Pertanika J. Sci. & Technol. 25 (S): 111 - 118 (2017)

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

# Statistical Optimisation of Process Parameters on the Efficiency of N-$TiO_2$ Dye Sensitised Solar Cell Using Response Surface Methodology (RSM)

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## ABSTRACT

In this study, nitrogen doped titanium dioxide-based dye-sensitised solar cell was successfully fabricated using screen printing technique to discover the optimisation of process parameters for the solar cell efficiency using response surface methodology (RSM). Parameter optimisation has been a major concern in solar cell fabrication. The selected parameters were: nitrogen concentration (15-25 mg of urea), the film thickness (25-60 µm) and dye loading time (12-24 hours), the optimum condition which yields the highest efficiency of 3.5% was at 15 mg nitrogen concentration, 25 µm film thickness and 24-hours dye loading time. Film thickness was found to have a significant influence on efficiency while the loading time exceeding 18 hours has the least significant effect.

*Keywords:* Dye-sensitised, solar cell, nitrogen, screen printing, optimisation

## INTRODUCTION

Energy, fresh water and air are the most important commodities for human existence. Fossil fuels such as petroleum, natural gas, and coal are the most widely used sources of energy for industrial and domestic purposes. The rapid depletion finite reserves and environmental concerns such as greenhouse gas emissions are some of the drawbacks of these highly efficient carbon-based fuels.

ARTICLE INFO

*Article history:*
Received: 24 August 2016
Accepted: 02 December 2016

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ISSN: 0128-7680 

Solar energy is a renewable source of energy that has attracted global attention as a substitute for fossil fuels owing to its numerous advantages of being a naturally infinite resource.

This study attempts to provide a unique design that optimises process parameters in the fabrication of N- doped-based DSSC which yields maximum efficiency for end-use electricity generation. The study also investigated the effects of nitrogen concentration, dye loading time and film thickness in the performance of N-$TiO_2$ –based DSSC using Surface Response Methodology (SRM) for the determination of the best-optimised model.

In order to achieve high conversion efficiency, there must be an efficient collection of nearly all the photogenerated electrons which means that the incident-photon to- current-efficiency should be close to unity under visible light region. This can be realised if the carrier diffusion length ($L_n$) is greater than the film thickness (d) (Grätzel, 2005)

$$L_n = \sqrt{D_e \tau_r}$$

where $D_e$ is the diffusion coefficient and $\tau_r$ is the electron life time. However, the film should be optimaly controlled as each $TiO_2$ particle is a potential electron trap.

Dye loading time needs to be optimised to ensure homogeneity of dye concentration in the $TiO_2$ pores as well as to prevent non-radiative decay of exciton and static quenching resulting from a large aggregation of dye molecules (Hardin, 2010). Nitrogen-doped $TiO_2$ has noble photovoltaic properties, therefore, it has received much attention due to the narrowing of the band gap and shifting of the absorption edge to the visible region of the solar spectrum.

Since its introduction in 1951 by Box and Wilson, RSM has been widely used as a unique statistical tool for engineering system design, optimisation and prediction of system's input-output relationship.

The mathematical model obtained from SRM enables reproducibility of the system optimal working condition by establishing an empirical relationship between variable factors and desired product response (Chowdhury et al., 2012; Khalid, 2012). In the current study, a statistical model has been developed based on varied experimental trails in order to determine the influence of the different process parameters on the overall performance of the fabricated Nitrogen-doped Titanium dioxide (N-$TiO_2$) - based Dye- sensitised Solar Cell (DSSC) device.

A quadratic model based on Central Composite Design (CCD) was developed and with Nitrogen concentration, Dye loading time and Film thickness as variable factors and cell efficiency as a response. The model was further improved using regression analysis and subsequent examination using analysis of variance (ANOVA) to determine its corresponding accuracy.

## MATERIALS AND METHODS

### Materials

Titanium Dioxide ($TiO_2$), Flouring Tin oxide (FTO) coated glass ($7sq^{-1}$), Di-2 Cis-bis (isothiocyanato) bis-bipyridyl-4-4'- dicarboxylato) ruthenium (ii) (N719) dye were all obtained from Sigma-Aldrich Co., (USA). Urea was purchased from R&M Chemicals and electrolyte was obtained from Kyutech Laboratory, Japan.

