The influence of light intensity, active area and excitation wavelength on the temporal response of a dye sensitized solar cell

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ABSTRACT

The temporal response of a biomimetic dye-sensitized solar cell (DSSC) is critically linked to the intensity of the incident light. When a DSSC is partially illuminated and the incoming light is of low intensity, the response time of the cell is prolonged dramatically. In this report, the major components of the DSSC are investigated to find the source and to provide a model of the driving mechanisms behind this delay. For low light level conditions, only deep traps states of the TiO₂ layer participate in electron transport resulting in a slow temporal response.¹ Increasing the illumination level thus increases the conductivity of the TiO₂ electrode by filling these trap states and increases the response time. This study shows a strong correlation between the light intensity, active area and excitation wavelength on the temporal response time of a DSSC.

Keywords: Solar cell, DSSC, biomimetic, temporal response, spectral response

1. INTRODUCTION

Biomimetic dye-sensitized solar cells (DSSCs), known as third generation solar cells, are based on the original design by Michael Grätzel, from the École Polytechnique Fédérale de Lausanne, who in 1991 developed a new type of solar cell which now bears his name.² A DSSC consists of a mesoporous, nanoparticle film of titanium dioxide (TiO_2) onto which a monolayer of dye is adsorbed, an electrolyte and two electrodes (figure 1). Light energy incident on the cell is converted to electricity on a molecular level, similar to the natural photosynthesis process, and is a regenerative, photoelectrochemical process by way of the electrolyte. While organic dyes can be used in the DSSC (i.e.: biomimetic), the lowest excited state of the dye must match the conduction band edge of the semiconductor and the absorption range of the dye should cover the widest range possible, e.g.: the whole visible spectrum.³ The purpose of the dye is to sensitize the TiO_2 layer to the visible and near-infrared part of the solar spectrum, i.e.: to enhance the wavelength acceptance of TiO_2 , as without it the nanoparticle layer would only respond to ultraviolet light.² The effective decrease in the large band gap of the semiconductor (3.2)eV) may be accounted for by assuming the introduction of 'new' dye surface states.² The range of wavelengths absorbed by a DSSC is governed by this effective band gap. Photons of incoming light with an energy greater than the effective band gap inject electrons into the conduction band of the semiconductor, with the excess energy partially lost to unwanted heating of the cell $(E = h\nu)$ where E is the energy, h is Plank's constant and ν is the frequency of the photon). The response of the DSSC to a particular wavelength is a function of the intensity of the light. Thus the spectral response of the cell to a white light source is the combination of its response to all wavelengths present in the source. Solar radiation is one such source with a mixture of ultraviolet, visible and infrared light $1-6 \,\mathrm{eV}$. However, this radiation is filtered by the atmosphere leaving harvestable photons in the range of 1-4 eV for solar cells. Taking into account variations in spectral irradiance worldwide, standardized test conditions (STCs) have been devised. These STCs consist of illumination of $100 \,\mathrm{mW} \,\mathrm{cm}^{-2}$, a spectral

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distribution of so called air mass (AM) 1.5, equivalent to wavelength distribution at ground level, and a solar cell temperature of 25° C.⁴

Gregg,⁵ Koide and Han⁶ have reported that one of the major differences between the DSSC and traditional, silicon-based solar cells is the lack of a depletion layer formed in the DSSC as the nanoparticles are smaller than the characteristic electron mean free pathway. Therefore, a large, local electric field is not present to help separate the electron-hole pairs as with the silicon-based cells. Instead, quasi-exciton states produced in the excited dye species are separated when the electron is injected into the nanoparticle film and positive charge carriers are transferred to the electrolyte. To enable effective electron transfer from the dye molecule's excited state into the semiconductor's conduction band, the lowest excited state of the dye should match the conduction band edge of TiO_2 .³

