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# Ultrafast metal mounted $TiO_2$ electrode preparation for dye sensitised solar cells using near infra red sintering

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## Abstract

A near infrared heating method is presented which directly heats metal substrates to very high temperatures within seconds. The technique is used to heat 1mm thick titanium metal coupons onto which 1 $cm^2$ area commercial $TiO_2$ pastes have been deposited giving assembled dye sensitised solar cell efficiencies which are equivalent or better than cells prepared using a convection oven. Near infrared heating for 12.5 seconds, corresponding to a line speed of 2 metres per minute, gave peak titanium temperatures of 545, 685, 817, 845 and 880 ºC yielding cells with efficiencies of 2.9, 2.8, 2.5, 2.3 and 1.9%. These compare to identically deposited metal mounted cells prepared in a conventional oven for 30 minutes at 500, 600 and 800 ºC of 2.9, 2.6 and 0.2%. The near infrared method is not only ultrafast but allows for a reasonably wide process window which renders it very suitable for roll to roll coating on metal surfaces.

**Keywords:** dye-sensitized, sintering, near infra red, rapid, radiation

## 1. Introduction

Dye-sensitized solar cells (DSC) have been developed over recent years as a viable low cost alternative to conventional silicon solar cells[1, 2]. The titanium dioxide based photo-anode is usually deposited from a paste which contains an organic binder. The standard method for bringing about the removal of binder, creating inter-particle connection and introducing porosity is through burning off the organic component by placing the coated electrode into a convection oven at 450 – 500 °C for 30 minutes[1, 3]. Several alternative methods have been proposed which can bring about the necessary processing of the $TiO_2$ in times of under 5 minutes and these include compression[4-6], microwaves[7] and laser [8-10] treatment. An ideal treatment should be flexible in terms of processing parameters, rapid and scalable.

Of current interest is the application of DSCs to flexible metal substrates[11-13] as this offers the potential benefits of cell flexibility and ease of scale-up for manufacturing by roll to roll processes giving rise to low cost building integrated photovoltaic materials. Roll to roll manufacturing is already widely used to make pre-finished coated metals for buildings and there are various new paint curing technologies that can replace convection ovens leading to lower energy and faster manufacturing routes. One such technique is Near Infrared (NIR) heating which delivers radiative curing to the metal substrate effectively heating the applied organic coating from the metal coating interface rather than from the air coating interface. NIR technology therefore holds potential promise in the sintering of $TiO_2$ layers mounted on metals since it can drive off organic moeties from the metal surface of the photo-anode and in particular it can do this extremely rapidly. In this short communication we demonstrate the effectiveness of the NIR treatment as compared to conventional oven treatment for a series of metal mounted DSCs on 1 mm thick Ti coupons.

## 2. Experimental

### *2.1 Near Infra Red Heating*

NIR radiation falls between visible and infrared on the electromagnetic spectrum. For the purpose of this work we will refer to the NIR region as being between 800-1500nm, since the lamps we have used have an output in the range 250-2500nm peaking between 800-1000nm [14]. These wavelengths can result in fast thermal heating of metal substrates. NIR curing technology is therefore becoming popular within coil coating industries for producing pre-painted galvanised steel strip for the construction sector [15].

Titanium dioxide is a good reflector of UV and visible radiation and that is why it is used widely in the coatings industry (coated with alumina or silica) to protect organic matrices in paint for example. $TiO_2$ pastes are however practically transparent to NIR and hence these wavelengths can be transmitted to the metal substrate where they are absorbed and result in rapid heating. Indeed, it was observation of the high energy density of NIR emitters and the rapid heating of metallic substrates through relatively transparent organic coatings that prompted this investigation of the use of NIR to drastically reduce binder removal times in the $TiO_2$ layers of DSCs.

### *2.2 $TiO_2$ deposition*

Prior to $TiO_2$ deposition a thermocouple was spot welded directly onto the underside of the metal surface. A thermocouple was applied to every sample tested and an individual temperature profile recorded. To enable deposition of the $TiO_2$ paste, a 1cm$^2$ mask of 2 layers of ~50μm Scotch™ adhesive tape height guide was applied to the surface of the 1mm thick titanium coupons (15 x 25 mm). A commercially available paste containing $TiO_2$ nanoparticles (Solaronix Ti-D) was placed onto the sample using a dropping pipette. Using a glass rod, this was drawn across the 1cm$^2$ exposed titanium surface. Immediately following deposition of the $TiO_2$ the tape was removed leaving the $TiO_2$ layer on the metal substrate ready for thermal processing via conventional or NIR ovens.