## Fabrication of DSSC device

The N-$TiO_2$ was prepared by mixing 500 mg of $TiO_2$ with the required amount of Urea as a source of nitrogen (from 15 mg to 25 mg) in a motor and carefully grounded until a homogenous mixture was obtained before it was annealed in a furnace at 500°C for 30 minutes. The fabrication of N-$TiO_2$-based photoanode was achieved using the following procedure, Initially, 500 mg of N-$TiO_2$ composite was mixed with a solution containing10 mL ethanol, 5 mL of distilled water and ethyl cellulose (1 g) in a 200 mL beaker and stirred for 12 hours using a magnetic stirrer to obtain an N-$TiO_2$ paste; subsequently, the paste was coated on an FTO-coated glass substrate by screen printing technique using a mesh with the desired thickness and the obtained film was sintered in a furnace at 450°C for 30 minutes. The resultant photoanode was immersed in an ethanolic solution of 0.2M N719 dye for required duration of between 12 and 24 hours. A complete DSSC device was assembled as follows: a platinum coated FTO glass cathode was placed on the photoanode separated by a polymer-based spacer and electrolyte solution was subsequently introduced into the cell through a pre-drilled hole on the cathode.

The current-voltage measurement was done using a solar simulator which provides AM 1.5 simulated solar radiation, I-V curve of the solar cell device was recorded by applying a bias voltage and simultaneously measuring the corresponding photogenerated current with a Keithly Source Meter (Keithly 2611, USA) under $100mWcm^{-2}$ light intensity.

## Experimental Design

Central composite Design (CCD) full factorial in the design-Expert software version 6.0.6 was used to evaluate three independent variables, namely amount of nitrogen, film thickness and dye loading time on five level points (see Table 1). This produced 20 experimental sets as represented in equation (1) below:

$$\textit{Number of experiment} = 2^k + 2k + 6 \quad (1)$$

Where k is the number of independent variables.

Table 1
*Independent variable coded levels*

| | | Level | | |
|---|---|---|---|---|
| Factor | Name | Centre | Low Level | High Level |
| $X_1$ | | 20 | 15 | 25 |
| $X_2$ | Film Thickness (µm) | 42.5 | 25 | 60 |
| $X_3$ | Dye loading time (h) | 18 | 12 | 24 |

The empirical model for the efficiency of N-$TiO_2$-based solar cell was developed by performing the experimental sets obtained from a complete design matrix as shown in Table 2.

Table 2
*VSM design matrix and experimental results*

| Run | $X_1$ | $X_2$ | $X_3$ | Y |
|---|---|---|---|---|
| 1 | 25 | 60 | 24 | 2.7 |
| 2 | 20 | 42.5 | 18 | 3.1 |
| 3 | 15 | 25 | 24 | 3.5 |
| 4 | 15 | 25 | 12 | 3.3 |
| 5 | 20 | 42.5 | 18 | 3.1 |
| 6 | 20 | 42.5 | 18 | 3.1 |
| 7 | 15 | 60 | 12 | 2.8 |
| 8 | 25 | 25 | 12 | 3.4 |
| 9 | 15 | 42.5 | 18 | 2.5 |
| 10 | 20 | 42.5 | 42 | 3 |
| 11 | 25 | 25 | 24 | 3.1 |
| 12 | 20 | 42.5 | 18 | 3 |
| 13 | 20 | 42.5 | 18 | 3 |
| 14 | 20 | 42.5 | 12 | 2.9 |
| 15 | 20 | 42.5 | 18 | 3.1 |
| 16 | 20 | 60 | 18 | 2.7 |
| 17 | 20 | 25 | 18 | 3.4 |
| 18 | 15 | 60 | 24 | 2.9 |
| 19 | 40 | 42.5 | 18 | 2 |
| 20 | 25 | 60 | 12 | 2.6 |

The relationship between the variable factors $X_1$, $X_2$, $X_3$ and the response Y is expressed as follows.

$$Y = F(X_1, X_2, X_3) \tag{2}$$

Where F represents the response function.

