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Performance and Stability of Dye-sensitized Solar Cells with Quasi-solid State Electrolytes base on N-methyl-quinoline Iodide

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Keywords: Polymer electrolyte, dye-sensitized solar cells (DSSCs), quasi-solid electrolytes

Abstract. We have fabricated dye-sensitized solar cells (DSSCs) with quasi-solid state electrolytes base on N-methyl-quinoline iodide and studied the performance and stability of the cells at different temperatures. The quasi-solid state electrolytes were prepared from polymer gel electrolyte based on N-methyl-quinoline iodide and iodine. Pure-anatase nanocrystalline TiO_2 films with absorption of standard N719 dye were employed as working electrodes. The maximum efficiency of the solar cells was 4.5 % under incident light of 100 mW/cm^2. The cells also showed excellent stability for several months under irradiation of sunlight. The ionic conductivity of the electrolytes and the performance of the cells at different temperatures were presented.

Introduction

The need of renewable energy with environmentally benign sources of production is a driving force for the search of energy. Due to dramatically growing demand and global warming, the harnessing of solar energy by converting sunlight to electricity using the photovoltaic properties of suitable semiconductor materials is one of the most elegant methods. Fortunately, the earth gains gigantic amount of energy from the sun about 3×10^{24} J a year or 10,000 times more than that world population currently uses. In other words, if solar cells with an efficiency of 10 % cover 0.1 % of the earth's surface, they will produce electricity enough for our present needs [1].

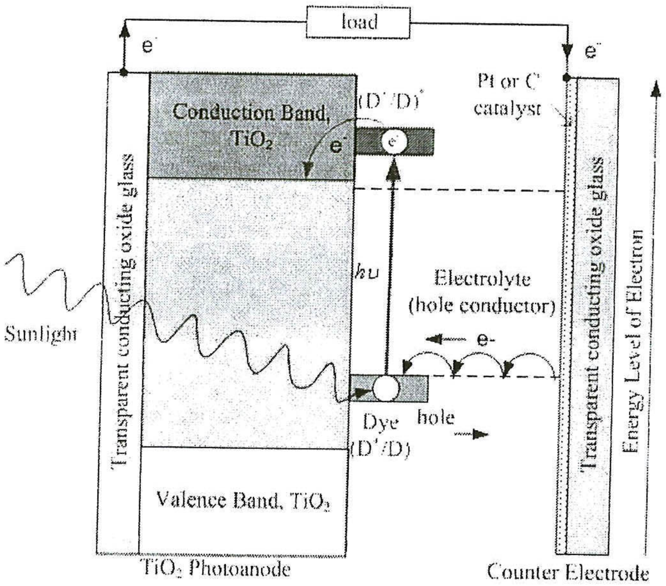

Figure1. Schematic energy diagram and electron-hole transfer processes of DSSCs.

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DSSCs are the photovoltaic devices of choice because of their high efficiency, low production cost, and environmentally friendly TiO_2 semiconductor materials. In general, DSSCs consist of three main components: a dye-covered nanocrystalline-TiO_2 layer on a transparent conducting oxide glass (TCO) substrate serving as working electrode, an iodide/triodide redox couple in liquid electrolyte, and a platinum-coated TCO glass substrate serving as a counter electrode. A simple energy diagram of DSSCs with electron-hole transfer process is shown in Fig.1. The use of volatile liquid electrolyte causes serious problems such as evaporation and leakage that result in lowering long-term stability. In addition, the liquid electrolytes make the manufacture of multi-cell modules difficult since the cells must be connected electrically but separated chemically, preferably on a single substrate [1]. To overcome theses problems, many research groups emphasise on the replacement of liquid electrolyte with solid or quasi solid-state hole conductors [2-4]. Although solid-state electrolytes solve some problems, the cells with solid-state electrolytes provide low energy conversion due to low electron injection efficiency. Quasi-solid-state electrolytes or polymer electrolytes with negligible vapour pressure have some advantages. They have high ionic conductivity, long-term stability, and good contacting and filling properties with nanocrystalline TiO_2 working electrode and counter electrode [5]. In this paper, we present the preparation and performance of DSSCs with Quasi-solid State Electrolytes base on N-methyl-quinoline Iodide.

Experimental

Titanium(IV) isopropoxide, $Ti[OCH(CH_3)_2]_4$ solution (Fluka) was used as received. TCO glass substrates are F-doped SnO_2 thin films with 8 Ω/sq were purchased from Solaronix SA, Switzerland. Nanocrystalline TiO_2 thin flims were synthesized by sol-gel dip-coating method. The procedure of synthesis for sol-gel is described elsewhere [6]. To fabricated working electrodes for desensitized solar cells, we deposited TiO_2 on TCO glass substrates followed by sintering in air at 450 °C for 30 min. After cooling down to 80 °C, the films were immersed in ruthenium dye sensitizer bis(tetrabutylammonium)-*cis*-di(thiocyanato)-*N,N'*-bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine)ruthenium(II) or N719 dye 0.4mM in acetonitrile for 24 hrs. Afterwards, the dye-sensitized TiO_2 electrode was rinsed with ethanol and dried in air. Finally, the working electrodes were dried in an oven and kept in oven at temperature of 80-90 °C. The crystal structures of the resulting films were identified by X-ray diffraction (XRD) technique with X'Pert-MPD System. To obtain platinized counter electrodes with platinum colloidal nanoparticles, we prepared platinized counter electrodes using electrodeposition method.

N-methyl-quinoline iodide was synthesized by adding 20 ml of quinoline into 18 ml of methyl iodide under vigorrous stiring at temperature of about 70-80 °C untill the resultant solution became the solid at room temperature. The process took time about 18 hrs. The solid product was cleaned to remove excess unreacted materials and residure and the kept in an oven at 50-60 °C for 24 hrs. The polymer based on *N*-methyl-quinoline iodide was produced as following procedures. 0.6 M *N*-methyl-quinoline iodide, 0.05 M iodine, and 0.05 M 4-tert-butylpyridine (TBP) were mixed with organic solvents under stirling to form a homogenous liguid electrolyte. This material will provide charge carriers. Then, polymer host poly(acrylonitrileco-styrene) of 17 % wt was added into the homogenous liguid electrolyte. The resultant was heated up to and maintaned at 80 °C in a closed flask to dissolve the polymer host. Once the polymer host was completely dissolved, the heater was turned off to cool down to room temperature. Finally, the polymer gel electrolyte was obtained.