Photoelectrodes prepared in this way and sintered under standard conditions at 500 ºC for 30 minutes gave a $TiO_2$ film thickness of 6.5 (±1) μm determined using stylus profilometry. Other heating regimes were also employed as detailed below. In order to simplify the process steps, in this instance, a typical post treatment with $TiCl_4$ was not attempted.

### *2.2.1 Preparation of $TiO_2$ photoelectrode –convection oven method*

Following removal of the Scotch tape the $TiO_2$ film was placed in a convection oven (Thermolyne – Thermo scientific) for sintering at 500ºC for 30 min. In addition, several other heating regimes were tested (see Table 1). A standard heating temperature (500 ºC) was tested at three heating times (1 min, 15 min and 30 min) and a standard heating time of 30 min was adopted for a series of temperatures (500, 600 and 800 ºC)

### *2.2.2 Preparation of $TiO_2$ photoelectrode – NIR method*

The NIR equipment used (AdPhos NIR/IR Coil lab LV2) operates by moving the sample to be heated on a glass platform at a set speed (as determined by the operator) under the NIR lamp (set at a pre-set but variable power level) exiting the other side. The lamps were only switched on when the sample platform entered the lamp field of view. Time spent under the lamp was recorded.

Altering both the platform speed and the NIR lamp power output enables a range of temperature profiles to be constructed. As such the samples were exposed at a range of power outputs for 12.5 seconds giving a range of peak metal temperatures (PMT) of between 545 and 880 ºC.

### *2.3 Device fabrication*

The $TiO_2$ coated metals prepared through different heating profiles were then sensitized by immersing them in 0.3mM dye (N719 from Dyesol) solution, namely [cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)-ruthenium(II)bis-tetrabutylammonium] in an acetonitrile/tert-butanol (1:1 vol:vol) solution for 16 – 20 hours.

Standard platinised counter electrodes were fabricated by deposition of 5mM hexachloroplatinic acid in 2-propanol onto the FTO coated glass and fired at 400ºC for 30 min. A single 0.5mm hole for introduction of the electrolyte had been pre-drilled into the counter electrode.

Devices of 1cm$^2$ were prepared by heat sealing the counter electrode to the dye coated $TiO_2$ film using 50µm Surlyn gaskets. The electrolyte solution (0.8M 1-propyl-3-methylimidazolium iodide (PMII), 0.3M benzimidazole, 0.1M $I_2$ and 0.05M guanidinum thiocyanate dissolved in 3-methoxypropionitrile) was introduced to the cell by vacuum injection and the remaining hole sealed with Surlyn and a circular microscope coverslip.

### *2.4 Current Voltage (I-V)and IPCE measurements*

The photovoltaic performance of the dye-sensitized solar cells were evaluated by a Müller solar simulator system with 1kW Xe lamp as light source. The cells were measured under the illumination intensity of 100 mW/cm$^2$, AM1.5, calibrated with a reference silicon solar cell (Fraunhofer ISE) with a built-in AM 1.5 filter together with a KG5 filter. The photocurrent generated under the applied voltage was recorded by a potentiostat.

The incident photo-to-current conversion efficiency (IPCE) of the dye-sensitized solar cells was measured with an IPCE system, assembled in the Bath photochemistry labs, in the spectrum range of 400 – 800 nm with the resolution of 5 nm. The illumination intensity at 550 nm determined by a silicon photodiode is 0.31 mA. A yellow filter was used to remove the second-order light diffraction at the wavelength above 550 nm.

## 3. Results and Discussion

Figure 1 illustrates the relative heating rates for 15 x 25 mm coupons of 1 mm Ti coated with $TiO_2$ paste and placed either in a convection oven at 500 ºC or passed under the NIR lamp unit with a lamp residence time of 12.5 seconds. It can be seen that the NIR lamp unit creates extremely rapid heating profile in the sample. The speed of heating is apparent in that the sample treated with NIR has cooled back to its initial temperature within 200 seconds, during which time the Ti coupon heated in a conventional oven is only just reaching an equilibrium temperature with its surroundings. Sufficient incident NIR clearly penetrates through the $TiO_2$ pastes to rapidly heat the Ti substrate. This rapid heating causes binder removal and possibly some degree of sintering of the $TiO_2$ particles. The added advantage is that heating the surface of the metal substrate should heat binder from bottom and drive it upwards and away from the metal surface. $TiO_2$ layers prepared on Ti coupons by NIR heat treatment appeared to have identical appearance, mechanical and adhesion properties to the metal surface as those heated in the conventional oven for 30 minutes.

