Contents lists available at ScienceDirect







journal homepage: www.elsevier.com/locate/electacta

High-performance and low platinum loading electrodeposited-Pt counter electrodes for dye-sensitized solar cells

Che-Yu Lin^a, Jeng-Yu Lin^{b,*,1}, Chi-Chao Wan^a, Tzu-Chien Wei^c

^a Department of Chemical Engineering, National Tsing-Hua University, Hsinchu 300, Taiwan

^b Department of Chemical Engineering, Tatung University, Taipei 104, Taiwan

^c Hsin-Chu Laboratory, Tripod Technology Corporation, IIC, 313R, No. 101, Kuang-Fu Rd., Hsinchu 300, Taiwan

ARTICLE INFO

Article history: Received 22 September 2010 Received in revised form 19 November 2010 Accepted 24 November 2010 Available online 2 December 2010

Keywords: Dye-sensitized solar cell Counter electrode Electrodeposition Additive

ABSTRACT

This study demonstrates platinum (Pt) counter electrodes with low charge-transfer resistance (R_{ct}), low Pt loading and high active surface area can be obtained within 30 s by using the direct-current deposition in the presence of 3-(2-aminoethylamino)propyl-methyldimethoxysilane (Me-EDA-Si) as an additive. The addition of appropriate Me-EDA-Si can not only enhance the current efficiency but also inhibit the growth of semicircle-like grains, thus resulting in Pt electrode with high active surface area. Consequently, the dye-sensitized solar cells (DSSCs) fabricated with so-prepared Pt electrodes exhibited cell efficiency of 7.39% while 0.01 vol% Me-EDA-Si was added, which is much superior to that with sputtered-Pt electrodes under the same assembly conditions.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, dye-sensitized solar cells (DSSCs) developed by Grätzel [1] have attracted much attention. One component of DSSCs, the counter electrode, plays an important role to accelerate the reaction, $I_3^- + 2e^- \rightarrow I^-$, and reduce the voltage loss during the catalytic reaction [2]. Platinum is the common catalyst material because Pt is more stable when in contact with the iodine-based electrolyte than other catalytic materials such as graphite [3,4] and conducting polymer [5,6]. In practice, sputtering is widely developed for depositing Pt film due to its stability and reproducibility. However, a large portion of the such deposited Pt is located inside the film and did not fully exhibit its catalytic function, rendering a waste of material [7,8]. Thermal decomposition is another alternative for fabricating the counter electrodes with low Pt loading, showing good performance and mechanical stability [9]. Yet the processing temperature needed is at least up to 450 °C, thus resulting in high energy consumption especially for large-scale production. Furthermore, the development of flexible DSSCs becomes a prominent issue and high-temperature process certainly is in conflict with the application of flexible polymeric substrate [10].

So new low-temperature and cost-effective processes have been explored. Polyvinylpyrrolidone (PVP)-capped Pt nano-clusters developed in our laboratory were deposited via a dip-coating method to fabricate counter electrode [7,11]. The cell efficiency could reach 5.28% with a Pt loading of 4.65 μ g cm⁻². But it still needs a post-treatment to minimize the shielding effect of PVP which could deeply decrease the catalytic ability of Pt catalyst.

Another effective approach to fabricate the Pt electrode is by electrochemical deposition. This approach can be further classified into two methods: electroless deposition (ELD) and electrodeposition (ED). The ELD technique was employed to fabricate Pt electrode with low charge-transfer resistance (R_{ct}) by suitable surface modification [8]. However, it is still in the early development stage. In addition, Chen et al. [12] used metallic substrates to fabricate Pt electrode by the displacement reaction. The best cell efficiency obtained was up to 7.29% with a Ni sheet as the substrate. Unfortunately, the Pt loading was also as high as \sim 487.5 µg cm⁻². The electrodeposition method is another simple and low cost process. Kim et al. pointed out that insufficient metal content resulted in a discontinuous film with inhomogeneous dendritic crystal by direct-current deposition [13]. So, pulse deposition was used to solve this problem. Because the metal ions can be supplied to the surface of the substrate during the pulse deposition so that the gradient of the metal ions can be eliminated, thus a uniform and well-dispersion Pt films can be obtained. Since sufficient Pt nuclei formed on the surface, the cell efficiency and the effective Pt active area could consequently be significant improved, as shown in

^{*} Corresponding author. Tel.: +886 2 25925252/2561 119; fax: +886 2 25861939. *E-mail address*: jylin@ttu.edu.tw (J.-Y. Lin).