Dye-sensitized nonocrystalline solar cells were assembled by following stapes. The prepared gel electrolyte was pasted onto the surface of dry-covered TiO_2 working electrode. The platinized counter electrode was pressed on top of the working electrode to form a DSSC. The cells have active areas of 0.25 cm^2. The current-voltage characteristic curves were measured with Keithley 2400 source meter. The Xenon arc lamp was used as an irradiation source and the intensity of the incident light was100 mW/cm^2. The current density was calculated based on the photocurrent and the area of the cells.

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Results and Discussion

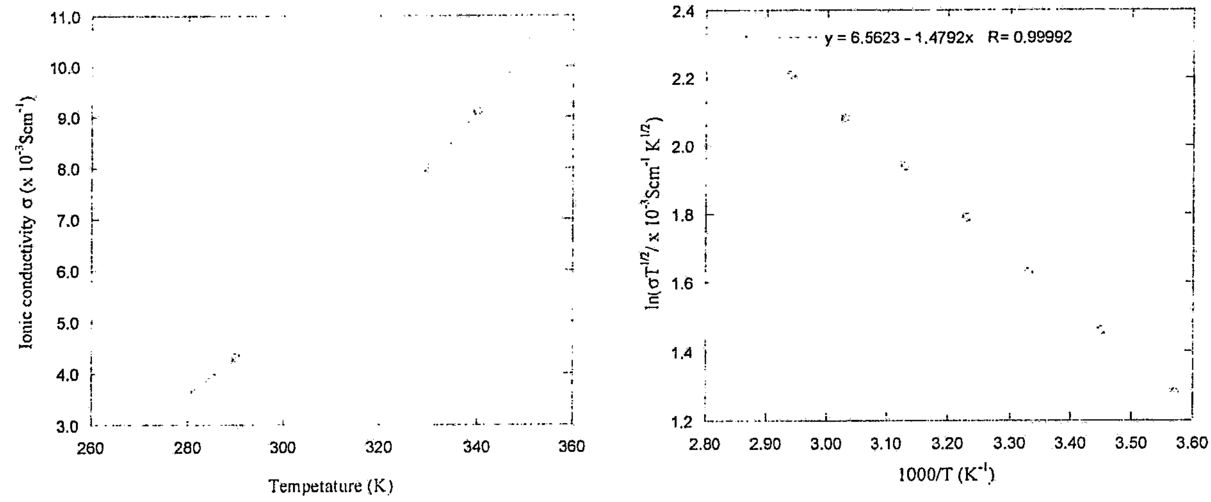

Figure1. Ionic conductivity plot (left) and semi-log plot (right) of the polymer gel electrolyte.

The variation of ionic conduction as a function of temperature and semi-log plot are shown in Fig 3. The variation of ionic conduction as a function of temperature is not linear, but semi-log plot of $\ell n(\sigma T^{1/2})$ and $\frac{1000}{T}$ is linear. The temperature dependence of ionic conductivity may be expressed by the modified Arrhenius equation which are called Vogel-Tammann-Fulcher equation (VTF)[7],

$$\sigma(T) = \sigma_0 T^{-1/2} \exp(-\frac{E_a}{RT}) \quad \text{or,} \quad \ell n(\sigma T^{1/2}) = -\frac{E_a}{RT} + \ell n(\sigma_0) \qquad (1)$$

where σ_0 is the pre-exponential factor, E_a the activation energy for ionic migration within solid, R is the molar gas constant, and T is the absolute temperature in Kelvin. The ionic conductivity increases as temperature increases. Due to the fact that the plot fits with modified Arrhenius equation, the mechanism of conductivity involves an intermolecular ion hoping as expected.

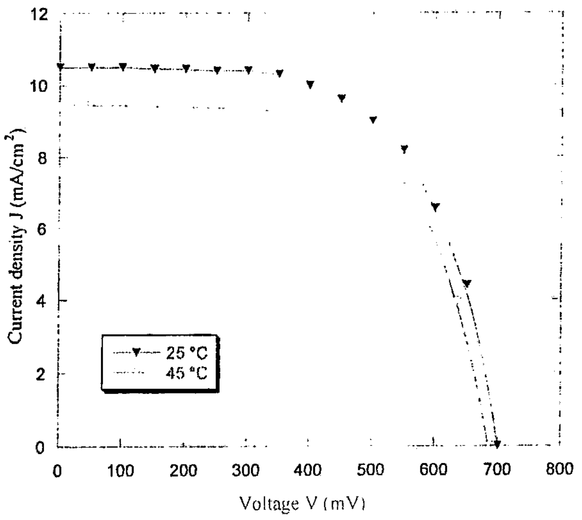

Figure 2. J-V curve of DSSC with the polymer gel electrolyte at different temperatures.

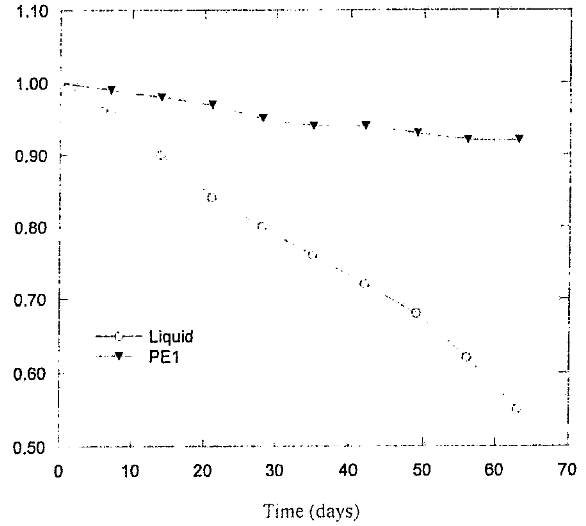

Figure 3. Long-term stability test of DSSC with the polymer gel electrolyte compared with liquid electrolyte

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The efficiency of polymer gel electrolyte of DSSC is shown in Fig 2. The highest efficiency of 4.5 % was obtained at operating temperature of 25 °C. When the operating temperature increased to 45 °C the efficiency slightly dropped to 3.9 %. The variations of short circuit current (dI_{sc}/dT) and open circuit voltage (dV_{oc}/dT) with respect to temperature are -0.05 mA/°C and -0.48 mV/°C, respectively while (dI_{sc}/dT) and (dV_{oc}/dT) of the cells with liquid electrolyte are 0.07 mA/°C [8] from -2.0 to -2.8 mV/°C [9] and, respectively. The normalized efficiency with respect to temperature of the cells with polymer electrolyte $\frac{1}{\eta}(\frac{d\eta}{dT})$ is -0.66 % while $\frac{1}{\eta}(\frac{d\eta}{dT})$ of silicon-based solar cells is -0.65 % [10]. This result shows that the performance of DSSCs with liquid electrolyte is comparable with silicon-based solar cells. Based on the duration of 64 days of observation, the long-term stability of DSSC with the polymer gel electrolyte is evidently superior to the DSSC with liquid electrolyte as shown in Fig.3.