Table 1 summarises the DSC efficiency, $V_{OC}$, $I_{SC}$ and fill factor (FF) data for the variety of 1 $cm^2$ DSCs manufactured on identical 15 x 25 mm 1mm thick Ti coupons heated using conventional and NIR ovens. Figure 2 shows graphically the rapid NIR heating efficiency (12.5 seconds) for binder removal at a PMT of around 500 ºC compared to treatment in a conventional oven for a range of time durations. It can be seen that as soon as the conventional heating time is reduced to 900 seconds (half the normal conventional heat treatment) the efficiency drops. At heating times of 1 minute clearly there is virtually no efficiency and this is hardly surprising given the heating profile in figure 1 since at this heating time the sample will have only attained a temperature of around 300 ºC. The drop in efficiency when reducing conventional heat treatment from 1800 to 900 seconds is mainly due to a reduction in fill factor. This suggests that even at this sintering time there is still some residual binder in the matrix and full porosity has not been attained. The NIR cell conversely though treated for only 12.5 seconds has comparable efficiency to the conventional cell prepared in 1800 seconds. The comparable fill factor suggests that despite the ultra-fast heating all of the binder has been removed and there is good particle-particle contact giving rise to a higher value of $I_{SC}$. This result alone indicates the promise of the NIR heating method for treating $TiO_2$ layers on metal substrates.

Another key criterion for a continuous industrial process is to have a wide process window to allow for sudden changes in line conditions (primarily line speed) caused by alterations in a subsequent or prior process. The second series of experiments performed with the NIR curing unit aimed to look at the effects of temperature surges in the oven on the final cell efficiency data. A series of NIR heating conditions were adopted giving peak Ti coupon temperatures of between 545 and 880 ºC. At the same time the conventional oven was used to prepare cells at 500, 600 and 800 ºC for 30 minutes. The energy conversion efficiency of the DSCs as a function of temperature by conventional sintering method and by near infra red fast sintering are shown in Figure 3 and cell characteristics are presented in greater detail in Table 1. It can be seen that the efficiencies obtained with the NIR unit are far less sensitive to the PMT attained (since this temperature is not maintained for long periods). In the range 545-817 ºC the cells are practically identical. At temperatures above this, the efficiency begins to drop as a result of a poor fill factor and cell current presumably as there is a reduction in active $TiO_2$ area. The same trend in falling fill factor and cell current is seen for convection cells at both 600 and 800 ºC. The fact that the $TiO_2$ layer seems to withstand such a high peak temperature is the subject of further investigation. At these temperatures a transition to lower surface area rutile structures would be expected (as is probably the case with conventional oven treatments at 600 and 800 ºC). It is possible given the typical heat profile illustrated in figure 1 that the NIR treated samples are simply not at this high temperature for long enough for significant changes in structure of the $TiO_2$ to occur. The fact that the NIR heating temperature has such a wide process window is technologically very important since when curing much larger strip widths of metal it is always more difficult to accurately control the heating profile particularly in a rapid heating situation. In addition, an important consideration is that the heating of the metal is stopped as soon as the NIR lamp is extinguished. Again this is not the case with a conventional gas oven where the oven temperature is maintained for a long time after the heating regime is changed due to the significant heat capacity of the refractory lining.

Figure 4 shows the incident photon-to-electron conversion efficiency (IPCE) of the DSCs prepared by NIR fast sintering (12.5 s) with different peak metal temperatures (PMTs) and by optimum conventional sintering at 500 $^{o}$C for 30 mins. As can be seen, the highest IPCE of the three DSC cell types created by NIR sintering and investigated here is obtained at PMT of 685 $^{o}$C. The trend in the variation of the IPCE is consistent with the trend of the short-circuit current density ($I_{sc}$) of the cells shown in Table 1. The IPCE of the DSC made by NIR fast sintering at 685 $^{o}$C is comparable to that of the DSC sintered at 500 $^{o}$C for 30 mins. A slightly higher IPCE of the DSC by NIR sintering at 685 $^{o}$C can be seen at the wavelength between 600-700 nm suggesting marginally better performance in this region. The IPCE is controlled by light harvesting efficiency and electron injection efficiency as well as electron collection efficiency. The detailed investigation of dye loading of the film, the $TiO_2$ particles size and degree of sinter as well as the kinetics of electron transport and electron transfer in the $TiO_2$ film of the DSC will clarify the contribution of each part to the IPCE spectrum of the cell. This is the subject of future work to be published elsewhere.

