A NEW COUNTER ELECTRODE BASED ON COPPER SHEET FOR FLEXIBLE DYE SENSITIZED SOLAR CELLS

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A new type counter electrode (CE) for flexible dye-sensitized solar cells (DSSC) has been fabricated using an industrial flexible copper (Cu) sheet as substrate and graphite as the catalytic material which applied by spraying method. Photovoltaic parameters like short circuit current (I_{SC}), open circuit voltage (V_{OC}) and fill factor (FF) were evaluated for fabricated cells. DSSCs with cell areas of 1 cm^2 fabricated with new type CE show higher solar-to-electricity conversion efficiency. The respective values are 5.29% and 3.38% for the graphite/ITO polymer based devices.

(Received August 6, 2010; accepted August 26, 2010)

Keywords: Flexible dye sensitized solar cells (DSSC), new counter electrode (CE), conversion efficiency (η)

1. Introduction

During the past two decades, dye-sensitized solar cells (DSSC) have emerged as one of the most promising candidates for useful photovoltaic applications in good quality of their low manufacturing cost and relatively high efficiency to convert solar energy into electricity [1-3]. Typically, a DSSC comprises a dye-covered nanocrystalline TiO_2 (titanium dioxide) electrode, electrolyte solution usually with a dissolved iodide/triiodide redox couple between the electrodes, and a counter electrode (CE). The total efficiency of the dye-sensitized solar cells depends on the optimization and compatibility of each of these constituents. The function of the CE is to transfer electrons arriving from the external circuit back to the redox electrolyte and to catalyze the reduction of the triiodide ion [4, 5]. Usually, Pt is used as the catalytic material and fluorine-doped tin oxide (FTO) glass or indium tin oxide (ITO) polymer as the substrate for a CE [1–5]. Although Pt exhibits excellent catalytic activity for electrolyte reduction and good electric conductivity, it is extremely expensive and has the problem of reserves for large scale application [6, 7]. The shape limitation and fragile feature will bring transport problem for the FTO glass based DSSCs [8]. Future large solar electric conversion systems will prefer materials plentifully available and easily handled. Therefore, it is necessary to develop inexpensive materials for CEs which also exhibit high electrical conductivity, good chemical stability and good catalytic activity to the reduction of electrolyte.

So far, cheap carbonaceous materials such as graphite, carbon black, activated carbon, hard carbon sphere, carbon nanotube, fullerene and graphene, have been employed as the catalytic materials on ITO polymer for the CEs [6, 7]. Meanwhile, novel substrates such as plastic foils have been used to fabricate flexible CEs to achieve the requirement for portable electricity and high-throughput industrial roll-to-roll production [8, 9]. However, the efficiency of the DSSC with

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this substrate is low and the improvements of their long time stability are also imperative for future large scale production.

Industrial copper sheet as substrate for graphite has very good electrical conductivity, high temperature resistance, low electrical resistance and good flexibility, which make it a good candidate to fabricate electrode. Both substrate and catalytic material are inexpensive materials, which give a good adhesion between the catalytic material and the substrate. The flexible DSSCs with this CE show better performance than graphite/ITO polymer based devices.

In this paper, we investigate performance graphite counter electrode based on copper sheet by current–voltage (I–V). The results are compared with graphite/ITO counter electrode based on polymer substrate, at similar condition.

2. Experimental

2.1. Preparation of counter electrodes

Copper substrates with cell areas of 1 cm^2 were cleaned in an ultrasonic bath (Elmasonic E 60H) with acetone and ethanol (50:50 V/V %) at 60°C for 1 hour and then air-dried. Transparent flexible substrates (Polyethylene terephthalate (PET), Indium Tin Oxide, (ITO) In_2O_3:SnO_2 2.5 cm × 2.5 cm, solaronix) were sonicated under same condition.

New type counter electrode with 50 µm thickness were produced by spraying graphite 33 (Kontakt Chemie) on the flexible copper sheet. The counter electrode was then put in the oven at 150°C for 24 h.

Graphite counter electrode based on ITO polymer substrate was prepared by similar method.