The basic performance of a DSSC can be evaluated through automated current-voltage (I-V) measurements, as described by Koide and Han.⁶ This automated testing procedure revealed a temporal response delay inherent to DSSCs, relative to traditional solar cells, which will be investigated in this study using a different approach. Spectral analysis combined with time dependant simplified voltammetry are presented here as important tools for understanding how new dyes, while assembled in a DSSC, respond to light of different wavelength and intensity. Variations in the manufacturing process and chemical composition of a DSSC have also been studied in detail using these techniques. In addition, the nanoparticle film has been characterized for thickness, average grain size and internal structure using imaging techniques; e.g.: scanning electron microscopy (SEM)(figures 1-4), focused ion beam (FIB)(figure 4) and atomic force microscopy (AFM)(not shown in this publication). Hence, the performance and structure of a DSSC may be investigated by the above mentioned techniques to yield information about the underlying physical mechanisms of the device, i.e.: electron generation, injection, transport, and the effect of grain size and thickness upon these electronic processes.

2. EXPERIMENTAL

Dye-Sensitized Solar Cell

A combination of preparation methods for the DSSC as described by O'Reagan et $al.^2$ and Grätzel⁷ has been followed in this study. The cell is composed of four main components: two electrodes, a semiconducting nanoparticle layer (TiO_2) , a monolayer of dye molecules adsorbed onto the TiO_2 layer and an electrolyte (figure 1). Each electrode consists of a glass slide, one side of which is coated with a conductive layer of fluorine doped tin dioxide SnO₂:F, which forms a transparent conducting oxide (TCO). Here, SnO₂:F is the preferred material for the TCO layer⁸ as it remains stable at high temperatures, up to $450 \, {}^{o}$ C, during the sintering process required for the manufacture of DSSCs. To one electrode, a nanoparticle layer of TiO₂ (thickness between 40-50 μ m) is applied and sintered to ensure good adhesion between the semiconducting particles, the TCO and for electronic conduction. This electrode is known as the anode or negative electrode. The counter electrode is coated with a thin graphite layer, which acts as a catalyst for the triiodide-to-iodide (I_3^-/I^-) regeneration process.⁹ The two electrodes are brought together and offset by 5 mm to allow for electrical contacts and held in place with a fixed mechanical pressure. Finally, the DSSC is activated with one or two drops of a liquid electrolyte, drawn into the cell via capillary action. The number of potential sensitizers available is vast and may be of a natural or synthetic origin. One of the most readily available natural dyes are the anthocyanins, the family of purple dyes found in raspberries and blackcurrants (molecular formula: $C_{1}5H_{11}O^{+}$). Natural, porphyrin-based sensitizers may be chemically modified to yield higher power conversion efficiencies of up to 7.1 %.¹⁰ However, synthetic dyes report the highest efficiencies of up to 11.3% at present¹¹ and are typically a Ruthenium-based complex: e.g.: NaRu(4,4'bis(5-hexylthiophen-2-yl)-2,2'-bipyridine)(4-carboxylic acid-4'-carboxylate-2,2'-bipyridine)(NCS)₂), C101.

Optical Setup

The spectrometer used in this study consists of a highly resolving, stepper motor controlled scanning grating monochromator (BM100) with a grating of 300 lines / mm and 1 m focal length. The procedure to calibrate the spectrometer was carried out using two laser sources at 632.8 nm and 532 nm. As a reference detector we have used a photodiode EG&G model UV-444B PN which provides a very linear response with a uniform quantum efficiency over the desired wavelength range or a BPW33 photodiode with a higher sensitivity across the spectrum. Photo-current and voltage measurements were quantitatively recorded with a *Keithley 6514* electrometer¹² which



Figure 1. Schematic of a DSSC.

offers superior resolution, sensitivity and dynamic range compared to a standard digital multimeter. It is a state of the art electrometer fitted with tri-axial connections which provides a sensitivity of less than 3 fA (current mode) and an input impedance of greater than $200 \text{ T}\Omega$ (voltage mode).