It is often the contention that the heating step causes sintering of the $TiO_2$ particles and that this improves efficiency. Whilst this is possible in conventional heating for 30 minutes, in this ultra-fast heat treatment using NIR it seems more unlikely. Perhaps more likely is extremely efficient binder removal given that the sample is heated from the metal surface up and binder will be driven out from below. Further work is in progress to examine the NIR heated films to evaluate possible sintering and also to examine the effects of NIR heat treatment on binder free pastes.

## 4. Conclusions

The data presented in this short paper has shown that NIR lamps can be used to rapidly heat metal substrates (Ti in this case) onto which $TiO_2$ pastes have been applied by doctor blading. The resulting DSCs have similar efficiencies to those produced by thermal treatment for 1800 seconds but NIR allows production within a time frame of as little as 12.5 seconds. The NIR heat treatment is already a technology that is applicable to roll to roll paint coating of metals and as such there is a potential for rapid technology transfer for the coil coating industry. The NIR heating method is so rapid that the films produced are more insensitive to peaks in temperature with a wide processing window of between 500 and 800 ºC. NIR seems to be very effective in binder removal as it heats the substrate directly and this appears to drive out organics from the film preventing them becoming trapped as can be the case with conventional ovens. Whilst this method is not appropriate to glass cells, NIR appears to be an extremely promising technology for the ultra-fast binder removal from $TiO_2$ pastes applied to metal surfaces. Further work is underway to evaluate the processing conditions required for stainless steel and construction steel materials which are a more cost effective support than metallic titanium.

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## Figure Legends

**Figure 1:** Typical heating profiles for NIR (solid black line) and convection cured (dashed grey line) samples shown for the first 200 seconds.

**Figure 2:** Comparison of the energy conversion efficiency of the DSCs (active area 1.0 cm$^2$) on 1 mm thick Ti coupons sintered for different times at 500 $^o$C and by near infra red fast sintering (12.5 s).

**Figure 3:** Comparison of the energy conversion efficiencies for the DSCs (active area 1.0 cm$^2$) on 1mm thick coupons sintered at different temperatures for 30 mins by conventional method and sintered for 12.5 s by near infrared fast sintering.

**Figure 4:** Incident photon-to-electron conversion efficiency (IPCE) for the DSCs on 1 mm Ti coupons sintered by a conventional method (500 $^o$C, 30 mins) and by near infrared fast sintering (12.5 s) at different temperatures.

**Table 1:** Comparative data between DSCs prepared on 1 mm Ti substrates using Solaronix Ti-D paste sintered using near infra red and conventional ovens.

| | **PMT (°C)** | **Time (s)** | **Efficiency (%)** | **Voc (V)** | **Isc (mA)** | **FF** |
|---|---|---|---|---|---|---|
| **NIR 1** | 545 | 12.5 | 2.9 | 0.76 | 6.2 | 0.61 |
| **NIR 2** | 685 | 12.5 | 2.8 | 0.77 | 6.6 | 0.55 |
| **NIR 3** | 817 | 12.5 | 2.5 | 0.77 | 5.4 | 0.61 |
| **NIR 4** | 845 | 12.5 | 2.3 | 0.76 | 5.5 | 0.54 |
| **NIR 5** | 880 | 12.5 | 1.9 | 0.79 | 4.5 | 0.53 |
| **Convection 1** | 500* | 1800 | 2.9 | 0.78 | 5.7 | 0.64 |
| **Convection 2** | 500* | 900 | 2.6 | 0.79 | 5.8 | 0.58 |
| **Convection 3** | 500* | 60 | 0.1 | 0.43 | 0.02 | 0.57 |
| **Convection 4** | 600* | 1800 | 2.6 | 0.84 | 4.8 | 0.65 |
| **Convection 5** | 800* | 1800 | 0.2 | 0.78 | 0.48 | 0.45 |

** conventional oven setting*

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