current flow at one of the interfaces of the semiconductor metal, i.e., rectifying action. Throughout the 1930's Neville Mott and Walter Schottky predominantly pioneered the development of a theory of metal semiconductor barrier layers.

The development of silicon electronics followed the innovation of a technique to manufacture *p – n* junctions in silicon in the 1950's. The *p – n* junction structure architecture produced superior rectifying action and photovoltaic performance¹.

Prior to 1953 the most efficient photovoltaic devices were selenium photocells with a maximum efficiency of 0.8 %. This changed dramatically in 1954 when D. M. Chapin, C. S. Fuller and G. L. Pearson combined their research to produce the first silicon solar cell with an efficiency of 6%. Other materials such as gallium arsenide, indium phosphide and cadmium telluride were studied for use in *p – n* junction photovoltaic devices, but silicon has remained the principal photovoltaic material. Silicon has benefitted from the advances of silicon technology from the microelectronics industry^{12,13}.

In the 1970's alternative energy sources research was spurred on by the energy crisis in the oil dependent western world. There was a growth in funding for research and development of photovoltaics and a variety of methods for reducing manufacturing and material costs while simultaneously improving device efficiency. Photochemical junctions were explored with a view to lower costs, and alternative materials included amorphous silicon, polycrystalline silicon and organic conductors. To improve efficiencies, tandem and other multiple band gap structures were developed¹.

With the discovery of the hole in the Ozone layer in 1985 there was a renewed wave of pressing concern for cleaner energy alternatives. In 1991 Brian O'Regan and Michael Grätzel reported a new concept of a solar cell that was based on biomimetics, specifically mimicking the photosynthesis process in plants⁴. This type of solar cell is known as a dye sensitised solar cell. To date their efficiencies are not a current threat to silicon solar cells, however it is hoped that one day these dye-sensitised solar cells will improve significantly to be considered for commercial use.

Photovoltaic production has expanded at a rate of 15 – 25% per annum since the latter half of the 1990's and this has allowed a reduction in manufacturing costs¹. Photovoltaics are finally starting to become competitive energy suppliers as conventional electricity supplies have become more expensive. One example of growth is in commercial solar panels for residential houses.

3. METHODOLOGY

We have implemented rudimentary dye-sensitised solar cells and performed measurements to characterise the current-voltage (I-V) values obtained. The dye-sensitised solar cells consist of two glass slides (4 cm × 2 cm), which have a layer of transparent conducting coating on one face of each slide as shown in Figure 1. Fluorine doped SnO₂ was our material of choice for the transparent conducting coating. Other oxides such as ZnO and SnO₂ can and have been previously investigated¹⁴.

By measuring the electrical conductivity to find the resistance of the glass slides, the transparent conducting coating was immediately distinguishable from the non-conducting face.

One basic method that was used for applying a monolayer of TiO₂ was masking three sides of the conductive face of the glass slide with Scotch tape. This formed a mould in which the TiO₂ solution could flow into. Another reason for masking the conductive glass was to allow for electrical contacts. Using a pipette, several drops of the commercial colloidal TiO₂ was transferred onto the slide and spread over the unmasked area evenly.

Once the TiO₂ dried the mask was removed with care. Sintering is required to adhere the TiO₂ layer onto the glass slide. Using a furnace at approximately 450°C the sintering time is roughly 5 – 10 minutes. The TiO₂ layer turns into a brownish colour, which is due to the organic matter in the TiO₂ layer reverting back to its former white colour once it has been successfully sintered on. The glass slide has to be cooled slowly after the sintering process to avoid thermal stress. This is the negative electrode.

One option is to dye the negative electrode. In this experiment dried Hibiscus flowers were soaked in a petri dish filled with boiling water. The slides were immersed face up in the solution for approximately 10 minutes to ensure that the dye had completely penetrated the TiO₂ layer. This was obvious by the purple-red staining of the TiO₂ layer. Tweezers were used to remove the slides from the petri dish and cold water was used to gently rinse off any excess dye. The slides were left face up to dry.

The counter electrode was formed by coating a light carbon layer over the transparent conducting coating of the second glass slide. Using a pencil, a graphite coating was applied to the surface of the transparent conducting coating and loose graphite particles were brushed away. This layer acts as the catalyst for the triiodide – iodide (I₃⁻, I⁻) regeneration reaction.

