

Short communication

Tandem dye-sensitized solar cell-powered electrochromic devices for the photovoltaic-powered smart window

Kwang-Soon Ahn^{a,*}, Sung Jong Yoo^c, Moon-Sung Kang^b,
Ji-Won Lee^b, Yung-Eun Sung^c

^a Energy Laboratory, Corporate R&D Center, Samsung SDI Co., Gyeonggi-do 449-577, South Korea

^b Energy and Environment Lab., Samsung Advanced Institute of Technology (SAIT), Gyeonggi-do 446-712, South Korea

^c School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, South Korea

Received 20 October 2006; received in revised form 15 December 2006; accepted 19 December 2006

Available online 12 March 2007

Abstract

Tandem dye-sensitized solar cell (DSSC)-electrochromic (EC) devices were realized using two-faced transparent conducting oxide (TCO). To supply sufficient voltage to drive the EC devices, two series connected, semitransparent DSSCs were fabricated with 7 nm-thick, dye-adsorbed TiO₂ and 4 nm-thick Pt layers. The two series connected, semitransparent DSSCs that were used had an open circuit voltage and short circuit current density of about 1.35 V and 3.96 mA cm⁻², respectively, at 1-sun. The tandem DSSC-EC devices showed an optical density difference of 1.2 at 750 nm and reasonable response times of about 60 and 45 s during the coloring and bleaching processes, respectively, indicating that the two series-connected, semitransparent DSSCs could be used as the power sources in the tandem photovoltaic-powered EC devices.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Dye-sensitized solar cell; Electrochromic device; Photovoltaic; Optical density difference; Response time

1. Introduction

The interest in the application of photovoltaic (PV) cells to low power devices such as small electronic devices and electrochromic (EC) devices has grown considerably, because of the striking energy savings which they allow [1–6]. PV-EC devices have two types of structures, viz. side-by-side and tandem structures. Benson et al. [2] reported that both designs are attractive and can reduce the installation cost of the EC windows by reducing or eliminating the electrical wiring and electrician labor costs. The PV cell is located around the perimeter and over the entire area of the EC window for the side-by-side and tandem structures, respectively. The bleached transmittance of the tandem Si-based PV-EC devices was less than that of the side-by-side devices [3,5,6], because the sunlight passes through both components in the tandem structures. Nevertheless, the tandem

structure may have other advantages, such as the fact that the PV cells may be used as an “energy window”, as well as the power sources of the EC devices.

Dye-sensitized solar cells (DSSCs) are known as one of the promising types of PV cells for use as energy windows [7–10], because they are less expensive and can be easily scaled up to large-area devices. The DSSC consists of a dye-sensitized TiO₂ layer, a Pt catalyst layer, and an electrolyte containing a redox couple (I^-/I_3^-) between them. When a DSSC is illuminated by sunlight, the adsorbed dye molecules on the surface of the mesoporous TiO₂ absorb the light and become excited. The absorption of light by the dye is followed by the injection of an electron from the excited state of the dye to the conduction band of the TiO₂ and its subsequent transfer to the transparent conducting oxide (TCO). Finally, the electron flows through the external circuit. The transparency of the DSSCs may be improved by developing adequate dye molecules and counter catalysts. On the other hand, Si-based PV cells have an intrinsic problem. Inorganic semiconductors like Si absorb intrinsically all wavelengths that correspond to energies above their energy bandgap. Therefore, the only solution to improve their transparency is to decrease the thickness of the Si-based PV cell. Gao et al. [6] reported

* Corresponding author. Present address: National Center for Photovoltaics, National Renewable Energy Laboratory, Golden, CO 80401, USA.
Tel.: +1 303 384 6469; fax: +1 303 384 6491.

E-mail addresses: kwang-soon.ahn@nrel.gov, kstheory@paran.com (K.-S. Ahn).