¹ ISE member.

^{0013-4686/\$ –} see front matter © 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2010.11.084

Preparation method	Additive conc.	Pt loading ($\mu g cm^{-2}$)	$R_{ m ct}$ ($\Omega{ m cm}^2$)	Solvent	μ (%)	Substrate	Preparation remarks	Ref.
Direct-current	0 vol%	1.06	5.83	MPN+TBP	2.19	FTO glass	Room temperature,	This work
deposition (ME-EDA-Si	0.001 vol%	2.07	4.91	MPN+TBP	4.93	FTO glass	30 s	
as an additive)	0.01 vol%	4.76	1.39	MPN+TBP	7.39	FTO glass		
	0.05 vol%	5.25	2.14	MPN+TBP	6.33	FTO glass		
	0.5 vol%	9.66	2.24	MPN+TBP	5.86	FTO glass		
Sputter	I	~ 100	2.03	MPN+TBP	6.01	FTO glass	Vacuum	
Sputter	I	200	2.36	MPN+TBP	5.46	Ni sheet	Vacuum	Ref. [12]
Constant potential (C ₁₆ EO ₈	$\sim 0.88 M^a$	5-10	$\sim 3.5^{a}$	MPN+TBP	7.6	FTO glass	450 °C, >2 h	Ref. [2]
as an additive)								
Pulse deposition (PVP as an	50 Mm	\sim 252 ^b	I	MPN+TBP	4.28	ITO glass	Room temperature	Ref. [15]
additive)								
Constant potential	I	${\sim}50$	1.2	ACN	~ 6.5	ITO glass	Room temperature	Ref. [14]
Pulse/direct deposition	I	~50	0.6	ACN	~ 6.5	ITO glass		
Pulse deposition	I	$\sim 3032^{b}$	$\sim 2^{a}$	I	5.03	FTO glass	Room temperature, >300 s	Ref. [13]
Direct-current deposition	I		$\sim 0.875^{a}$		3.68	FTO glass		
Electroless deposition	I	34.55	1.24	MPN+TBP	6.71	FTO glass	60 °C, >1 h	Ref. [8]
PVP-capped Pt	I	4.65	$\sim 2.75^{a}$	MPN+TBP	5.28	ITO glass	270 °C, >20 min	Ref. [7]
Chemical deposition	I	487.5	1.72	MPN+TBP	7.29	Ni sheet	67–70°C, 5–20 min	Ref. [12]
^a Value calculated based on the re	eferences' informatio	п.						

I.

Value calculated by 100% current efficiency.

Table 1. Tsekouras et al. [14] demonstrated the cell efficiency can reach ~6.5% with a combination of pulse and constant potential deposition. Yoon et al. [2] employed octaethylene glycol monohexadecyl ether ($C_{16}EO_8$) as a deposition additive to prepare the Pt counter electrodes and achieved a higher efficiency of 7.6%. However, the procedure needs further annealing ($450 \,^{\circ}$ C) to remove the $C_{16}EO_8$ and the total procedure takes more than 2 h. Song et al. [15] further modified the pulse deposition process by using PVP as additive. Nevertheless, the cell efficiency of the DSSC was just 4.28%. The major reason might be due to the shielding effect of the long-chain PVP molecules.

In this article, we proposed a simple, fast (within 30 s) and room-temperature process by means of direct-current deposition in the presence of an additive, Me-EDA-Si generally used as a self-assembly monolayer (SAM) to modify the surface for wide applications, especially in the electronics industry [8,16,17]. The morphology and deposition rate of the Pt counter electrodes were examined by a field-emission scanning electronic microscopy (FESEM). The other characterizations for serving as a counter electrode, such as Pt loading, R_{ct} and the cell efficiency were also carried out.