In this study, light sources of different power levels used to excite the DSSC include: $\approx 1 \, \text{kW}$ xenon arc lamp, 20 W incandescent lamp and 11 W fluorescent light. Although the Xe arc lamp offers the highest output intensity, incandescent sources yield a smoother spectral output. The Xe arc lamp is used in solar simulators for calculating power conversion efficiencies for all types of solar cell technologies, as it mimics the solar spectrum closely through similar emissions in the ultraviolet, visible and infrared. Efficiencies are tested in recognized international test centers under standard test conditions.⁴ A normal incandescent light bulb usually has a tungsten filament which heats to 2500 K. A halogen lamp has added some halogen elements (bromine or iodine) which allows the filament to burn hotter up to 3000 K. Some have a dichroic reflector which reflects the IR back onto the lamp filament which aids in it's heating. The DSSCs spectral response is measured using the highly resolving scanning grating monochromator which exposes the cell to a tailored excitation wavelength which is scanned through the wavelength range of interest. We have recorded the solar cell and the photodiode responses individually and subsequently divided one by the other to obtain the cells true spectral response. The spectral response (SR) at a given wavelength λ is defined by

$SR(\lambda) = J_{ph} (\lambda) / I(\lambda)$

where $J_{ph}(\lambda)$ is the total photogenerated short circuit current density at a given wavelength λ and $I(\lambda)$ is the spectral irradiance of the incident light.

A FEI Quanta 3D dual beam scanning electron microscope (SEM) equipped with a highly spatially resolving electron field emission gun (FEG) and a highly spatially resolving Gallium ion gun was employed for imaging and depth profiling of the TiO_2 structures providing a resolution of down to 1.5 nm.

3. RESULTS AND DISCUSSION

In this report, the internal structure of the TiO₂ layer that forms the basis of a DSSC, was characterized via SEM. Information regarding TiO₂ thickness and grain-size are shown in figure 2,3,4 which provide an important insight into the structure and size of the TiO₂ layer which is mandatory for the development of a model regarding the underlying, physical mechanisms of a DSSC, i.e.: electron generation, injection and transport. In order to evaluate the absolute thickness of the layer, a focused ion beam (FIB) was used to sputter atoms from the TiO₂ layer until it reached the substrate below. Results show an average grain size of 45 nm (figure 2-4 show SEM images at three different magnifications) and average thickness of 20.8 μ m (figure 5).

Building on this imaging analysis, evaluation of open-circuit voltage (V_{oc}) for assembled DSSCs has been carried out under varying test conditions with white light sources of various power outputs. The purpose of these experiments was to investigate the reasons behind the slow temporal response in a DSSC. To establish a reference for the temporal response and maximum V_{oc} reached for a DSSC, a full cell (active area of 450 mm²) was illuminated by a white light source. The temporal response and maximum V_{oc} were found to be in the



Figure 2. SEM image of sintered nanoparticle TiO₂ layer, magnification $8000 \times$ and scale bar $5 \,\mu$ m.



Figure 3. SEM image of sintered nanoparticle TiO₂ layer, magnification $35000 \times$ and scale bar $2 \,\mu$ m.

order of 7-10 seconds and 265 mV, respectively, which will be used as a reference for subsequent experiments. However, these values are dependent on the intensity of light used which show higher V_{oc} and faster response times at higher light levels. Open-circuit voltage measurements are the focus of this study, in spite of the cell being a current source, because the measured internal impedance of the cell ($k\Omega$) is small compared to a normal current source which in theory has an infinitely high impedance.

To ensure that the presented results cannot be attributed to basic, electronic RC-integrator type characteristics, firstly the internal impedance of the DSSC was measured through I-V curves. This yielded an impedance in the low k Ω range which is considerably less than that of the measuring devices, and therefore the only potential contributor to the temporal characteristics, as the cell is in parallel with the electrometer/voltmeter. Using realistic values for the capacitance ($\leq 1 \text{ nf}$) and the above impedance ($\approx 1 \text{ k}\omega$) would yield temporal responses



Figure 4. SEM image of sintered nanoparticle TiO_2 layer, magnification $100000 \times$ and scale bar 500 nm. Average particle size 45 nm.