2.2. Flexible DSSC fabrication

For preparation of photoelectrode, normal doctor blade technique was applied to fabricate the TiO_2 film [11]. Firstly, ITO with surface resistivity ~60 Ω/sq were sonicated with acetone and ethanol (50:50 V/V %) at 60°C for 1 h. Subsequently, TiO_2 paste(Ti-Nanoxide D-L series, solaronix) was sonicated for 1 h to form an easily mobilized gel and then a little of the gel was spread onto a transparent flexible substrates in advance surrounded with a adhesive 3M tapes (having a thickness of ~50 µm) as spacers. The prepared photo electrode was placed in the oven (Memert UFE 500) and sintered at 120°C for 24 hours. The photoelectrode were sensitized by immersing them in ruthenium dye solution (535-bisTBA, Solaronix) for 24 h. Dye solution was prepared by dissolving 20 mg of Ruthenium 535-bisTBA in 100 ml ethanol 99.9% (Merck). The immersed TiO_2 electrode in dye Ruthenium 535-bisTBA was removed and rinsed with ethanol and was dried at room temperature for 1 hour. The immersed TiO_2 electrode in dye solution was removed and rinsed with ethanol and dried at room temperature for 1 h. The dye-covered nanocrystalline TiO_2 film and the counter electrodes were assembled into sealed sandwich-type cells applying one drop of electrolyte (MPN-100) and sealing with Amosil 4.

2.3. Measurements

The photocurrent-voltage characteristics were measured with a potentiostat (chi660a) under illumination. A 1000 W Xenon lamp was employed as the light source in conjunction with an IRA-25S filter (Schott, USA) to get rid of the UV light. The light intensity corresponding to AM 1.5 (100 mW/cm2) was calibrated using a standard silicon solar cell. The scanning electron microscopy (SEM Philips XL30) image of the top view of CE was obtained with a SEM Philips XL30 model.

3. Results and discussion

3.1. Sheet resistance

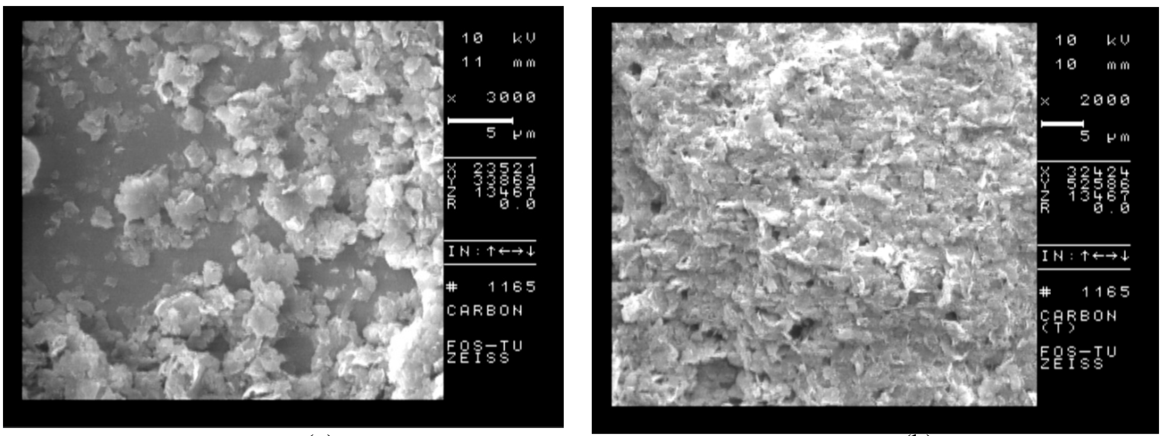
Electrical resistance of counter electrode is an important factor to influence DSSC's efficiency. The high resistances of the substrate for electrode lessen the fill factor of the cell as result reduce photoelectrical conversion efficiency. As seen from Table 1, the resistance of platinum counter electrode is about 20 Ω/sq, while the resistance of new counter electrode we designed is only 2Ω/q. This would cause decreased effect to cells' efficiency.

Table.1. Square resistance comparison of both counter electrodes.

Counter electrode	Cu/ graphite	ITO/ graphite
Sheet resistance (Ω/q)	2	20

3.2. Morphology of new counter electrode

Fig.1 shows scanning electron microscopy image of the surface graphite film coated on copper sheet before and after sintering process. The film is about 50μm thick and the graphite have homogenously and sponge-like structure on copper sheet after sintering process. As it is shown in Fig.1 no fracture on the surface of the coated layer after sintering is seen indicating excellent inter-particle connectivity.



(a) (b)

Fig.1 SEM images of new type counter electrode (a) before and (b) after sintering.

3.3. Adhesion Test

Evaluating the mechanical properties of thin films is a difficult task. We believe that adhesion test is probing the Cu/graphite and ITO/Graphite interface. As can be seen from Fig. 2, the ITO/graphite film is detached much faster upon sonication than Cu/ graphite film. The loss of graphite on ITO substrate is observed during the sonication test and only bare graphite on Cu substrate that apparent when observed either in the microscope fringes. Therefore, we infer that it is the ITO/graphite interface that constitutes the weakest point of the structure and that is disrupted first by the ultrasound treatment. This result is that we used of Cu substrate as counter electrode for flexible DSSCs. Correlation between these observations and the long-term stability of photo electrochemical cells based on these films remains to be done.