2. Experimental

2.1. Preparation of Pt counter electrodes

First, the fluorine-doped tin oxide transparent glasses (FTO 13 Ω/\Box , NSG) were ultrasonically cleaned sequentially in detergent, acetone (Mallinckrodt Chemicals) and distilled water (DI water) for 10 min, and then stored in isopropyl alcohol (IPA, ECHO Chemicals). The electrodeposition was carried out with an electrochemical analyzer system, CHI 627C (CH Instruments, USA). All experiments were done in a three-electrode cell, including a Pt plate as counter electrode and an Ag/AgCl electrode as reference electrode (Bioanalytic System, 3 M KCl) and FTO glasses with an exposed area of 0.64 cm² as the working electrode. The base solution consisted of 10 mM of PtCl₄ (Merck) and 0.05 M of HCl (ECHO Chemicals). 3-(2-Aminoethylamino)propyl-methyldimethoxysilane (Me-EDA-Si, Fluka) was served as additive and added to the base solution in concentrations ranging from 0% to 0.5%. A constant current density of 10 mA cm⁻² was employed for electrodeposition.

2.2. Characterization of electrodeposited-Pt counter electrodes

High-resolution filed emission scanning electron microscopy (FE-SEM, Hitachi S4700I) was used to study the morphology of the various Pt electrodes. The Pt loading of the as-prepared electrode was examined by an inductively couple plasma-optical emission spectrometer (ICP-OES, Perkin Elmer Optima-2000DV). Prior to the ICP measurement, the Pt electrodes were placed in agua regia with agitation for 24 h to dissolve the Pt. The contact angle tests were conducted using a digital microscope (AM211, Dinolite Pro.) to investigate FTO surface modification. To further investigate the catalytic activity of the Pt electrodes for tri-iodine reaction, its charge-transfer resistance (R_{ct}) was measured by means of an electrochemical impedance spectroscopy (EIS) with a symmetric test cell with two identical electrodes. These two electrodes were wrapped with thermoplastic hot-melt Surlyn leaving an exposed area of 0.64 cm². The electrolyte for EIS tests contained 0.5 M 4tertpbutylpyridine (Aldrich), 1 M 1,3-dimethylimidazoliumiodine (Merck), 0.15 M iodine (J.T. Baker), and 0.1 M guanidine thiocyanate (Aldrich) in 3-methoxypropionitrile (Acros) solution. The EIS tests were carried out using a computer-controlled electrochemical interface system (Solartron Analytical, SI 1286) and HF frequency response analyzer (Solartron Analytical, SI 1255), and the

Ĩ

The list of various Pt counter electrodes reported for use in DSSCs

Table

Т



Fig. 1. Top-view FESEM images of (a) pure FTO; (b) sputtered-Pt counter electrode; electrodeposited-Pt counter electrodes prepared in the presence of (c) 0vol%; (d) 0.001 vol%; (e) 0.01 vol%; (f) 0.05 vol% and (g) 0.5 vol% Me-EDA-Si, respectively.

impedance data covered frequency range from 0.1 Hz to 100 kHz. In addition, cyclic voltammetric (CV) tests were employed to compare the relative active surface area.

2.3. Preparation of the TiO₂ photoanode

To measure the cell efficiency of DSSC with as-prepared Pt counter electrode, the cell was assembled with TiO₂ photoanode, as previously described [18]. The TiO₂ photoanodes were prepared by screen-printing double-layer TiO₂ with a total thickness of ~14 μ m on the FTO substrate, which were supplied by Tripod Technology and the effective area was 0.283 cm². The first layer as the interlayer was ~12 μ m thick and the second layer with light-scattering anatase TiO₂ particles was ~2 μ m thick. Before the assembly, the TiO₂ photoanodes were immersed into the organic sensitizer N719 (0.3 mM N719 dye in an ethanol solution, Everlight Chemical Industry Co.) solution at 40 °C for 4 h to ensure the dye was adsorbed and totally covered on the TiO₂ photoanodes.

2.4. DSSCs assembly and photovoltaic performance

After dye adsorption, the photoanode was assembled with Pt counter electrode with a hot-pressing machine and thermoplastic Surlyn (30 μ m thick, DuPont) at 120 °C and 3.5 kg cm⁻² pressure. The DSSCs were then ready for cell efficiency tests (photocurrent–voltage curve, *I–V* curve). The electrolyte also used in the EIS test was injected into the cells. The *I–V* curves were measured with a computer-controlled Keithely 2400 source meter under illumination by a Yamashita Denso YSS-150A solar simulator (AM 1.5, 100 mW cm⁻²).

