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# Estimating the temperature of the active layer of dye sensitised solar cells by using a "second-order lumped parameter mathematical model"

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ABSTRACT

This study presents a method for estimating the temperature reached by the active layer of dye sensitised solar cells (DSSC) by applying a mathematical model based on a second-order lumped parameter model which takes into account the thermal resistance and heat storage capacities of the different layers of the DSSC. To obtain the input necessary for the application of the mathematical model, an instrumentation system was developed capable of continuously recording the temperature of the external surfaces of both the photoelectrode and the counter-electrode of the DSSC when the sample is irradiated by a light source at 1000 W/m$^2$. The results obtained when the mathematical model is applied show that the lowest root-mean-square error value is obtained for a DSSC absorptivity of 90%. These conditions lead to overheating with regard to the room temperature of 36 K, results which are in agreement with others reported in the literature involving different methods to the one in this article. Also, the methodology proposed can be used for estimating the temperature reached for others photovoltaic devices based on semiconductor thin film.



## 1. Introduction

Under normal working conditions, the temperature reached by solar cells, usually referred to as the Normal Operating Cell Temperature (NOCT), is approximately 45–50 °C (Raga and Fabregat-Santiago, 2013). The efficiency of silicon solar cells decreases by about 10% with regard to the nominal figure, whereas dye sensitised solar cells (DSSCs) have a maximum energy conversion at temperatures close to the NOCT, decreasing when this temperature is exceeded (Raga and Fabregat-Santiago, 2013). This behaviour leads to changes in their electrical parameters, such as the open-circuit potential ($V_{OC}$) and the short-circuit current density ($J_{sc}$). In the case of silicon (monocrystalline or amorphous) solar cells, $V_{OC}$ decreases and $J_{sc}$ increases with temperature (Gallardo et al., 2012; Kondo et al., 1997; Wenham et al., 1994). In the case of DSSCs, the higher $J_{sc}$ and the lower $V_{OC}$ (Gallardo et al., 2012; Odonnell and Chen, 1991; Usami et al., 2009; Wenham et al., 1994) values at higher temperatures lead to a decrease in their efficiency. However, this kind of measurements is performed without clearly establishing the temperature of the active layer of the DSSCs. Moreover, another effect of the increase in temperature of the semiconductor material is a decrease in the band gap value (Berginc et al., 2007; Odonnell and Chen, 1991). For this reason, estimating the temperature reached by the active layer of the solar cell is an interesting topic in this research field.

Increases in temperature may be caused by two factors: heating by the incident light source (sunlight) and photon energy levels in excess of the band gap of the semiconductor material used to make the solar cells. In the first case, the radiation responsible for this heating is the infra-red region of the solar spectrum, while in the second, the energy exceeding the band gap is transformed into heat energy, which increases the temperature of the system. Thus, the direct estimation of the temperature under normal working conditions is practically impossible due to the dimensions and configuration of DSSCs, traditional instruments being incapable of making direct measurements. As a result, it is necessary to develop alternative methods that, while not performing a direct measurement of the temperature of the active layer, are able to provide an accurate estimation.

Also, it is necessary to understand the stability mechanism of the temperature effect on the DSSC performance. The stability of the DSSC is affected by external (light soaking and temperature) and internal (thermal stability of dye, leakage of electrolyte,

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sealing, etc.) factors, being the internal ones influenced by the external ones. As reported Lund et al. (2014), to study the stability of the cell, typical methods used are: stand-alone thermal stress at different temperatures (from negative temperature values to 85 °C approx.), artificial light intensity soaking test at 1000 W/m$^2$ (1 sun) or a combination of both methodologies. In turn, in the range from −20 °C to room temperature (Xue et al., 2012), the DSSCs suffer a decrease of efficiency due mainly to a decrease in $J_{sc}$ caused by the decrease of light harvesting of the photoelectrode efficiency. There is an increase of $V_{OC}$ and $FF$ that suppressed the decrease of $J_{sc}$. Lund et al. (2014) showed the study of the performance of a DSSC under a stress test of 1000 h at 40 °C under constant irradiation power of 1 sun. They found that the changes in $J$–$V$ parameters during the test were due to changes in the electrochemical performance of the cell. These changes are the increase of the series resistance of the DSSC and charge transfer resistance at the counter electrode. Variations in the resistance of the photoelectrode produced that $J_{sc}$ and $V_{OC}$ were slightly decreased. Also, Bari et al. (2011) kept DSSC samples inside a climatic chamber in the dark at different constant temperature from 60 °C to 85 °C, and measured the electrical parameters periodically. They observed a negligible variation of the electrical parameters compared with the values showed by a reference cell. They found a decrease in $V_{OC}$ and $J_{sc}$, being the last one stronger. This fact produced a decrease in the maximum output power of the cell. Also at 60 °C and only 10 h of storage, an increase of efficiency was found, due to annealing induced by temperature which can improve the overall performance of the DSSC.