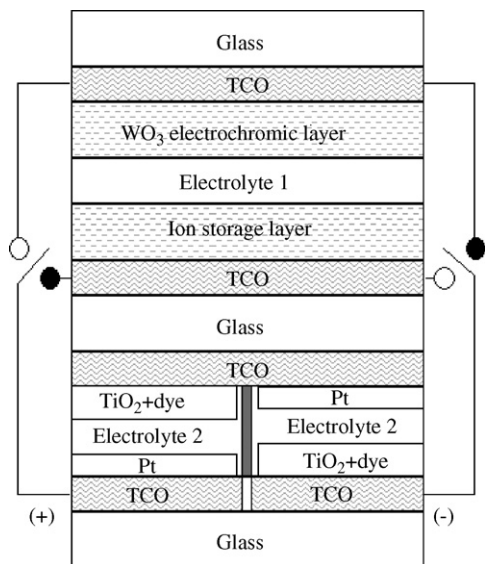


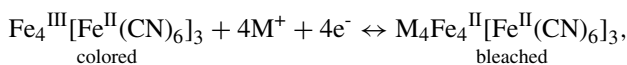
Fig. 1. Schematic diagram of tandem DSSC-EC device.

that the bleached transmittance of the tandem PV-EC cell was below 35%, even when the PV thickness was reduced to about 60 nm. Further more, this extremely thin thickness may result in serious problems, such as electrical short circuits, which make it difficult to produce large-area devices. Therefore, the tandem structure with the DSSC and EC devices is expected to be more useful than the tandem Si-based PV-EC devices.

The tandem DSSC-EC device requires a transparent DSSC that outputs enough voltage to drive the EC device. The mesoporous TiO_2 layer in the DSSCs is able to make it transparent, because of its wide bandgap of about 3.4 eV. The DSSC's transparency may be significantly affected by the kind and amount of dye molecules used to absorb the light. The former is related to the absorption property of the dye molecule itself and the latter is related to the physical treatment of the mesoporous TiO_2 layer. The amount of the attached dye molecules may be reduced by decreasing the thickness of the mesoporous TiO_2 layer. However, reducing the amount of dye molecules may decrease the performance of the DSSC, due to the generation of a lower number of electron-hole pairs. Therefore, the use of highly efficient dye molecules would make it possible to obtain more transparent, highly efficient DSSCs. In addition, a semitransparent Pt layer with a thickness of a few nanometer can be used, which would provide sufficient room to make several types of DSSC module. EC devices typically operate above 1 V [11,12], but the single DSSC can only provide about 0.7 V, because the open circuit voltage (V_{oc}) is determined by the potential difference between the conduction band level of the TiO_2 and the redox couple. Therefore, two series-connected DSSCs are required in order to provide a high enough operating voltage for the EC device.

In this paper, tandem DSSC-EC devices were fabricated using two-faced transparent conducting oxide (TCO), as shown in Fig. 1, in which two series-connected DSSCs were used and a WO_3 layer and prussian blue (PB) were used as the electrochromic (EC) and ion storage (IS) layers, respectively, for the

complementary EC devices. The generally accepted EC switching principles are as follows: [13]



where M^+ can be Li^+ , K^+ , or H^+ . The two series-connected DSSCs provided a driving voltage of about 1.35 V which is sufficient for the EC device of the WO_3 -PB system. The self-powered EC devices also had an optical density difference (ΔOD) of about 1.2 at 750 nm and reasonable response times of about 60 and 45 s during the coloring and bleaching processes, respectively, indicating that the tandem DSSC-powered EC devices would be useful for PV-powered smart windows.

2. Experimental

The tandem DSSC-EC devices were fabricated as shown in Fig. 1. Two DSSCs were connected in series in order to provide a high enough driving voltage for the EC devices. One-faced and two-faced SnO_2 on glass (Asahi glass Co., $10 \Omega \square^{-1}$) were used as the transparent conducting oxide (TCO). The one-faced SnO_2 layer was etched using a laser etching system for the fabrication of the two series-connected DSSCs. The transparent, mesoporous TiO_2 films (film thickness: 7 μm , active area: 24 cm^2) were prepared by sintering TiO_2 paste (ST21, Ishihara Sanyo Co.)-coated layers on the TCOs at 450 $^\circ\text{C}$ for 30 min, for which the detailed process is described elsewhere [14]. The mesoporous TiO_2 films were then cooled to 80 $^\circ\text{C}$ and immersed in an ethanol solution of a ruthenium-complex (N719, Solaronix Co.) over-night to allow for the adsorption of the dye, followed by rinsing in ethanol and drying in a 50 $^\circ\text{C}$ oven. The semitransparent, 4 nm-thick Pt layers were deposited using a sputtering system. The edges of the cell and the etched part on the TCO were sealed and separated with a 60 μm -thick Surlyn (Dupont Co.). The electrolyte (referred to as electrolyte 2 in Fig. 1) was then introduced into the cell, which was composed of 0.6 M 1-propyl-3-methyl imidazolium iodide, 0.05 M iodine, 0.05 M LiI, and 0.5 M 4-tert butylpyridine in acetonitrile.