Figure 5. SEM image using the FIB to evaluate the absolute thickness of the TiO₂ layer, magnification 5000× and scale bar 10 μ m. Average height 20.8 μ m.

on the ns-scale. Further evidence is provided by a comparison of two measuring devices of strongly deviating internal impedances (200 T Ω and 10 M Ω for the Keithley and the Caltek, respectively) as shown in (table 1). The virtually identical temporal responses demonstrate that possible RC time constants from external devices are also not the source of the reported temporal delay.

By reducing the active area of the cell and maintaining the same conditions as the in reference experiment above, it is possible to investigate whether the total amount of injected electrons, which need to be replenished by the electrolyte, have an effect on the temporal response. An opaque mask, with an aperture of 50 mm^2 (3 mm by 17 mm) replicating the output slit dimensions of a monochromator is attached to the front of the DSSC. This

aperture allows a small amount of the incident light through, leaving the bulk of the solar cell in darkness. The cell is allowed to reach maximum V_{oc} and this value is used as a reference point. Then the cell is covered with an opaque medium until no light conditions are reached. Next the cell is uncovered and the time taken to reach 95% of V_{oc} again is measured (table 2). The experiments were repeated several times and the average values were taken. Reduced active area (while maintaining the photon density) results in a slower response time. In comparison to the reference experiment these results show a substantial increase in the temporal response. If the electrolyte was the 'bottle-neck' in the temporal response, then by reducing the active area thus reducing the number of electrons to be replenished, it would yield a faster time response. However, this is not the case as the temporal response delay is still present.

Keithley/ s	Caltek/ s	
7.09	9.21	
7.81	8.71	
7.90	9.93	
7.71	9.31	
8.85	8.90	
7.87^{\dagger}	9.21^{\dagger}	
Average time [†]		

Table 1. Average response times of the Keithley 6514 electrometer $(200 \text{ T}\Omega)$ versus Caltek digital multimeter $(10 \text{ M}\Omega)$.

Next in order to investigate if the TCO plays an important role in the temporal response, the mask orientation was varied from vertical (i.e.: between the electric contact points) to horizontal (i.e.: across the cell). Although it was expected that the vertical positioning would yield a faster response time due to its proximity to the electrical contacts, the horizontal mask shows a faster result (table 2). From this we can conclude that the TCO is not the main contributor to the delay in temporal response.

	Daylight	Fluorescent
INO IVIASK		
V_{oc} max.	$265\mathrm{mV}$	$274\mathrm{mV}$
V_{oc} min.	$25\mathrm{mV}$	$25\mathrm{mV}$
$\mathrm{Time} \longrightarrow \mathrm{V_{oc}}$	$5\mathrm{s}$	$4\mathrm{s}$
Horizontal mask		
V_{oc} max.	$165\mathrm{mV}$	$82\mathrm{mV}$
V_{oc} min.	$35\mathrm{mV}$	$25\mathrm{mV}$
Time \longrightarrow V _{oc}	$47\mathrm{s}$	$30\mathrm{s}$
Vertical mask		
V_{oc} max.	$180\mathrm{mV}$	$100\mathrm{mV}$
V_{oc} min.	$40\mathrm{mV}$	$40\mathrm{mV}$
$\mathrm{Time} \longrightarrow \mathrm{V_{oc}}$	$42\mathrm{s}$	48 s

 $^{\dagger}\mathrm{Cell}$ active area $50\,\mathrm{mm^2}$ / $450\,\mathrm{mm^2}$

Table 2. Response times and maximum V_{oc} for vertical and horizontal mask orientation illuminated with daylight and fluorescent light. Mask area of 50 mm². Full cell area 450 mm².