Thus, this study presents an estimation of the temperature reached by the active layer of titanium dioxide, because it is an interesting parameter affecting to the DSSC performance. This involved developing a mathematical model that simulates the thermal behaviour under illumination of the active layer of solar cells under working conditions that are as similar as possible to reality using data obtained with the authors' own instrument system. This system has been developed and adapted from a previous system designed by the authors (Gallardo et al., 2012) which is able to measure and record the external surface temperature data from the electrode and counter-electrode of a complete, operating DSSC, as well as the air temperature at two points outside of the irradiation zone.

The mathematical model used to estimate the temperature of the active layer of the solar cell is based on a lumped parameter method for modelling the thermal response of the cell, taking into account the thermal resistance and the energy storage capacity of each layer of material that it is composed of Lorenz and Masy (1982) first developed a first-order lumped parameter model for the thermal response of building materials consisting of two thermal resistances and one capacitance. Later, Gouda et al. (2002) showed that an increase in accuracy is possible with a second-order model composed of three resistances and two capacitances. The thermal resistances and capacitances are the characteristic parameters of the model and need to be adjusted by their comparison with a reference. In this study, the adjustment of the characteristic parameters of a second-order lumped parameter model was performed by comparing the results obtained by this model with the experimental data available. The boundary conditions or input data for the model were the experimental measures of air temperature and radiant temperature of the surroundings, as well as the incident radiation. The results or output data of the model are the surface temperatures on both sides of the solar cell. In this adjustment, an optimization method was applied that is similar to the one proposed by Underwood (2014). The method is based on a multiple objective function search algorithm to minimise the root-mean-square error between the surface temperatures obtained by the model and experimentally. Finally, after adjusting the characteristic parameters of the model, the temperature of the active layer was calculated.

## 2. Experimental

### 2.1. Preparation of the DSSCs

For the experimental tests, two DSSCs were used that were assembled in our laboratory (Navas et al., 2012) and which were named C1 and C2. Both are assembled following the same methodology and using the same semiconductor suspension. The procedure is homemade and therefore small differences in the performance of the cells can be found. This kind of solar cell consists of two assembled parts: an electrode and a counter-electrode. The assembly of the DSSC can be resumed in the following steps:

1. A semiconductor suspension was prepared using nanoparticulated $TiO_2$ (Degussa P25), added to a mixture of ethanol and an aqueous solution of $HNO_3$ (pH = 3–4). Polyethylene glycol (MW: 6000, Panreac) was used as a surfactant. These components were mixed in a planetary ball mill for 2 h.
2. A thin film of the paste obtained was deposited onto the electrode using the doctor blade method. FTO coated transparent glass plates (2 × 1.5 cm$^2$, thickness of 2.2 mm, sheet resistance ∼ 15 Ω square$^{-1}$), supplied by Pilkington, were used as the electrode. The deposited films were dried in an ethanol atmosphere for 1 h and then sintered at 450 °C for 1 h. The thickness of the deposited films was about 10 ± 0.5 μm.
3. The sintered films deposited onto the electrode were immersed in an ethanolic solution of dye Ru535 (formerly named as N3, $C_{26}H_{20}O_{10}N_6S_2Ru$, supplied by Solaronix).
4. A thin film of Pt was deposited onto the glass used as the counter-electrode. The Pt film was obtained by decomposing a small amount of a 0.02 M solution of $H_2PtCl_6{\cdot}xH_2O$ (purity ∼ 38% Pt, Sigma Aldrich) in 2-propanol (purity 99.5%, Panreac) at 380 °C.
5. The electrolyte used was a mixture of 0.5 M 4-tert-butylpyridine (TBP, purity 99%, Sigma Aldrich), 0.1 M LiI (purity 99.9%, Sigma Aldrich) and 0.05 M $I_2$ (purity 99.8%, Panreac) in 3-methoxypropionitrile (purity 98%, Fluka).
6. Finally, the electrode and the counter-electrode were assembled using a surlyn film (thickness: 25 μm).

As an example, Fig. 1 shows an image of one of the two samples used in the study.

### 2.2. Characterization of the DSSCs

To determine the properties of the assembled cell, a photovoltaic characterization was carried out making it possible to

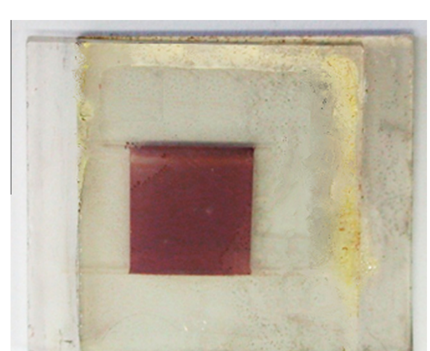

**Fig. 1.** A DSSC used in this study.