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A theoretical study on third generation photovoltaic technology: dye-sensitized solar cells

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Abstract. A numerical model has been developed to investigate the performance of dye-sensitized solar cells (DSSCs) under extreme weather conditions. The main purpose of this work is to simulate the temperature influence on the overall efficiency of DSSCs with a consideration of the voltage loss at titanium dioxide (TiO_2)/ transparent conductive oxide (TCO) interface. Appropriate simulation input parameters are chosen to reflect the extreme winter weather conditions of Fargo, North Dakota. It is found that at the temperature 250 K (ca. -20 °C), the maximum power output is about 23 W/m^2 which is about 50% lower than the value at 340 K (ca. 70 °C). The study reveals that low temperature conditions have serious detrimental effects on the DSSCs' performance.

Key words

Dye-sensitized solar cells, temperature dependence, Schottky barrier model, J-V characteristics

1. Introduction

Ever-increasing oil price caused by the fossil fuel depletion becomes the driving force to develop the renewable energy technologies. Given the fact that solar radiation on the earth surface amounts to 3.8 million EJ per year, which is approximately ten thousand times more than current energy needs [1,2], it is desirable to tap in the solar radiation in the form of light-electrical conversion. In order to achieve this goal, various photovoltaic devices like organic, inorganic, hybrid solar cells were fabricated in succession. In spite of high conversion rate of silicon-based solar cells, the high module cost and complicated production process restrict their application to astronautic and aeronautic technology. For domestic and other commercial applications, research has been focused on organic solar cells for their inherent low module cost and easy fabrication. In addition, organic solar cells achieve their lightweight and flexibility advantage over conventional silicon-based crystalline solar cells.

In 1991, Oregan and Gratzel built the first dye-sensitized nanocrystalline solar cells whose photoelectric energy conversion rate reached 7.1% and incident photon to current conversion efficiency was about 80% [3]. This seminal report has stimulated great research interest to improve the efficiency of dye-sensitized solar cells, and the state-of-the-art efficiency is over 10% [4], a level deemed as necessary for commercial use by leading dye-sensitized solar cell providers [5].

On the annual basis, North Dakota receives about 60 percent of total possible sunshine hours [6] (i.e., sufficient for the application of photovoltaic device). However, the large temperature variations between summer and winter conditions have long presented a challenge in design and implementation of dye-sensitized solar cells. The objective of this research is to investigate the influence of ambient temperature variation on the performance of dye-sensitized solar cells. In this paper, a theoretical model integrating a thermionic emission model into a diffusion model is developed to evaluate the device performance under extreme weather conditions. The results of the theoretical simulation are compared with experimental data. The details of the theoretical modeling and parametric analysis are discussed as follows.

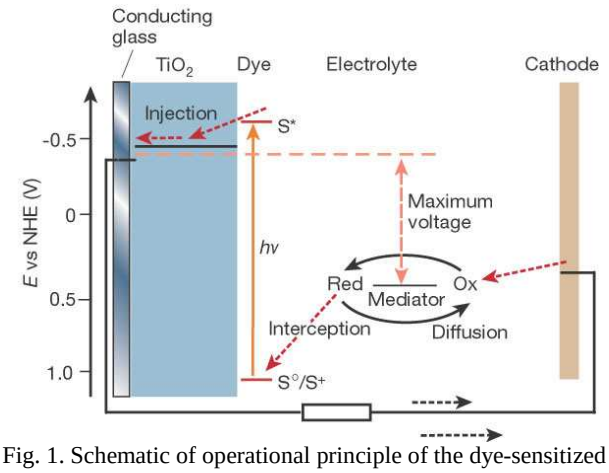


Fig. 1. Schematic of operational principle of the dye-sensitized solar cell. [7]

2. Mathematical Modeling

In theory, the maximum voltage generated in DSSCs is determined by the difference between the quasi-Fermi level of the TiO_2 and the redox potential of the electrolyte, about 0.7 V, e.g. the open-circuit voltage under solar illumination conditions. However, the voltage loss at the TiO_2/TCO interface should be taken into account in practical cases where such loss is not negligible in magnitude. Therefore, the reference photovoltage can be calculated as,

$$V = V_0 - V_1 \tag{1}$$

where V_0 is the potential difference between quasi-Fermi level of TiO_2 (E_F) and the redox potential of electrolyte (E_{redox}), and V_1 is the voltage loss at the TiO_2/TCO interface.