3. Results and discussion

The top-view FE-SEM images of pure FTO glass, sputtered-Pt film and electrodeposited-Pt films are shown in Fig. 1. From Fig. 1a and b, it can be found that the sputtered-Pt deposit is highly bright with



Fig. 2. Top-view FESEM images of electrodeposited-Pt counter electrodes with various deposition time in the base solution containing (a) 0 vol% and (b) 0.01 vol% Me-EDA-Si.

a mirror-like surface and its surface morphology naturally resembles that of pure FTO substrate, which is consistent with previous observation [2]. Fig. 1c shows that the semicircle-like Pt particles were obtained from the base solution. However, the inhomogeneous distribution of Pt particles was observed on the FTO surface even after 30s direct-current deposition. According to Kim et al. [13], the use of dc electrodeposition tended to form dendritic crystal because the formation of nuclei inferior to the growth of existing crystals. Such effect decreased the surface area of Pt counter electrode, eventually resulting in the decay of catalytic activity and cell performance. In contrast, the electrodeposited-Pt electrodes deposited at various concentrations of Me-EDA-Si (Fig. 1d-g) were significantly different from that without Me-EDA-Si. The Pt deposits with highly coarse active surface area were observed from bath with Me-EDA-Si, thus solving the inhomogeneous Pt particle distribution and the dendritic crystal morphology while DC deposition was employed. For the base solution containing 0.001 vol% Me-EDA-Si (Fig. 1d), the film was similar to that deposited in the absence of Me-EDA-Si, but rough surface with non-uniform dispersion could be observed. With 0.01 vol% and 0.05 vol% Me-EDA-Si added, the films became much rougher, and nodular structure with elongated, rod-like grains was observed. The grain size was about 100 nm in length and 30 nm in width. Although these two images seemed similar, there was still some difference between them. Partial aggregation of the nodular structures leads to clustering in the case of 0.05 vol% Me-EDA-Si. With 0.01 vol% Me-EDA-Si in the base solution, the nodular structure was well dispersed and less aggregation was observed on the FTO surface, thus resulting in much more active surface area. When 0.5 vol% Me-EDA-Si was added in the base solution (Fig. 1g), the deposit was charcoal gray with both platelike grains and clusters. The above observation indicates that the electrodeposited-Pt film obtained from the base solution containing 0.01 vol% Me-EDA-Si in 30s direct-current deposition seems more attractive than others because it shows the highest surface area. Moreover, the presence of Me-EDA-Si seems to inhibit the semicircle growth of Pt particles.

The Pt loading was analyzed by an ICP-OES. Apparently, the loading of Pt increased with the increase in the concentration of Me-EDA-Si, as shown in Table 1. The Pt loading in the absence of Me-EDA-Si was only about $1.06 \,\mu g \, \mathrm{cm}^{-2}$. Nevertheless, the deposition was found to speed up while adding Me-EDA-Si into the deposition bath. The more Me-EDA-Si was added, the higher current efficiency was obtained. Fig. 2 presents the FESEM images of electrodeposited-Pt electrodes in the presence (0.01 vol%) and absence (0 vol%) of Me-EDA-Si. There is an apparent discrepancy in the surface morphology for just 2 s deposition. The formation of nuclei with 0.01 vol% Me-EDA-Si was much more than that with-

out Me-EDA-Si. Also we could hardly find any nucleus formation on the FTO surface after 2 s or 5 s electrodeposition. These results imply that Me-EDA-Si may act as an accelerator during Pt electrodeposition as further supported by the following quantitative study. As the Me-EDA-Si concentration increased from 0.001 up to 0.5 vol%, the Pt loading was 2.07 μ g cm⁻², 4.76 μ g cm⁻², 5.25 μ g cm⁻² and 9.66 μ g cm⁻², respectively. A comparison of Pt loading between different coating methods are summarized in Table 1. The Pt loading of the sputtered-Pt electrode was ~100 μ g cm⁻² in this work, certainly much higher than our product. Kim et al. [13] also used direct-current deposition to prepare Pt counter electrode, but the Pt loading was much higher than our sample as shown in Table 1.