Summary

We have succeeded in making polymer gel electrolyte of DSSC based on base on N-methyl-quinoline iodide with the efficiency of 4.5 %. The polymer gel electrolyte has ionic conductivity and exhibits intermolecular ion hoping mechanism. Its long-term stability is better than the liquid electrolyte and the effect of temperature on the power drop in the DSSCs with polymer gel electrolyte is comparable with crystalline silicon solar cells.

Acknowledgements

The authors would like to thank the National Research Council of Thailand and Ubon Ratchathani University for funding.

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THE EFFECT OF TEMPERATURE ON THE PERFORMANCE OF DYE-SENSITIZED SOLAR CELLS USING NANOSTRUCTURED TiO_2

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ABSTRACT

It is realized that the performance of solar cells decreases as temperature increases. In this work, we present the influence of temperature on the electrical parameters and performance of dye-sensitized solar cells (DSSCs). The cells consist of nanostructured-TiO_2 film working anodes and sputtered-platinum counter electrodes. TiO_2 Nanocrystalline films were prepared by sol-gel dip-coating method on transparent conducting oxide (TCO) glass substrates. Ultra-thin platinum films were deposited on TCO glass substrates by dc magnetron sputtering to make the counter electrodes. The current (I) and voltage (V) characteristics and the efficiency of the cells were carried out as a function of temperature in the range of 20 – 70 °C. The open circuit voltage (V_{oc}) and short circuit (I_{sc}) of the cells decrease as temperature increases which results in lowering the efficiency of the cells. The temperature dependence of I_{sc} is very sensitive when compared with conventional solar cells. .

KEY WORDS

Temperature dependence, dye-sensitized solar cells, nanostructured TiO_2, performance, renewable energy

1. Introduction

In recent years, the increase of oil price and realization of the global warming have become continuously serious throughout the world. To cope with the problems, many efforts have been made to search for renewable and clean sources of energy. The harnessing of solar energy to convert sunlight to electricity using appropriate photovoltaic materials is one of the most elegant methods. Dye-sensitized solar cells (DSSCs) are potentially low cost photovoltaic solar conversion devices. Since the discovery of DSSCs in 1991 by M.Grätzel [1], the research and development in the field of DSSCs have been done extensively. To date DSSCs with efficiency over 10 % have been reported [2]. Current research in this field is concentrating on improving nanostructured TiO_2 working electrodes, replacing volatile liquid electrolytes with solid state electrolytes to enhance the lifetime of the cells [3], and synthesising more effective sensitizers to increase the efficiency of the cells.

In general, it is well recognized that the performance of traditional solar cells such as Si and GaAs based solar cells decrease when temperature increases [4-6]. This phenomenon is well understood [4]. Many reports on efficiency of DSSCs were performed with 1 sun illumination, but the temperature of the DSSCs during its characterization was not specified. Moreover, only a few papers reported temperature dependence on the performance of DSSCs. The paper by M. Berginc et al. [7] studied the effect of temperature on the performance of DSSCs with P25 based on propyl-methyl-imidazotium iodide electrolyte and found that when temperature increases from 4.4 to 41.0 °C the current density increases from 2 mA/cm^2 to 7 mA/cm^2 while the voltage decreases slightly from 0.7 to 0.6 mV. The current decreases if the temperature exceeds 41 °C. The cells gave maximum efficiency of 2.6 % at 41.0 °C. Yet, P.J. Sebastián et al. [8] have studied DSSCs with rutile-phase nanocrystalline TiO_2 and found that at elevated temperatures the current density decreases slightly from 3.4 to 3.3 mA, but the voltage decreases from 0.77 to 0.67 V temperature increases from 30 to 80 °C. The current density of Sebastián's group differs from Berginc's group in that it decreases. In this work, we present the effect of temperature on the performance of dye-sensitized solar cells using pure anatase-nanostructured TiO_2 films as working electrodes at different temperatures ranging from 20 to 70°C.

2. Experimental

All chemicals employed were analytical grades of the best available purity. Titanium (IV) isopropoxide, $Ti[OCH(CH_3)_2]_4$ solution was used as received. TCO glass substrates are F-doped SnO_2 thin films with 10 Ω/sq. Nanocrystalline TiO_2 thin flims were synthesized by sol-gel dip-coating method. The procedure of synthesis for sol-gel is described elsewhere [9]. To fabricated working electrodes for DSSCs, we deposited TiO_2 on TCO glass substrates followed by sintering in air at temperature about 450°C for 30 min. The crystal structures of the thin films were identified by X-ray diffraction (XRD) technique with X'Pert-MPD System. The thickness of TiO_2 films was increased by means of consecutive dip-coating process. The calcined films were immersed in standard N719 dye for 24 hr. Next, the dye-sensitized TiO_2 electrodes were rinsed with ethanol and dried in an oven at temperature of 80 °C. The counter electrodes were prepared by following steps. TCO glass substrates were first washed in a liquid detergent solution, then rinsed in deionized water twice, and finally were ultrasonically cleaned again in warm alcohol and acetone mixture of 1:1 volume ratio about 80 °C for another 20 minutes and blown dry in nitrogen gas. Ultra-thin platinum thin films were deposited by DC magnetron sputtering on cleaned TCO glass substrates with thickness about 50-100 nm. The films were annealed in air at temperature about 450 °C.

For DSSC assembly and cell performance measurement, we have used a standard method described in the well-known literature [10] which is simple and feasible. After the electrodes were dried and warm, a drop of the liquid electrolyte (tetrapropy-lammoniun iodide) was dropped onto the surface of the dye-sensitized TiO_2 working electrode. Pt-coated TCO glass substrates serve as counter electrodes were placed above the working electrode. The two electrodes were clipped together and were sealed with silicone to prevent the leak of the electrolyte. The active areas of the samples are 0.25 cm^2. To measure I-V curve characteristics at different temperatures, we placed LakeShore DT-470 semiconductor diode sensor under the cells. At low temperature, we cooled the cells by placing near liquid nitrogen and at high temperature; we heated the cells by placing the cells over a hot plate. The current-voltage characteristic curves were measured with Keithley 2400 source meter. The current density was calculated based on the current and the area of the cells. The Pyranometer Sensor (CM11, Kipp & Zonen, Netherlands) with sensivity of 5.12×10^{-6} V/Wm^{-2} was used to measure the intensity of the light. 100 W Xenon arc lamp was used as an irradiation source.