The EC devices (active area: 25 cm^2) were fabricated on the opposite TCO side of the two series-connected DSSC. WO_3 films were deposited using a sputtering system with a W metal target. WO_3 sputtering was performed under pure O_2 at a working pressure of 2×10^{-2} Torr. The WO_3 films were sputterdeposited at an RF power of 100 W for 60 min at room temperature (RT), for which the detailed process was described elsewhere [11,12]. The PB layers were electrochemically deposited in an aqueous solution containing 0.1 M KCl, 0.1 M HCl, 5 mM $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$. The TCO was cathodically polarized at a current density of 30 $\mu\text{A cm}^{-2}$ to form the PB layers, the detailed description of which was mentioned elsewhere [13]. The thicknesses of the WO_3 and PB layers were about 400 and 300 nm, respectively, as determined by a laser profilometer (NanoFocus Co., μ -scan). Before assembling the EC and IS layers, one electrode should be pre-charged with protons for the complementary EC device [11–13].

We previously reported that the EC devices initially prepared from fully bleached EC and IS layers for the charge-unbalanced EC devices could provide good bleached-state transmittances over a wide range of charge capacity ratios ($R = Q_{IS}/Q_{EC}$, where Q_{IS} and Q_{EC} are the charge capacities of the IS and EC layers, respectively) and were less sensitive to the R value [12]. Therefore, the electrodeposited PB layers were fully bleached before assembling the EC and IS layers. The pre-charging of the PB layers was performed at a current density of 0.1 mA cm^{-2} in a $5 \text{ mM H}_2\text{SO}_4$ aqueous electrolyte and the R value was 1.2. Finally, the complementary EC devices were fabricated by laminating with the sulfonated styrene-(ethylene-butylene)-styrene triblock copolymer that was used as the electrolyte (referred to as the electrolyte 1 in Fig. 1), following a procedure described elsewhere [11,12,15].

Photocurrent–voltage (I – V) measurements of the two series-connected DSSCs were performed using an AM 1.5 solar simulator (Eko Co., MP-160) and a Xenon lamp (100 mW cm^{-2}) as a white light source. The transmittance spectra of the tandem DSSC-EC devices were measured after the coloring and bleaching processes under 1-sun illumination, and their in situ transmittance (633 nm) was also measured to evaluate the EC response time, which was described in detail elsewhere [16,17].

3. Results and discussion

Fig. 2 shows the photocurrent–voltage (I – V) curve of the two series-connected DSSCs under 1-sun illumination. The open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF), and efficiency of the two series-connected DSSCs used here were 1.35 V, 3.96 mA cm^{-2} , 0.54, and 2.9%, respectively. Therefore, the V_{oc} (1.35 V) of the two series-connected DSSCs can provide a high enough voltage to drive the EC devices. The low cell efficiency of 2.9% may be caused by the low I_{sc} value. It is known that the I_{sc} value can be increased by increasing the amount of adsorbed dye and the Pt thickness [7–10,18]. However, semitransparent DSSC is required for tandem DSSC-EC devices and the amount of adsorbed dye and the thickness of the Pt layer were therefore minimized by reducing the thicknesses of the mesoporous TiO_2 layer ($7 \mu\text{m}$) and Pt layer (4 nm), thus leading to the low I_{sc} value and cell efficiency. Nevertheless, this I_{sc} value could provide enough current density to oper-

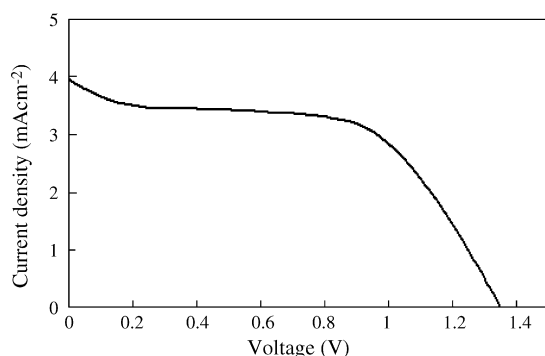


Fig. 2. Photocurrent–voltage curve of two series connected DSSCs under 1-sun illumination.