Fig. 3 shows the chronopotentiometric studies to investigate the function of Me-EDA-Si during Pt deposition. It can be observed that the depolarization effect can be observed within the first 5 s of electrodeposition while the deposition bath was in the presence of Me-EDA-Si. The overpotential in the presence of 0.01 vol% Me-EDA-Si was less than that obtained in the base solution with the first 5 s of deposition. With further increasing Me-EDA-Si concentration to 0.5 vol%, a very rapid drop in overpotential was found at the interval. Generally, the decrease in the overpotential could facilitate electrodeposition, thus resulting in an enhanced deposition rate [20]. This also indicates that an enhanced deposition rate can be



Fig. 3. (a-c) Chronopotentiometric measurements were conducted on clean FTO substrates in the base solution, base solution containing 0.01 vol% Me-EDA-Si, and base solution containing 0.5% Me-EDA-Si, respectively. (d) Electrodeposition was carried out on the Me-EDA-Si modified FTO in the base solution. The inset figure is the results of contact angle test in the base solution containing 0.01 vol% Me-EDA-Si.



Fig. 4. Schematic of the proposed mechanism of Me-EDA-Si on Pt electrodeposition.

obtained in the presence of ME-EDA-Si, which is in accordance with the finding from ICP-OES results. Therefore, Me-EDA-Si is likely to act as an accelerator during the Pt electrodeposition. To further realize in more detail regarding the function of Me-EDA-Si during electrodeposition, a FTO surface was modified with Me-EDA-Si prior to electrodeposition by dipping it into the solution containing 1 vol% Me-EDA-Si for 10 min and then the electrodeposition in the base solution was carried out. The change in overpotential of the pre-modified FTO substrate similar to that obtained in the base solution containing 0.5 vol% Me-EDA-Si can be observed, as shown in Fig. 3. Based on this result, we proposed that Me-EDA-Si was firstly anchored with the OH⁻ functional group on the FTO surface at the start of the electrodeposition. Moreover, we found that Me-EDA-Si can anchor with the FTO surface in a very short time by means of the contact angle measurement, as shown in the inset of Fig. 3. An obvious increase in the contact angle on the FTO surface was observed no more than 2 s due to the attached Me-EDA-Si, indicating that the interaction between FTO and Me-EDA-Si was very rapid. Consequently, a mechanism of Me-EDA-Si on Pt electrodeposition can be proposed, as schematically shown in Fig. 4. Firstly, Me-EDA-Si compounds diffuse faster than [PtCl₆]²⁻ ions from bulk solution into the diffusion layer in the base solution containing Me-EDA-Si due to the attraction of OH⁻ functional group on the FTO surface. Then Me-EDA-Si compounds can anchor with OH- functional group on the FTO surface [8,16,17] and their amino group can provide the binding sites for the [PtCl₆]²⁻ ions, resulting in attracting more $[PtCl_6]^{2-}$ ions. Thus the deposition rate can be enhanced.

To evaluate the catalytic activity of the Pt electrode toward tri-iodine reaction, EIS analysis was conducted with a symmetric test cell. Based on the theory of EIS, series resistance (R_s) , chargetransfer resistance (R_{ct}) and Nernst diffusion impedance (R_D) could be determined by this method from high-frequency region to lowfrequency region. However, R_{ct} is the most important among these three types to measure the catalytic activity in the early stage. It represents the electron-transfer resistance between the electrolyte and the Pt counter electrode. In general, a smaller R_{ct} indicates a high activity and consequently high cell conversion efficiency. Fig. 5 illustrates the Nyquist plots of the various Pt electrodes. The R_{ct} values of around 5.83, 4.91, 1.39, 2.14 and 2.24 Ω cm² can be obtained while the base solution containing 0 vol%, 0.001 vol%, 0.01 vol%, 0.05 vol% and 0.5 vol% Me-EDA-Si, respectively. The smallest R_{ct} value was observed for the electrode deposited with 0.01 vol% Me-EDA-Si, implying that the electron transferability was more facile from the counter electrode to I3- ion. This also indicates that its catalytic activity is superior to others due to its well-dispersive nodular structure. Furthermore, the R_{ct} of the electrodeposited-Pt electrode with 0.01 vol% Me-EDA-Si was smaller than that of the sputtered-Pt electrode $(2.03 \,\Omega \,\text{cm}^2)$, even with a much lower Pt loading in the former case, implying the catalytic activity of electrodeposited Pt electrode was higher than sputtered Pt electrode because of the former has a relative high surface area.