3. Results and Discussion

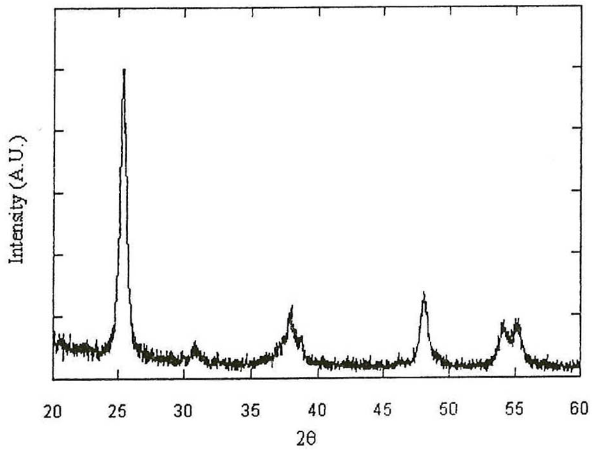

Figure 1. XRD patterns of pure anataseTiO_2 thin films on TCO glass substrate

Fig. 1 shows XRD pattern of the specimen TiO_2 film. The data analysis shows that TiO_2 film is a pure anatase phase. The crystallite size was estimated by applying the Scherrer's equation to the full width at half maximum (FWHM) of (101) peak,

$$d = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where d is the average crystallite size, λ is the X-ray wavelength, β s the broadening of the diffraction line measured as the full width at half maximum intensity (FWHM), and θ is the corresponding diffraction angle. The average of crystallite size is 10 nm in diameter. The Scanning Electron Microscope (SEM) image shows the film is composted of many spherical crystals of TiO_2 and the size is bigger than that of obtained by XRD calculation because nanoparticles of TiO_2 aggregate and become clusters.

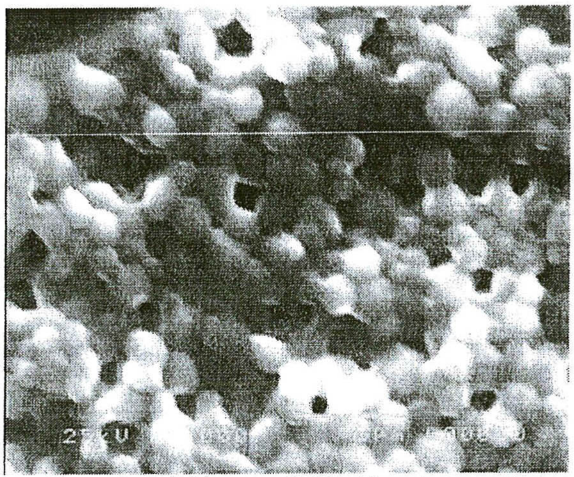

Figure 2. SEM image of TiO_2 film photoanode

We measured the cells which produced IV curves at different temperatures shown in Fig. 3. The photovoltaic parameters for the cells are summarized in Table 1. The light-to-electricity conversion efficiency can be calculated the following equations:

$$\eta = \frac{P_{output}}{P_{input}} \times 100 \tag{2}$$

$$\eta = \frac{(J \cdot V)_{max}}{P_{input}} \times 100 \tag{3}$$

$$\eta = \frac{(J_{sc} \times V_{oc})}{P_{input}} \times FF \times 100 \tag{4}$$

where J_{sc} is the short-circuit current density (mA/cm^2), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power (mW/cm^2) and $(JxV)_{max}$ is the product of the current density and voltage in the IV curve at the point of maximum power out put. The incident light was sunlight with the power of 100 mW/cm^2.

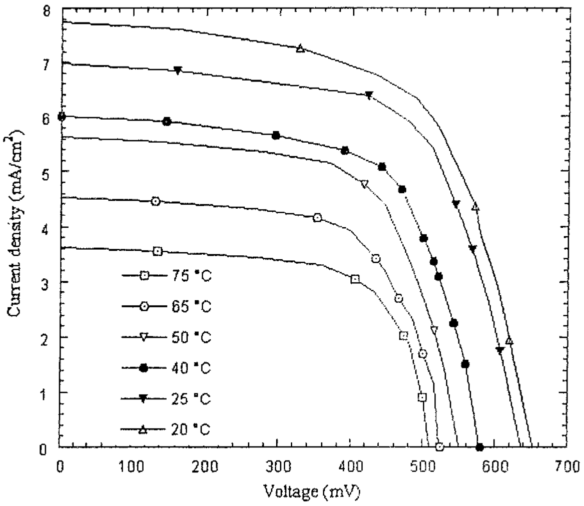

Figure 3. J-V curves of the DSSCs with different temperatures

Table 1
Photovoltaic data of the dye-sensitized solar cells with different temperatures

J_{sc}(mA/cm^2)	V_{oc}(V)	FF	η (%)	T (°C)
3.60	0.50	0.66	1.20	75
4.75	0.52	0.68	1.68	65
5.60	0.55	0.69	2.13	50
6.00	0.58	0.70	2.43	40
7.00	0.64	0.70	2.46	25
7.75	0.65	0.68	3.43	20

The data show that the open circuit voltage (V_{oc}) and shot circuit (I_{sc}) of the cells decrease as temperature increases as shown in Table 1. The efficiency of the cells decreases as temperature increases as shown in Fig 3 and 4. Our data are different from previous results reported by M. Berginc et al. [7], but are likely similar to the results published by P.J. Sebastián et al. [8]. The average rates of change of V_{oc} and I_{sc} with respect to temperature, dV_{oc}/dT and dI_{sc}/dT are -2.36 and -0.07, respectively. The decreasing rate with respect to temperature of the open voltage, dV_{oc}/dT, of the cells is similar to the conventional solar cells, but the decreasing rate with respect to temperature of the short circuit, dI_{sc}/dT, is very large when compared with the conventional solar cells [4-6]. These results differ from the previous data [7-8] in that the variation of I_{sc} in temperature our data is very sensitive.