Under steady-state conditions of irradiated dye-sensitized solar cells, transport of the photoinjected electrons in TiO_2 mesoporous films can be described by the diffusion model [8]. In this simple diffusion model, two assumptions were proposed: (i). electrons are transported via diffusion. (ii). diffusion length is constant; i.e. recombination process is assumed to be of first order. Hence, the governing equation can be expressed as,

$$Dn''(x) - \frac{n(x) - n_0}{\tau} + \Phi\alpha e^{-\alpha x} = 0 \tag{2}$$

where D is the diffusion constant of the electrons in the film, $n(x)$ the excess electron density, n_0 the electron density in the dark ($n_0 = 10^{16}\ cm^{-3}$), τ the electron lifetime, Φ the incident light intensity, and α the reciprocal absorption length.

Under short-circuit conditions, the electrons at the TCO/TiO_2 interface are efficiently drawn off as a photocurrent, and electrons reaching the outermost part of the film $x = d$ will be reflected and will diffuse back into the inner layers of the film (i.e. negligible current flow at $x = d$). The boundary conditions for substrate/electrode illumination are:

$$n(0) = n_0 \tag{3}$$

and

$$\left(\frac{dn}{dx}\right)_{x=d} = 0 \tag{4}$$

The analytical solution of the short-circuit current density J_{sc} can be expressed:

$$J_{sc} = \frac{\left[-L\alpha\cosh\left(\frac{d}{L}\right) + \sinh\left(\frac{d}{L}\right) - L\alpha e^{-d\alpha}\right] L\alpha q\Phi}{(1 - L^2\alpha^2)\cosh\left(\frac{d}{L}\right)} \tag{5}$$

where q is the elementary charge of electron equal to $1.6 \times 10^{-19}\ C$; L is the electron diffusion length equal to $\sqrt{D\tau}$; and d is the thin film thickness.

When dye-sensitized solar cells operate under illumination, electron density in the conduction band of TiO_2 is increased to n as one boundary condition and another boundary holds as Eq. (4).

$$n(0) = n \tag{6}$$

Solving the diffusion equation with these boundary conditions gives the photocurrent as,

$$J = J_{sc} - \frac{qDn_0}{L}\tanh\left(\frac{d}{L}\right)\left(e^{\frac{qV}{kTm}} - 1\right) \tag{7}$$

Rearranging Eq. (7) yields the expression for the voltage as a function of the photocurrent, i.e. the J-V characteristics.

$$V_0 = \frac{kTm}{q} ln\left(\frac{L(J_{sc} - J)}{qDn_0\tanh\left(\frac{d}{L}\right)} + 1\right) \tag{8}$$

where k is the Boltzmann constant equal to $1.38 \times 10^{-23}\ m^2 kg s^{-2} K^{-1}$, and m is the ideality factor equal to 4.5.

Since TCO substrate is a high doped semiconductor or metal, their contact with TiO_2 can be simulated with Schottky barrier model [9]:

$$J = A^* T^2 \exp\left(-\frac{\Phi_b}{kT}\right)\left(\exp\left(\frac{qV_1}{kT}\right) - 1\right) \tag{9}$$

and

$$A^* = \frac{4\pi m^* q k^2}{h^3} \tag{10}$$

where h is the Planck constant equal to $6.626 \times 10^{-34}\ m^2 kg\ s^{-1}$, m^* is effective electron mass equal to 5.6 times the electron mass m_e [10], A^* is the Richardson constant of TiO_2 equal to $6.71 \times 10^6\ Am^{-2}K^{-2}$, and Φ_b is the Schottky barrier height. The voltage loss can be expressed as a function of photocurrent.

$$V_1 = \frac{kT}{q}\ln\left(1 + \frac{J}{A^* T^2 \exp\left(-\frac{\Phi_b}{kT}\right)}\right) \tag{11}$$

The J-V relationship is obtained by substituting Eq. (8) and Eq. (11) into Eq. (1).

$$V = \frac{kTm}{q} ln\left(\frac{L(J_{sc} - J)}{qDn_0\tanh\left(\frac{d}{L}\right)} + 1\right) - \frac{kT}{q}\ln\left(1 + \frac{J}{A^* T^2 \exp\left(-\frac{\Phi_b}{kT}\right)}\right) \tag{12}$$