As reported above, alterations in active area have been seen to produce changes in the temporal response. The following experiment, uses monochromatic light and various aperture sizes, to investigate the dependance of the

temporal response on the excitation wavelength. Wavelengths were chosen according to the absorption spectrum of the anthocyanin dye¹³ and the bandgap of TiO₂, at 391, 565 and 597 nm, corresponding to 3.16, 2.19 and 2.07 eV, respectively. In order to avoid direct photon absorption by the TiO₂ layer, a wavelength close to energies below 3.2 eV which is the TiO₂ band gap is chosen. The intensity levels were fixed for each excitation wavelength. The *Keithley* electrometer is programmed to monitor the response of the cell from no light (minimum V_{oc}) to full light conditions over 120 seconds. It was found that the temporal response is inversely proportional to the active area of the cell and directly proportional to the wavelength of the light. As the aperture is reduced, the intensity of the illumination is decreased and the temporal response at each wavelength increases. Additionally, while all the responses are in the similar order of magnitude, the temporal response is faster for shorter wavelengths.

Finally, at these particular wavelengths, the light flux is adjusted by means of an aperture ranging from a maximum of 1 mm to a minimum of 0.23 mm and corresponding temporal responses were compared. Since the aperture by itself has a strong effect on the temporal response, we will only compare changes of the temporal response at aperture sizes as reported in figures 6, 7, 8. For all intensity levels, the 391 nm was faster, suggesting that the kinetic energy of the excited electrons must play a role in the temporal behavior. However, the differences are not the dominating effect compared to changes of the active area as reported earlier.



Figure 6. True measured data points of the temporal response with logarithmic fit at 391 nm for three selected aperture sizes (function $P_1^* \log(x-P_2)+P_3^*(x-P_4)+P_5$) and is in good agreement with the measured data.

Hishikawa *et al.* have reported that longer wavelengths of light have a deeper penetration depth in DSSC and result in longer, average electron path through the TiO₂ and hence a slower temporal response.¹⁴ This may be explained by the fact that incident light at higher wavelengths (597 nm) has to be absorbed by the dye first and then inject an electron in to the TiO₂ whereas light at UV wavelengths (391 nm) are absorbed faster due to the proximity of the TiO₂ band gap. However, this is not the only model that can be applied to explain the temporal response in a DSSC.¹ As described by Hagfeldt and Grätzel, in low light level conditions only deep traps states participate in the electron transport causing a low diffusion coefficient. Measurements have shown that the diffusion of electrons is characterized by a distribution of diffusion coefficients, related to the hopping of electrons via surface traps at different depths. These electron traps are localised energy states just below the conduction band edge of the TiO₂ semiconductor. Increasing the light intensity raises the electron motion. Increasing the illumination level thus increases the conductivity of the TiO₂ electrode by filling the trap states. Therefore the temporal response is critically linked to the integral intensity of the incident light.

4. CONCLUSION

The slow temporal response of a DSSC has been investigated via spectral and imaging analysis in this report. The major components of the DSSC were systematically assessed and it was found that the illuminated area



Figure 7. True measured data points of the temporal response with logarithmic fit at 565 nm for three selected aperture sizes (function $P_1^* \log(x-P_2)+P_3^*(x-P_4)+P_5$) and is in good agreement with the measured data.



Figure 8. True measured data points of the temporal response with logarithmic fit at 597 nm for three selected aperture sizes (function $P_1^* \log(x-P_2)+P_3^*(x-P_4)+P_5$) and is in good agreement with the measured data.

relative to the total area of the TiO_2 layer dominates the prolonged temporal response. Furthermore keeping the photon flux constant showed that mask orientation and excitation wavelength only have a minimal impact on the temporal response. Thus it can be concluded that the TCO and the electrolyte play minor roles in the temporal response at the above presented timescale. The prolonged temporal response may be explained by the proposed model which states that at low light conditions only deep trap states participate in electron transport. Given that the underlying processes (e.g.: electronic excitations, electron conduction and injection) are typically in the ultra-fast time scale (ns-fs), future research is needed to fully understand the mechanisms of the above reported temporal timescales which are in the order of tens of seconds.

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