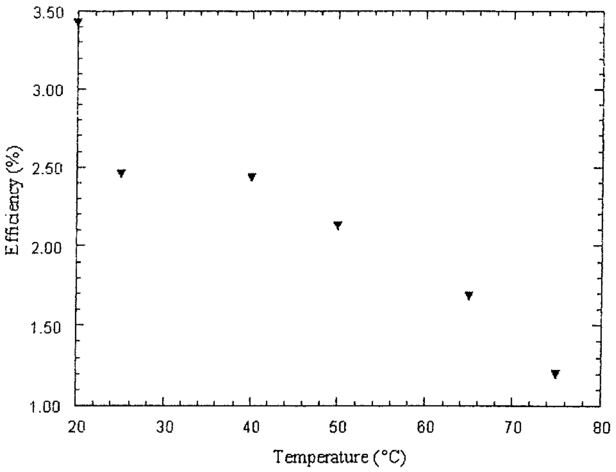

Figure 4. The plot of the efficiency of the cells as a function of temperature

4. Conclusion

We have successfully fabricated pure anatase TiO_2 films on the top of TCO glass substrates and used TCO glass substrates with ultra-thin platinum coating as counter electrodes. As temperature increases form 20 °C to 75 °C, the short circuit current and open voltage of the cells decrease. The fill factors and performance of the cell also decrease when temperature increases. These results are different from previous reports by other groups. The temperature dependence of V_{oc} dye-sensitized solar cells with nanocrystalline anatase TiO_2 is similar to the conventional solar cells, but the I_{sc} decreases significantly as temperature increases when compared with conventional solar cells.

Acknowledgements

The authors would like to thank Ubon Rachathanee University and National Research Council of Thailand for financial support.

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Fabrication and Properties of Dye-Sensitized Solar Cells Using Indium Tin Oxide-Coated Stainless Steels as Counter Electrodes

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Abstract: A new configuration of dye-sensitized solar cells (DSSC) using Indium Tin Oxide (ITO)-coated stainless steel as counter electrodes was proposed and investigated. The purposes of ITO-coated stainless steel replacement for ITO glass counter electrodes are to dissipate heat from the cells and to reduce production cost. The working electrodes are made of natural dye absorbed-TiO_2 nanocrystalline film on the top of transparent tin oxide (TCO) glass. The TiO_2 was prepared by sol-gel dip-coating method. The counter electrodes are ITO-coated stainless steel with Pt coated particles on the top of ITO thin film. The ITO thin film was deposited by DC magnetron sputtering. The ITO thin film on stainless steel can prevent corrosion of stainless steel counter electrodes. The dye-sensitized solar cells exhibit high conversion efficiency of 2.74 %which is comparable to those of prepared by the traditional method namely ITO glasses both working electrodes and counter electrodes.

Keywords: ITO-coated stainless steel, counter electrode, dye-sensitized solar cells, nanocrystalline titania (TiO_2), renewable energy

1. INTRODUCTION

The need of renewable energy sources and environmentally friendly energy is potential driving force for the search of new sources of energy in the 21st century due to dramatically growing demand and global warming. The harnessing of solar energy to convert sunlight to electricity using appropriate semiconductor materials is one of the cleverest methods. Fortunately, the earth gains gigantic amount of energy from the sun about 3 x 10^{24} J a year or 10,000 times more than that world population currently uses. In other words, if solar cells with an efficiency of 10 % cover 0.1 % of the earth's surface, they will produce electricity enough for our present needs [1]. Dye-sensitized solar cells (DSSC) are devices of choice because their high efficiency, low production cost, and environmentally friendly materials. In general, DSSCs are composted of three main components: (1) a dye absorbing nanocrystalline-TiO_2 layer on a TCO glass substrate as a working electrode, (2) an iodide/triodide redox couple in an organic solvent or polymer or solid as an electrolyte, and (3) a platinum-coated TCO glass substrate as a counter electrode. Stainless steel substrates were introduced in DSSCs by Kang et al [2] as working electrodes. Our group presented DSSCs using tainless steel sheet counter electrode with an efficiency of 2.7 %. Yet, they could not resist corrosion. They become rusted within months. However, the use of the TCO glass counter electrode may be difficult to dissipate heat from the cells resulting in lowering the cell performance. To transfer heat out of the cells and to protect corrosion, we propose DSSCs with a ITO-coated stainless steel with Pt catalyst as counter electrodes.

2. METHODOLOGY

All chemicals employed were analytical grades of the best available purity. Titanium (IV) isopropoxide, $Ti[OCH(CH_3)_2]_4$ solution was used as received. TCO glass substrates are F-doped SnO_2 thin films with 10 Ω/sq. Nanocrystalline TiO_2 thin flims were synthesized by sol-gel dip-coating method. The procedure of synthesis for sol-gel is described elsewhere [3]. To fabricated working electrodes for DSSCs, we deposited TiO_2 on TCO glass substrates followed by sintering in air at temperature of 450-500 °C for 30 min. The crystal structures of the thin films were identified by X-ray diffraction (XRD) technique with X'Pert-MPD System. TiO_2 layers on the substrates could be thickened by means of consecutive dip-coating process. The calcined films were immersed in standard N3 dye for 24 hr. Next, the dye-sensitized TiO_2 electrodes were rinsed with ethanol and dried in an oven at temperature of 80 °C. The counter electrodes were prepared as follows. Stainless steel substrates were first washed in a liquid detergent solution, then rinsed in deionized water twice, and finally were ultrasonically cleaned again in warm alcohol and acetone mixture of 1:1 volume ratio about 80 °C for another 20 minutes and blown dry in nitrogen gas. ITO thin films were deposited by DC magnetron sputtering on the stainless steel foils of about 0.25 mm thickness. The films were annealed in air at different temperatures ranging from 200 to 450 °C. The resultant ITO-coated stainless steel were deposited Pt to make a catalyst. Pt catalyst was deposited on ITO-coated stainless steels by dropping of H_2PtCl_6 solution with repetition of the heat treatment at 400 °C for 30 min.

For DSSC assembly and cell performance measurement, we have used a standard method described in the well-known literature [4] which is simple and feasible. After the electrodes were dried, a drop of the liquid electrolyte (tetrapropy-lammoniun iodide) was dropped onto the surface of the dye-sensitized TiO_2 working electrode. ITO coated stainless steels with Pt catalyst serve as counter electrodes were placed above the working electrode. The two electrodes were clipped together and were sealed with silicone to prevent the leak of the electrolyte.