The $R_{\rm ct}$ values for various Pt counter electrode are also summarized in Table 1. Although the Pt loading increased with increasing concentration of Me-EDA-Si, the $R_{\rm ct}$ did not follow the same tendency. On the contrary, a minimum $R_{\rm ct}$ of $1.39 \,\Omega \,{\rm cm}^2$ was found as 0.01 vol% Me-EDA-Si was added in the base solution. Besides, large $R_{\rm ct}$ might be attributed to insufficient Pt or the relative sparse active surface areas on the counter electrode.

To further confirm the results from SEM and EIS analysis that the counter electrode made by dc deposition in the presence of 0.01 vol% Me-EDA-Si possesses high active surface area, CV analysis was done to characterize the relative active surface areas of the Pt electrodes. Fig. 6 shows the CVs of sputtered-Pt and electrodeposited-Pt electrodes measured in iodine electrolyte at 50 mV s⁻¹ scan rate. It is well-known that the reaction occurs on the counter electrode of DSSCs is $I_3^- + 2e^- \rightarrow 3I^-$. Consequently, only the cathodic reaction is considered in the CV test. According to previous report [7,11], the reaction of I^-/I_3^- redox mediator occurred between -0.4 V and 0.4 V, and thus this interval was chosen as the scan range. In this interval, the anodic peak is contributed by the reaction (1) in an anodic sweep and the cathodic peak is contributed by the reaction (2) in a cathodic sweep, respectively.

$$3I^- \rightarrow I_3^- + 2e^-$$
(Anodicpeak) (1)

$$I_3^- + 2e^- \rightarrow 3I^-(Cathodicpeak)$$
 (2)

As shown in Fig. 4, the oxidation and the reduction peak of I^-/I_3^- for the different electrodes were similar but increased current density can be observed when the electrode was prepared with 0.01 vol% Me-EDA-Si. Compared with these three counter electrodes, the electrodeposited-Pt counter electrode obtained in the



Fig. 5. EIS results for different Pt counter electrodes.



Fig. 6. Cyclic voltammetrics for the sputtered-Pt counter electrode and electrodeposited-Pt counter electrodes prepared in the presence of 0 vol% and 0.01 vol% Me-EDA-Si.

presence of 0.01 vol% Me-EDA-Si as a working electrode indeed demonstrated the largest current density for the reaction of I^-/I_3^- . The superior performance is related to high active surface area as studied by other workers [7,13,19].

The I-V curves of the as-prepared DSSCs are shown in Fig. 7, and the corresponding photovoltaic parameters are listed in Table 1. The performance of the DSSC with Pt counter electrode electrodeposited with 0.01% Me-EDA-Si additive (Pt loading \sim 4.76 µg cm⁻²) shows a short circuit current (J_{sc}) of 17.45 mA cm⁻², open circuit voltage (Voc) 0.68 V, fill factor (FF) 0.62, thus yielding a 7.39% cell efficiency (η) . As for the DSSC with a sputtered-Pt counter electrode (Pt loading $\sim 100 \,\mu g \,\mathrm{cm}^{-2}$), the J_{sc}, V_{oc} and FF were 14.9 mA cm⁻², 0.66 V, and 0.61 and a resultant η of 6.01% Moreover, we noticed that the J_{sc} and the η values of the DSSCs with electrodeposited-Pt counter electrodes increased gradually with the Me-EDA-Si concentration up to 0.01 vol% and then decreased with further addition of Me-EDA-Si. This observation is indeed in consistency with the EIS results. In addition, although the loading of Pt increased with increasing Me-EDA-Si concentration, the cell efficiency reached a maximum when 0.01 vol% Me-EDA-Si was added in the base solution. This might be attributed to the relative highest active surface area in this particular case, as observed from the EIS and CV data,



Fig. 7. I-V curves of the DSSCs assembled with various Pt counter electrodes.

the η value of the DSSC with electrodeposited-Pt counter electrode in the presence of 0.5 vol% Me-EDA-Si in the base solution was only 5.86%. The η value decreased dramatically with higher Pt loading on the FTO surface, indicating that most of the Pt became useless due to Pt aggregation.

Comparison of data as shown in Table 1 further indicates the successful decrease of Pt loading with the use of Me-EDA-Si without loss of high cell efficiency under the similar preparation method. Although there were efficiencies reported higher than 6–7% in the literature, they usually involve optimal combination of all the components in DSSC or usually on a very small substrate. In any case, a higher η (7.39%) for our low Pt-loading counter electrode than the corresponding sputtered-Pt counter electrode (6.01%) means we should be able to further improve our cell efficiency with existing technology.