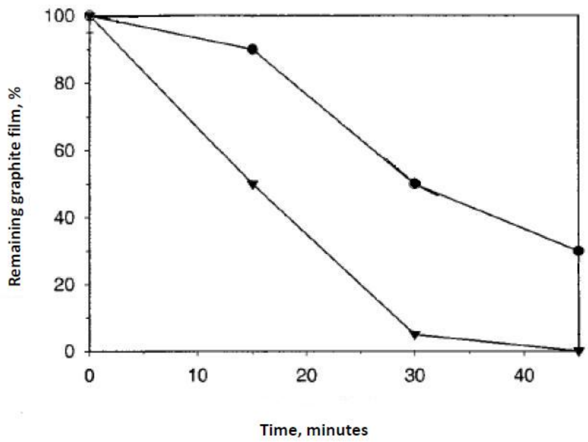


Fig.2 *Results of the adhesion test performed by sonication of the graphite films in water: ▲Cu / graphite film; ● ITO/ graphite films;*

3.4. Photovoltaic performance

The I-V curve for two fabricated cells with different counter electrode is shown in Fig .3.

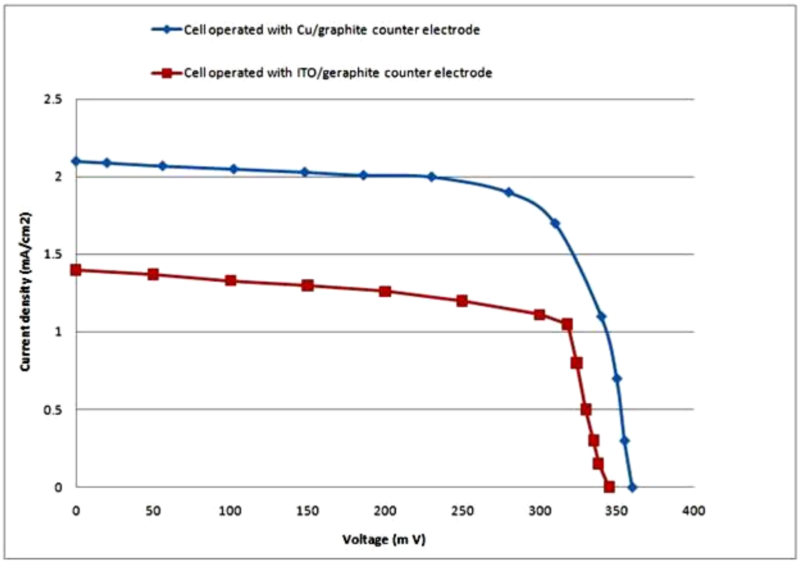


Fig. 3. Photocurrent–voltage characteristics for flexible DSSC with different counter electrode measured under illumination of 100mWcm−2 (AM 1.5).

The fill factor for DSSC was calculated from equation (1) where P_{max} is the maximum electrical power obtained; I_{SC} and V_{OC} are the short-circuit current density and open-circuit voltage, respectively.

$$FF = \frac{P_{max}}{I_{sc} \times V_{oc}} \quad (1)$$

The conversion efficiency of the dye sensitized solar cell is obtained from equation (2) Where I is the intensity of incident light; A is the active area illuminated by halogen lamp [12].

$$\eta = \frac{Isc \times Voc \times FF}{I \times A} \quad (2)$$

The values of V_{OC}, I_{SC}, FF and cell efficiency (η) for both cells with different counter electrode of active area 1cm^2 illuminated by a halogen lamp with an incident light of 100 $mWcm^{-2}$ are shown in Table2. As seen in table the FF values for both cells with different counter electrode are equal, and types of counter electrode used in this work have no effect on FF. The use of Cu/graphite counter electrode facilitates the electron transfer process to regenerate the electrolyte in the cell explaining the higher I_{SC}, V_{OC} and η values over the ITO/graphite counter electrode.

Table.2. Photovoltaic performance for fabricated cells.

Fabricated flexible DSSC	**V_{OC} (mV)**	**I_{SC} (mA/cm^2)**	**FF**	**η**
Cell operated with ITO/graphite counter electrode	345	1.40	70	3.38
Cell operated with Cu/graphite counter electrode	360	2.10	70	5.29

4. Conclusions

A new type counter electrode consisting of copper substrate, high conductive, low electrical resistance, and catalyzed graphite film was proposed in this paper. This kind of new counter electrode has advantages of simple preparation, low cost, low resistance and good adhesion, which can improve obviously photoelectric conversion efficiency from 3.38% to 5.29%.

Acknowledgment

This research is financially supported by Iranian Research Organization for Science and Technology (IROST), Iran. The authors would like to thank college of science, University of Tehran for preparing gold sputtering counter electrode and SEM images.

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