The positive and negative electrodes are placed together so that the catalyst-coating electrode is placed on top of the TiO₂ layer. The two glass slides are offset as to allow the entire TiO₂ layer to be covered by the counter electrode and the bare side of the transparent conducting coating is exposed. Binder clips were used to hold the glass slides together. To activate the cell the electrolyte solution (triiodide – iodide) was placed at the edge of the glass slides and capillary action drew the solution down to stain the TiO₂ layer. The exposed sides of the cell were used as the contact points⁵.

4. RESULTS

For this solar cell dried Hibiscus flowers were used for the dye and a carbon coating was used for the counter electrode. Other cyanin dyes were explored such as raspberry and blackberry juice, however the observed current values were far lower than that of the Hibiscus flowers. Using a 20 W 12 V halogen lamp as a light source, set 20 cm from the solar cell and using the circuit described in Figure 2, the current and voltage can be measured.

Figure 2. Circuit schematic for measuring the current-voltage characteristics of the solar cell.

This circuit comprises a 10 K potentiometer, a voltmeter, an ammeter and a solar cell under test. By varying the potentiometer and exploiting the relationship between current and voltage from Ohm's Law a current-voltage curve is obtained as illustrated in Figure 3.

$$V = IR . \quad (4.1)$$

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

From the knee of the curve, the maximum product of current and voltage was obtained. This value can be used to calculate the efficiency of the solar cell. The power density of the cell is given by the product of the photocurrent density by the voltage,

$$P = JV. \quad (4.2)$$

The solar cell will reach a maximum power point, $P_{\max}$, which will occur at a maximum voltage, V_m , with a corresponding current density, J_m , which can be seen graphically in Figure 3. The fill factor is the ratio of the maximum obtainable power to the theoretical power.

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}}. \quad (4.3)$$

The conversion efficiency, η , of the solar cell can be calculated by measuring fill factor, FF , the power density, P , and the photocurrent density, J , at short circuit, J_{sc} , and the open circuit photovoltage, V_{oc} .

$$\eta = \frac{J_{sc} V_{oc} FF}{P_s}. \quad (4.4)$$

The key quantities J_{sc} , V_{oc} , FF and η of a solar cell are the crucial performance characteristics. When testing a solar cell all four quantities must be defined for a particular illumination. 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.

The fill factor was determined to be 0.542 where $J_m = 0.26$ mA, $V_m = 266$ mV, $J_{sc} = 0.29$ mA and $V_{oc} = 389$ mV.

5. DISCUSSION AND CONCLUSION

The results for the presented DSSCs were not measured under ideal testing conditions. A basic and inexpensive DSSC is capable of producing a small photocurrent. However the efficiencies of these DSSCs are far below 1%. At the time of testing the solar cells, a solar simulator was unavailable and an uncalibrated light source was used. Therefore the power conversion efficiency could not be accurately calculated and hence it was omitted.

Altering the materials in the DSSC can have a significant and positive effect, although the downside is that there is a rise in production cost. An example of upgrading the DSSC would be to substitute the graphite catalyst coating for a platinum coating. Another alternative for a considerable increase in efficiency would be to use a ruthenium dye. Ruthenium dyes are currently the best dyes for DSSCs¹⁴. Another feature is the sealing of the DSSCs. The DSSCs used were not sealed. By implementing these alternatives the efficiency of a DSSC can dramatically improve to approximately 10 – 11%^{15, 16}.

Hibiscus can be used as a suitable and inexpensive dye for dye sensitized solar cells⁵. One of the most notably dyes used in dye sensitized solar cells with high power conversion efficiencies is ruthenium^{15,16}. The disadvantage of ruthenium is that it is costly and for our measurements hibiscus was a more suitable dye as it was easily sourced and inexpensive. Another organic dye which will be examined is porphyrin.

In an effort to characterise the DSSC an automated testing rig will be designed in which multiple solar cells will be tested under the same light source in the same time frame. Various dyes, different cell architectures and cell longevity will all be examined. This will allow for a quick comparison of different solar cells.

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