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD pattern of TiO_2 film. The data analysis shows that TiO_2 film is a pure anatase phase. The crystallite size was estimated by applying the Scherrer's equation to the full width at half maximum (FWHM) of (101) peak. The average size is 10 nm in diameter. Fig. 2 shows XRD patterns of ITO films on stainless steel at different annealing temperatures. The lattice parameters of ITO as deposited is slightly increased, but the impurity phases were not observed. We further increased annealing temperatures to 450 °C, but the structure of the films remains the same.

The efficiency of DSSCs in different types of counter electrodes was reported in our previous work [5]. In this work, we compare different DSSC counter electrodes: stainless steel, stainless steel with Pt catalyst, TCO glass with Pt catalyst, and ITO-coated stainless steel with Pt catalyst substrates as counter electrodes.

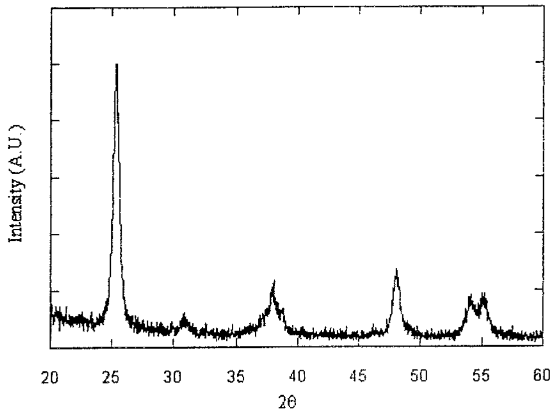

Fig. 1 XRD patterns of pure anataseTiO$_2$ thin films on TCO glass substrate.

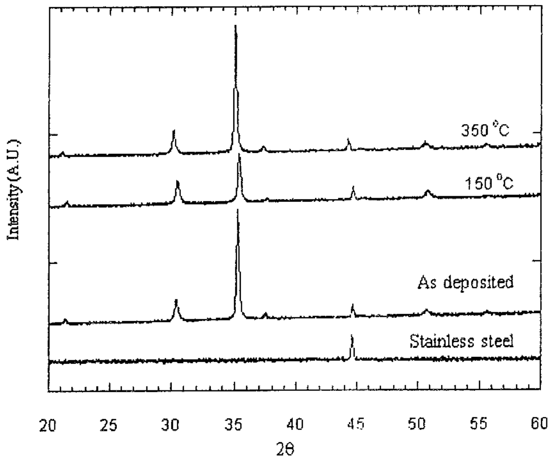

Fig. 2 XRD patterns of ITO thin films on stainless steel with different annealing temperatures.

We measured several cells which produced IV curves resembling those in Figure 2. The photovoltaic parameters for the cells are summarized in Table 1. The IV curves of the best specimens with TiO$_2$ films with different counter electrodes are shown in Figure 2. The light-to-electricity conversion efficiency can be calculated the following equations:

$$\eta = \frac{P_{out}}{P_{in}} \times 100 \qquad (1)$$

$$\eta = \frac{(J \times V)_{max}}{P_{light}} \times 100 \qquad (2)$$

$$\eta = \frac{(J_{sc} \times V_{oc})}{P_{light}} \times FF. \times 100 \qquad (3)$$

where J_{sc} is the short-circuit current density (mA/cm^2), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power (mW/cm^2) and $(JxV)_{max}$ is the product of the current density and voltage in the IV curve at the point of maximum power output. The incident light was sunlight with the power of about 80 mW/cm^2.

Table 1 Photovoltaic data of the dye-sensitized solar cells with different counter electrodes

Type of counter electrodes	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η%
ITC-coated SS with Pt catalyst	6.90	0.53	0.60	2.74
TCO glass with Pt catalyst	6.80	0.54	0.59	2.70
w/o coated SS with Pt catalyst	6.70	0.50	0.50	2.09
SS w/o Pt catalyst	5.90	0.49	0.49	1.73

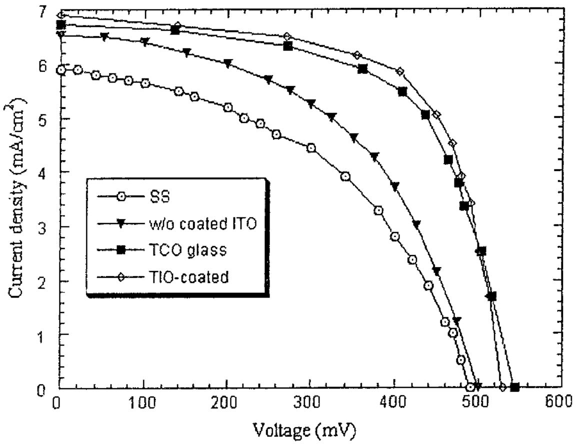

Fig. 3 JV curves of the DSSC with different counter electrodes: stainless steel (SS), stainless steel with Pt catalyst (w/o coated ITO), TCO glass with Pt catalyst (TCO glass), and ITO-coated stainless steel with Pt catalyst (ITO-coated).

The data show that the efficiency of the cells with a stainless steel counter electrode is 1.73 % and the efficiency of the cell with a Pt catalyst stainless steel counter electrode increases slightly to be 2.09 %. This result means that the electron transfer rate at the interface between the electrolyte and the counter electrode increases because of the catalytic activity of the platinum particles deposited on the surface of the stainless steel. However, the efficiencies of the cells with stainless steel and Pt catalyst stainless steel counter electrodes are lower than that of the cell with Pt catalyst TCO counter electrode yielding 2.70 %. The efficiency of DSSC with Pt catalyst ITO-coated stainless steel is 2.74 %. This may result from the interface between stainless steel and TiO_2 is improved by the thin layer of ITO. The fill factors (FF) of the stainless steel and platinum-coated stainless steel counter electrodes are 0.49 and 0.50 respectively which are not significantly different. Fill factor gives important intrinsic information related to the cells such as internal resistance. We also observed that ITO-coated stainless steel can resist corrosion. When ITO-coated stainless steel with Pt catalyst is used as counter electrodes, the internal resistance of the cells is decreased which results in increasing of the fill factors. Therefore, coating ITO on stainless steel can reduce the resistance of interface between stainless steel and semiconductor TiO_2 before coating platinum catalyst.