In this case, a polynomial model based on Taylor's expansion series (Khuri & Mukhopadhyay, 2010) was chosen and represented as follows:

$$Y = bo\sum(bixi) + \sum_1^k bijxixj\ (i, j = 1, 2, \ldots\ldots, k) + e \tag{3}$$

Putting the predicted solar cell efficiency Y and the variable $X_1$, $X_2$, $X^3$ representing the amount of nitrogen, film thickness and dye loading time respectively, equation 3 is expressed as:

$$f(x) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 \quad (4)$$

## RESULTS AND DISCUSSION

### Development of Regression Model

At the end of the experiment, a carefully selected regression model based on the highest order polynomial was developed for the DSSC efficiency (Y) as dependent variable while the independent variables $X_1$, $X_2$, $X_3$ represent amount of nitrogen (weight of urea), film thickness and dye loading time respectively. The empirical model is represented in equation (5) as below:

$$Y = 3.05 - 0.067X_1 - 0.3X_2 + 0.027X_3 - 0.05X_1^2 + 0.04X_2^2 - 0.009X_3^2 - 0.013X_1X_2 - 0.063X_1X_3 + 0.037X_2X_3 \quad (5)$$

the linear terms $X_1$, $X_2$, and $X_3$ represent the effect of the individual variable on the efficiency while the multiple variable terms show the interaction of variable on the response and the quadratic effect was represented by the squares of the terms.

The predicted versus actual efficiency plot is shown in Figure 1, from the plot, the predicted value was observed to be closer to the experimental value of the solar cell efficiency, the coefficient of determination ($R^2$) is calculated to be equal to 0.9680 which shows a near unity correlation between the predicted and actual cell efficiency which is an indication of the effectiveness of the developed model.

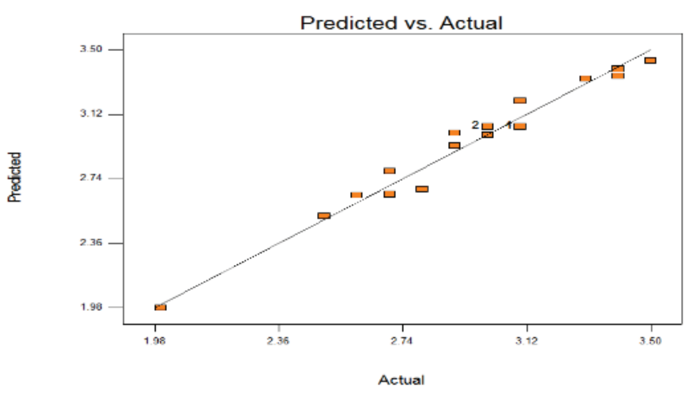
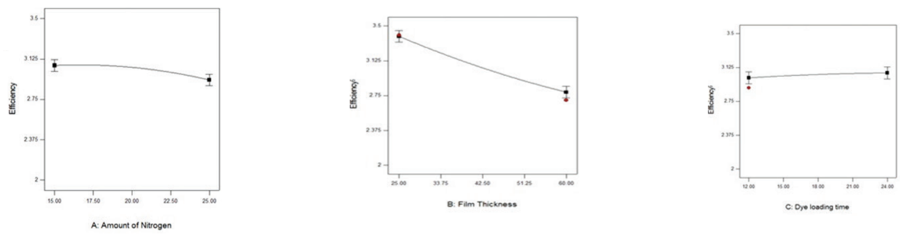



*Figure 1.* Plot of predicted against actual values




(a) (b) (c)

*Figure 2.* Response surface plot for efficiency dependence on (a) amount of nitrogen, (b) Film thickness and (c) dye loading time

Figure 2(a), (b) and (c) shows the effect of the amount of nitrogen, film thickness and dye loading time on the overall efficiency of the solar cell. Figure 2(a) shows the dependence of the cell performance on the film thickness, efficiency decreased 3.2% to 2.8% as the thickness increases from 25 microns to 60 microns which is attributable to an increase in recombination sites along the electron path length.

The optimal nitrogen concentration was found to be 15 and 17 mL and there was no strong dependence of cell efficiency with an increase in nitrogen concentration (Guo et al., 2011) as the efficiency decreases by only 0.1% as the nitrogen concentration was increased from 15 to 25 mL as shown in Figure 2(b). Additionally, there was no strong dependence of efficiency on the increase in dye loading from 12 hours to 24 hours.