4. Conclusions

We have developed a process whereby low Pt-loading counter electrode can be prepared in very short period by dc electrodeposition with appropriate addition of Me-EDA-Si. The Me-EDA-Si additive serves as an accelerator so that the counter electrode can be electrodeposited within only 30s. Moreover, the addition of Me-EDA-Si can inhibit the growth of semicircle-like Pt grains, thus resulting in the formation of high active surface area. The DSSC with the electrodeposited-Pt counter electrode prepared in the presence of 0.01 vol% Me-EDA-Si already demonstrated a fairly high cell efficiency of 7.39% with very low Pt loading (~4.76 μ g cm⁻²) in our preliminary experiment without optimization. The improved performance of the DSSC was attributed to the increased relative active surface areas and the small charge-transfer resistance (1.39 Ω cm²). The whole process took only 30s and was under ambient atmosphere, and no high temperature post-annealing was required.

Acknowledgment

The authors are very grateful to the National Science Council in Taiwan for its financial support under Contract No. NSC-99-2221-E-036-038.

References

- [1] M. Grätzel, Nature (London) 414 (2001) 338.
- [2] C.H. Yoon, R. Vittal, J. Lee, W.S. Chae, K.J. Kim, Electrochim. Acta 53 (2008) 2890.
- [3] Z. Huang, X. Liu, K. Li, D. Li, Y. Luo, H. Li, W. Song, L. Chen, Q. Meng, Electrochem. Commun. 9 (2007) 596.
- [4] G. Calogero, F. Bonaccorso, O.M. Marago, P.G. Gucciardi, G.D. Marco, Dalton Trans. 39 (2010) 2903.
- [5] K.M. Lee, W.H. Chiu, H.Y. Wei, C.W. Hu, V. Suryanarayanan, W.F. Hsieh, K.C. Ho, Thin Solid Films 218 (2010) 1716.
- 6] J.G. Chen, H.Y. Wei, K.C. Ho, Sol. Energy Mater. Sol. Cells 91 (2007) 1472.
- [7] J.L. Lan, Y.Y. Wang, C.C. Wan, T.C. Wei, H.P. Feng, C. Peng, H.P. Cheng, Y.H. Chang, W.C. Hsu, Curr. Appl. Phys. 10 (2010) s168.
- [8] C.Y. Lin, J.Y. Lin, J.L. Lan, T.C. Wei, C.C. Wan, Electrochem, Solid State Lett. 13 (2010) D77.
- [9] N. Papageorgiou, W.F. Maier, M. Gratzel, J. Electrochem. Soc. 144 (1997) 876.
 [10] M. Toivola, J. Halme, K. Miettunen, K. Aitola, P.D. Lund, Int. J. Energy Res. 33
- (2009) 1145. [11] T.C. Wei, C.C. Wan, Y.Y. Wang, C.C. Chen, H.S. Shiu, J. Phys. Chem. C 111 (2007) 4847
- [12] C.M. Chen, C.H. Chen, T.C. Wei, Electrochim, Acta 55 (2010) 1687.
- [13] S.S. Kim, Y.C. Nah, Y.Y. Noh, J. Jo, D.Y. Kim, Electrochim. Acta 51 (2006) 3814.
- [14] G. Tsekouras, A.J. Mozer, G.G. Wallace, J. Electrochem. Soc. 155 (2008) K124.
- [15] Y.J. Song, J.K. Oh, K.W. Park, Nanotechnology 19 (2008) 355602.
- [16] P.C. Hidber, W. Helbig, E. Kim, G.M. Whitesides, Langmuir 12 (1996) 1375.
- [17] D. Qu, K. Uosaki, Chem. Lett. 35 (2006) 258.
- [18] H.R. Jhong, D.S. Wong, C.C. Wan, Y.Y. Wang, T.C. Wei, Electrochem. Commun. 11 (2009) 209.
- [19] P. Li, J. Wu, J. Lin, M. Huang, Z. Lan, Q. Li, Electrochim. Acta 53 (2008) 4161.
- [20] M. Tan, J.N. Harb, J. Electrochem. Soc. 150 (2003) C420.