4. CONCLUSION

We have successfully fabricated pure anatase TiO_2 films on the top of TCO glass substrates and used ITO-coated stainless steel foil with Pt catalyst as a counter electrode. The light-to-electricity conversion efficiencies of the best specimens were2.84 %, 2.70%, 2.09%, and 1.73 % for Pt catalyst ITO-coated stainless steel, TCO glass with Pt catalyst, stainless steel with Pt catalyst, and stainless steel counter electrodes, respectively. The low efficiencies of the cells with stainless steel derive from high internal resistance of the interface between stainless steel and semiconductor materials, TiO_2. The cell with Pt catalyst stainless steel counter electrode yields higher efficiency than stainless counter electrode without Pt catalyst because catalytic activity of platinum particles is a crucial factor for performance of the dye-sensitized solar cells. The cell made of ITO-coated stainless steel electrode gives efficiency higher than the cell made of without ITO-coated stainless steel electrode because ITO film reduce internal resistance and improve the contact between TiO_2 and stainless steel.

5. ACKNOWLEDGMENTS

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Fabrication and properties of dye-sensitized solar cells using stainless steel as counter electrodes

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We propose the new configuration of dye-sensitized solar cells using a stainless steel (SS) foil as counter electrodes. The working electrodes are composed of natural dye absorbing TiO_2 nano-film on the top of transparent conducting oxide (TCO) glass. The counter electrodes are made of platinum-coated stainless steel. The dye-sensitized solar cells exhibit high conversion efficiency which is comparable to those of prepared by the traditional method namely TCO glasses for both working electrodes and counter electrodes.

1. INTRODUCTION

Due to dramatically growing demand and warming, the need of renewable energy sources and eco-friendly environment energy is considered a potential force for power requirements for the 21st century. The harnessing of solar energy to convert sunlight to electricity using appropriate semiconductor materials is one of the cleverest methods. Fortunately, the earth gains gigantic amount of energy from the sun about 3×10^{24} J a year or 10,000 times more than that world population currently uses. In other words, if solar cells with an efficiency of 10 % cover 0.1 % of the earth's surface, they will produce electricity enough for our present needs [1]. Dye-sensitized solar cells are the photovoltaic devices of choice because their high efficiency, low production cost, and environmentally friendly materials.

In general, dye-sensitized solar cells are composed of three main components: a dye-absorbed nanocrystalline-TiO_2 layer on a transparent conducting oxide glass (TCO) substrate as working electrode, an iodide/triodide redox couple in an organic solvent or polymer or solid as an electrolyte, and a platinum-coated TCO glass substrate as a counter electrode. To the best of our knowledge, no other research groups used stainless steel as counter electrodes except for working electrodes [2-3]. The use of TCO counter electrodes makes cost of the cells expensive and heavy. Furthermore, the use of the TCO glass counter electrode may be difficult to dissipate heat from the cells resulting in lowering the cell performance. To transfer heat out of the cells, we fabricate the dye-sensitized solar cells with a platinum-coated stainless steel as a counter electrode.

2. EXPERIMENT

Titanium(IV) isopropoxide, $Ti[OCH(CH_3)_2]_4$ solution was obtained from Fluka and used as received. TCO glass substrates are F-doped SnO_2 thin films with 10 Ω/sq were purchased from Solaronix SA, Switzerland. Nanocrystalline TiO_2 thin films were synthesized by sol-gel dip-coating method. The procedure of synthesis is described elsewhere [4]. To fabricate working electrodes for desensitized solar cells, we deposited TiO_2 on TCO glass substrates followed by sintering in air at 450-500 °C for 30 min. The crystal structures of the thin films were identified by X-ray diffraction (XRD) technique with X'Pert-MPD System. TiO_2 layers on the substrates could be thickened by means of consecutive dip-coating process. The calcined films were immersed in ruthenium dye, cis-$Ru(SCN)_2L_2$ (L = 2.2' -bipyridyl-4,4'-dicarboxylate) for 12 hrs. Afterwards, the dye-sensitized TiO_2 electrode was rinsed with ethanol and dried in air.

Stainless steel foils of about 0.25 mm thickness were used as a counter electrode. The counter electrodes were prepared as follows. Stainless steel substrates were first washed in a liquid detergent solution for 20 minutes, then rinsed in deionized water twice, and finally ultrasonically cleaned again in warm alcohol and acetone mixture of 1:1 volume ratio about 80 °C for another 20 minutes and blown dry in nitrogen gas. Platinum was coated on stainless steels by means of electrodepositing with chloroplatinic acid (H_2PtCl_6) as a source of platinum catalyst.

For dye-sensitized solar cell assembly and cell performance measurement, we have used a standard method described in the well-known literature [5] and briefly described as follows. After the electrodes were dried, a drop of the liquid electrolyte (tetrapropyl-ammonium iodide) was dropped onto the surface of the dye-sensitized TiO_2 working electrode. Pt-coated stainless steel counter electrode was placed above the working electrode. The two electrodes were clipped together and were sealed with silicone to prevent the leak of the electrolyte.

The photovoltaic test of the dye-sensitized TiO_2 nanocrystalline solar cells with stainless steel counter electrode was carried out by measuring current-voltage characteristic curves under natural sunlight with the power of about 80 mW/cm^2. The current-voltage characteristic curves were measured with Keithley 2400 source meter. The current density was calculated based on the current and the area of the cells. The Pyranometer Sensor (CM11, Kipp & Zonen, Netherlands) with sensitivity of 5.12×10^{-6} V/Wm^{-2} was used to measure the intensity of the sunlight. The heat dissipation from the cells was determined by the reduction of the cell temperatures after blowing with an electric fan.

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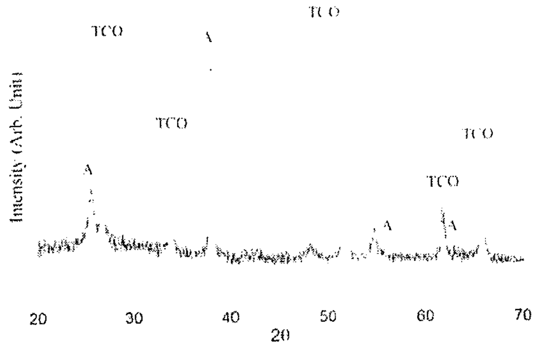

FIGURE 1. XRD pattern of nanocrystalline TiO_2 thin film on TCO glass substrate: A = Anatase TiO_2 and TCO = $F:SnO_2$ thin film glass substrate.

The temperature of the cells was measured by LakeShore DT-470 silicon diode temperature sensors with 10 μA current source. The sensor was attached at the counter electrode of the cell. The wind speed was measured by MicroPro Digital Anemometer.

3. RESULTS AND DISCUSSIONS

X-ray diffraction patterns of TiO_2 films deposited on TCO glass substrates are shown in Fig. 1. The pattern of calcined (400 °C) TiO_2 corresponds to pure anatase phase. The crystallite size was estimated by applying the Scherrer equation to the full width at half maximum (FWHM) of (101) peak of anatase. The average size is 10 nm in diameter.