Table 3
*Summary of statistical parameters for the ANOVA regression model*

| Model summery | |
|---|---|
| Source | Quadratic |
| Standard deviation | 0.086 |
| $R^2$ | 0.9680 |
| Adjusted $R^2$ | 0.9392 |
| Sum of Squares | 1.12 |
| Degrees of freedom | 3 |
| Mean square | 0.37 |
| F value | 50.25 |

## Current vs. Voltage curve

The J-V curves of the solar cells prepared under different conditions are shown in Figure 3 (A= highest thickness, B= lowest thickness and C= highest dye loading time) and from the plot it is clear that sample B and sample C have the same open circuit voltage - the difference between the Lowes Unoccupied Molecular Orbital (LUMO) and the redox potential of the electrolyte (Roy et al., 2010). However, the reduction in film thickness which is also a reduction of carrier

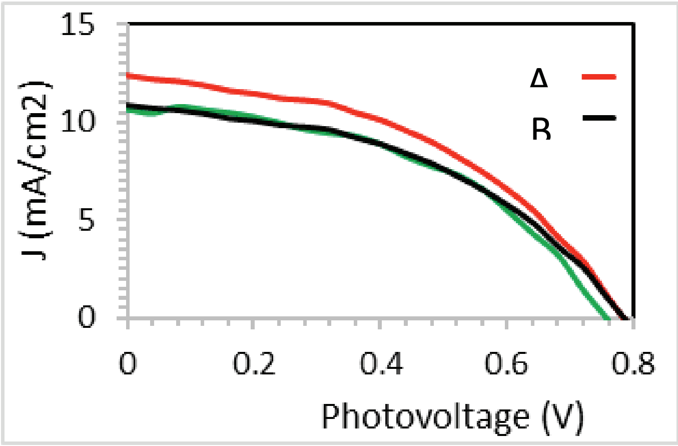



*Figure 3.* Current- Voltage relationship of DSSC under different process condition

Table 4
*Analysis of Variance (ANOVA) and lack of fit test response of the developed quadratic model*

| Source of Variance | Sum of Squares | Degree of freedom | Mean Squares | F Values | Prob > F |
|---|---|---|---|---|---|
| Model | 2.25 | 9 | 0.25 | 33.6 | < 0.0001 |
| $X_1$ | 0.18 | 1 | 0.18 | 24.46 | 0.0006 |
| $X_2$ | 0.9 | 1 | 0.9 | 120.78 | < 0.0001 |
| $X_3$ | 0.00711 | 1 | 0.00711 | 0.95 | 0.3517 |
| $X_1^2$ | 0.98 | 1 | 0.98 | 131.89 | < 0.0001 |
| $X_2^2$ | 0.007217 | 1 | 0.007217 | 0.97 | 0.3483 |
| $X_3^2$ | 0.0088 | 1 | 0.0088 | 1.18 | 0.3027 |
| $X_1X_2$ | 0.00125 | 1 | 0.00125 | 0.17 | 0.6908 |
| $X_1X_3$ | 0.031 | 1 | 0.031 | 4.19 | 0.0678 |
| $X_2X_3$ | 0.011 | 1 | 0.011 | 1.51 | 0.2473 |
| Residual | 0.075 | 10 | 0.007452 | | |
| Lack of Fit | 0.061 | 5 | 0.012 | 4.59 | 0.06 |
| Pure Error | 0.013 | 5 | 0.002667 | | |
| Total | 2.33 | 19 | | | |

diffusion length, leads to an increase of current density from 10.8mA $cm^2$ in sample B to 12.4 mA $cm^2$ in sample C due to the low electron-hole recombination. The lower efficiency of the sample is attributed to the high film thickness.

## CONCLUSION

A statistical model was developed using response surface methodology through sequential experimental settings to determine the ideal number of different variables influencing the efficiency of N-$TiO_2$ based DSSC, the optimum condition was at 15mg nitrogen concentration, 25 µm photoanode film thickness and 12 hour dye loading time. The model was useful in ensuring efficiency by restricting the process variable for efficient output in industrial applications.

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