Performance parameters such as cell fill factor (FF) and cell efficiency (η) were calculated using the following equations:

$$FF = \frac{V_{max} J_{max}}{V_{oc} J_{sc}} \tag{13}$$

$$P_{max} = V_{max} \times J_{max} \tag{14}$$

where J_{sc} is the short-circuit current ($mA\ cm^{-2}$), V_{oc} the open-circuit voltage (V), and P_{max} the maximum power output. J_{max} and V_{max} are corresponding to current and voltage values where the maximum power output is reached in J-V curve.

Table I. Primary simulation parameters used in this work

Parameter	Value	Ref.
Light intensity, $\Phi\ (cm^{-2}s^{-1})$	1.0×10^{17}	
Light absorption coefficient, $\alpha\ (cm^{-1})$	5000	[11]
Electron lifetime, $\tau\ (ms)$	10	[12]
Ideality factor, m	4.5	[11]
Electron diffusion coefficient $D\ (cm^2s^{-1})$	2.3×10^{-5}	[11]
Richardson constant $A^*\ (Am^{-2}K^{-2})$	6.71×10^{6}	[12]
Electron concentration in dark condition $n_0\ (cm^{-3})$	10^{16}	[13,14]

3. Results and Discussion

In dye-sensitized solar cells, the back reaction of electron from the conducting glass substrate to triiodide ions is an important loss mechanism especially at maximum power point and open circuit. Under an open circuit condition, the voltage loss at TCO/TiO_2 is determined by temperature, Schottky barrier height, and recombination current. The recombination current varied in a wide range depending on the material composition of TCO substrates and the existence of a blocking layer. In this study, the recombination current density of value $J = 0.0001\ Am^{-2}$ was chosen [15]. At TiO_2/TCO interface, the voltage loss variation against temperature and Schottky barrier height is plotted in Fig. 2. It is found that lowering temperature results in an increase of voltage loss, and when Φ_b value is beyond c.a. $0.6\ eV$ a significant voltage loss occurs. Figure 2 shows (red line) that there exists critical threshold value. When the Schottky barrier height is below this critical value, the temperature effect on voltage loss is inappreciable and the voltage loss is negligible. This conclusion serves as a useful guide for TCO materials selection indicating lower Φ_b is more suitable for obtaining higher open circuit voltage. These simulation results are consistent with the experimental studies, in which fluorine doped tin oxide ($\phi_b < 0.6\ eV$) was used as the TCO material [9].

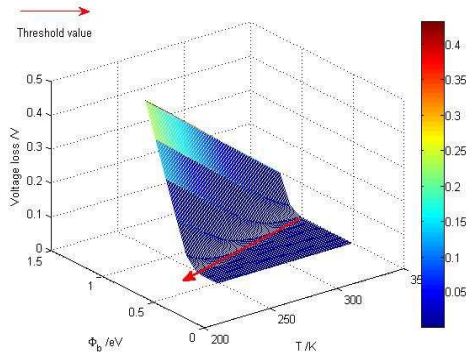


Fig.2. Variation of voltage loss at TiO_2/TCO contact with temperature and Schottky barrier.

Assuming $\phi_b = 0.6\ eV$, the open-circuit voltage (V_{oc}), maximum power output (P_{max}), and overall conversion efficiency (η) are calculated and listed in Table. II. The effect of temperature on DSSC J-V characteristics are illustrated in Fig. 3. It could be seen that, when temperature increases, the thermal energy also increases to excite more electrons from the valence band to the conduction band of TiO_2. This alleviates interfacial voltage losses resulting in a better device performance.

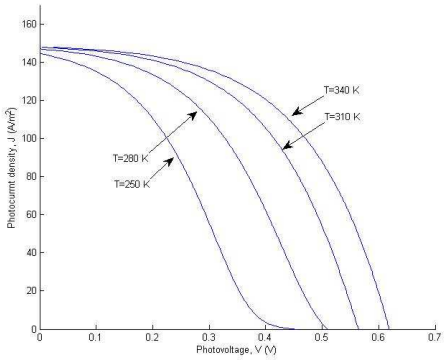


Fig. 3. Effect of operating temperature on DSSC J-V characteristics.