We have reported the dye-sensitized solar cells with TCO glass substrates as both electrodes in our previous work [6]. In this work, we compare the dye-sensitized solar cells with a stainless steel substrate as counter electrode. We measured several cells which produced IV curves resembling those in Fig. 2. The IV curves of the best specimens with TiO_2 films with different counter electrodes are shown in Fig. 2. The photovoltaic parameters for the cells are summarized in Table 1. The light-to-electricity conversion efficiency (η) can be calculated by the following equations:

$$\begin{aligned}\eta &= \frac{P_{out}}{P_{in}} \times 100 \\ &= \frac{(J \times V)_{max}}{P_{light}} \times 100 \\ &= \frac{FF \times (J_{sc} \times V_{oc})}{P_{light}} \times 100\end{aligned}$$

where J_{sc} is the short-circuit current density (mA/cm^2), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power (mW/cm^2) and $(J \times V)_{max}$ is the product of the current density and voltage in the IV curve at the point of maximum power output. The incident light was sunlight with the power of about 80 mW/cm^2.

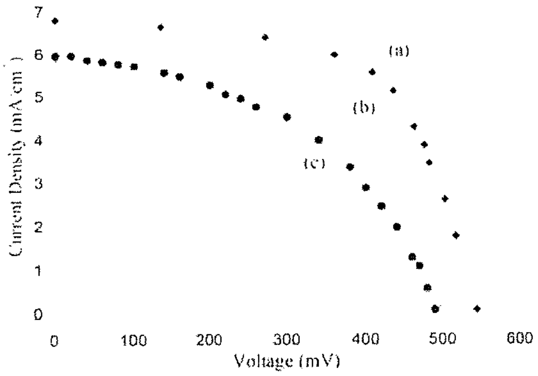

FIGURE 2. IV curves of the dye-sensitized solar cells fabricated by using different substrates as counter electrodes. (a) TCO, (b) Pt-coated stainless steel and (c) stainless steel.

TABLE 1. Photovoltaic data of the dye-sensitized solar cells with different counter electrodes measured at the cell temperature of 30°C.

Counter electrode	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η%
TCO	6.80	0.54	0.59	2.70
SS Pt-coated	6.70	0.50	0.50	2.09
SS	5.90	0.49	0.49	1.73

The sample marked counter electrode TCO stands for the traditional dye-sensitized solar cells made of TCO glass substrates for both working and counter electrodes. The TCO counter electrodes are always coated with platinum-catalyst. Our TCO counter electrodes were also coated with platinum-catalyst. The SS Pt-coated sample represents the sample made of platinum-coated stainless steel counter electrode. And SS sample denotes the sample made of stainless steel counter electrode without platinum catalyst.

The photovoltaic properties of dye-sensitized with different counter electrodes are shown in Table 1 and IV curves are presented in Fig. 2. The data show that the efficiency of the cells with a stainless steel counter electrode is 1.73 % and the efficiency of the cell with a platinum-coated stainless steel counter electrode increases slightly to be 2.09 %. This result means that the electron transfer rate at the interface between the electrolyte and the counter electrode increases because of the catalytic activity of the platinum particles deposited on the surface of the stainless steel. However, the efficiencies of the cells with stainless steel and platinum-coated stainless steel counter electrodes are lower than that of the cell with TCO counter electrode yielding 2.70 %. The fill factors (*FF*) of the stainless steel and platinum-coated stainless steel counter electrodes are 0.49 and 0.50 respectively which are not significantly different. Fill factor gives important intrinsic information related to the cells such as internal resistance. When the stainless steel and platinum-coated stainless steel are used as counter electrodes, the internal resistances of the cells increase resulting in decreasing of the fill factors. It is possible to reduce the resistance of interface between stainless steel and semiconductor TiO_2 by vacuum deposition of TCO on a stainless steel foil before platinum-coated.

TABLE 2. Photovoltaic data of the dye-sensitized solar cells with different counter electrodes when left in sunlight for 1 hour from 11.00-12.00 o'clock (T_i) and then continuously blown for 1 hour from 12.00-13.00 o'clock (T_f) and $\Delta T = T_i - T_f$.

Counter Electrode	T (°C)	J_{sc}	V_{oc}	FF	η%
TCO	$T_i = 51$	5.6	0.50	0.57	1.99
	$T_f = 40$	6.0	0.49	0.58	2.13
SS-Pt coated	$T_i = 50$	6.0	0.47	0.47	1.65
	$T_f = 28$	6.1	0.50	0.51	1.94

When the cells were left in the sunlight for 1 hour from 11.00-12.00 o'clock, we measured the cell temperature and labeled as T_i. Then, the cells were continuously blown for 1 hour from 12.00-13.00 o'clock, we recorded as T_f. We observed that the temperatures of the cells with TCO counter electrode and platinum-coated stainless steel electrode are reduced from 51 to 40 °C and 50 to 28 °C, respectively as shown in Table 2. The differences of the temperatures, $\Delta T = T_i - T_f$, of TCO counter electrode and platinum-coated stainless steel are 9 °C and 22 °C, respectively. These data show that the platinum-coated counter electrode can dissipate heat from the cell better than TCO counter electrode. It was also found that lowering cell temperature results in increasing the efficiency of the cells.

It was observed that the stainless steel electrodes have become rusted. Then, further development will be put to overcome this obstacle by coating thin film of indium-tin-oxide on stainless steel to protect oxidation before covering with platinum catalyst.

4. CONCLUSIONS

We have successfully fabricated nanocrystalline TiO_2 thin films on the top of TCO glass substrates and used stainless steel foil as a counter electrode. The light-to-electricity conversion efficiencies of the best specimens were 2.70%, 2.09% and 1.73 % for TCO, Platinum-coated stainless steel, and stainless steel counter electrodes, respectively. The low efficiencies of the cells with stainless steel derive from high internal resistance of the interface between stainless steel and semiconductor materials, TiO_2. The cell with platinum-coated stainless steel counter electrode yields higher efficiency than stainless counter electrode because catalytic activity of platinum particles is a crucial factor for performance of the dye-sensitized solar cells. Although the cell with platinum-coated counter electrode slightly yields lower efficiency than the cells with TCO counter electrode, it provides better heat dissipation that results in enhancing the efficiency of the cell and makes the efficiency comparable to that of the cell with TCO counter electrode.

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