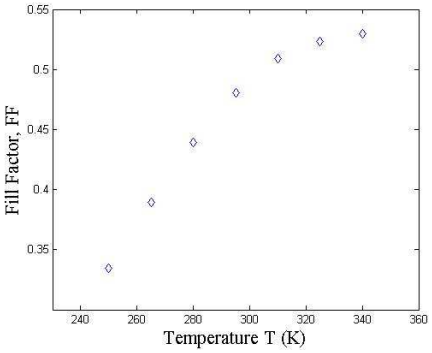
Table II. Effect of the operating temperature on the performance of DSSCs

T	V_{oc}	J_{sc}	FF	P_{max}	η
K	V	mA cm^{-2}		W/m^2	%
250	0.45	14.83	0.33	22.57	2.26
280	0.51	14.83	0.44	33.21	3.32
310	0.56	14.83	0.51	42.57	4.26
340	0.62	14.83	0.53	48.61	4.86

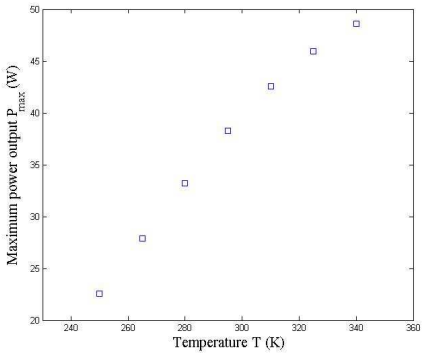
The effect of operating temperature on DSSC fill factor and maximum power output is plotted in Fig. 4. It is found that both the fill factor and maximum power output increases simultaneously as the temperature increases. When the temperature is over 310 K, the fill factor tends to be steady. This phenomenon indicates that at high temperatures, the thermal energy influence on the DSSCs' performance is attenuated.

In this work, the extended cold weather has proven to be detrimental on cells performance as well as on their service life because of the fact that electrolytes freeze rapidly, causing the system to fail—sometimes as even during sunny days. To maintain higher working temperature, two ways are suggested to efficiently utilize solar energy:

i. to design and fabricate an insulated cell-housing that is compatible with the regional environmental conditions.
ii. to design and fabricate a mounting arm that could allow the panel to be inclined at an optimum tilt angle to maximize the incoming solar radiation.



(a)



(b)

Fig. 4. Effect of operating temperature on DSSC fill factor (a) and maximum power output (b).

4. Comparison with experimental data

As it is shown in Fig. 5, the predicted results using the model developed in this study agrees well with the experimental data obtained by M. Berginc et al [16], especially when I_2 concentration is lower than 0.09 M. Also, the results clearly reflect that low operating temperature have an adverse effect on the performance of DSSCs.

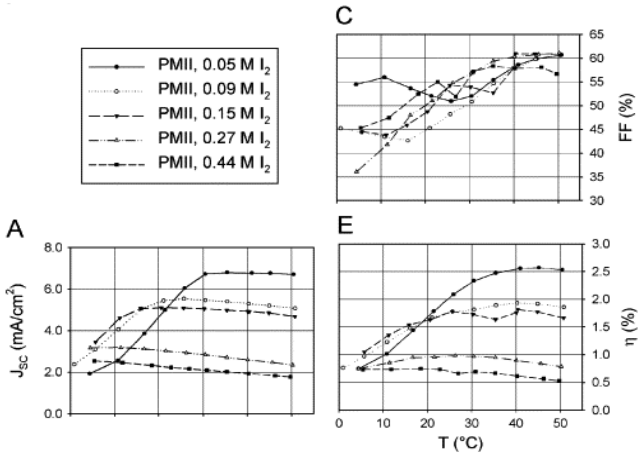


Fig. 5. Effect of operating temperature on DSSC J_{sc} (A), fill factor (C) and efficiency (E). [16]

5. Conclusion

A simple model of a DSSC is derived which could predict the effect of temperature on performance factors such as voltage loss at TCO/TiO_2 interface and the J-V characteristics. The simulated results are in a good agreement with experimental data. The present study has shown that at low temperatures like -20 °C, the maximum power output drops to a value about half lower than that it could have attained at 70 °C, indicating the significance of operating temperature on the DSSCs' performance particularly in extreme weather condition.

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