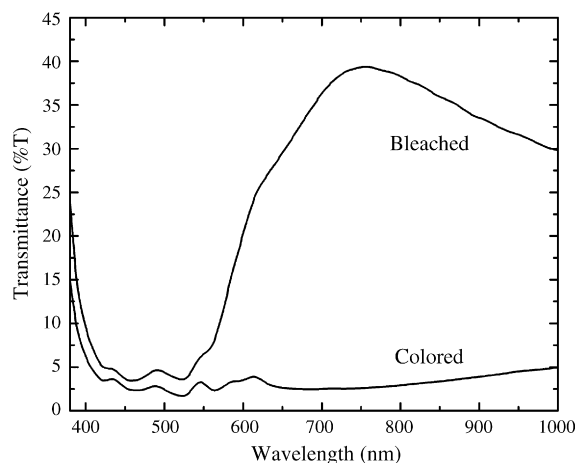


Fig. 3. Transmittance spectra of tandem DSSC-EC device after the coloring and bleaching processes under 1-sun illumination.

ate the EC devices at a reasonable speed, as will be discussed later.

Fig. 3 shows the transmittance spectra of the tandem DSSC-EC device obtained after the coloring and bleaching processes under 1-sun illumination, in which the 100% transmittance was calculated relative to that of air. The bleached-state transmittance below 650 nm was remarkably decreased due to the light absorption of the dye molecules in the DSSC, indicating that the transmittance could be increased by using a smaller amount of dye or a dye which absorbs in the UV range. The tandem DSSC-EC device had a good transmittance change (ΔT) and ΔOD of 36.7% and 1.2 at 750 nm, respectively, indicating that the two series-connected, semitransparent DSSCs can be used as the power sources in the tandem PV-powered EC devices.

The in situ transmittance (633 nm) was also measured to evaluate the response time during the coloring and bleaching processes of the tandem DSSC-EC device. Fig. 4 shows the in situ transmittance curve of the tandem DSSC-EC device during the coloring and bleaching processes under 1-sun illumination, where (–) switching means that it is switched in the solid circle and (+) switching means that it is switched in the open circle in Fig. 1. The tandem DSSC-EC device had reasonable response times of about 60 and 45 s during the coloring and bleaching processes, respectively. The I_{sc} value of the two series-

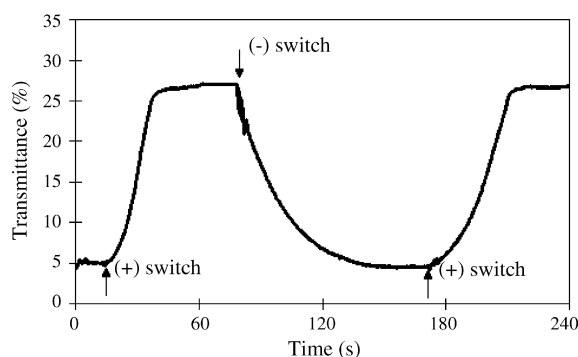


Fig. 4. In situ transmittance (633 nm) curve of tandem DSSC-EC device during the coloring and bleaching processes under 1-sun illumination.

connected DSSCs may affect the EC response speed [19]. For the EC device employed, a charge capacity of 23 mC cm^{-2} was required to finish the coloring or bleaching process. Therefore, to have a response time of about 45 s, a current density of only about 0.5 mA cm^{-2} from the two series-connected DSSCs was required, indicating that the I_{sc} value of the two series-connected DSSCs in Fig. 2 could provide enough current to operate the EC device. It also indicates that other, as yet unknown, rate-limiting factors exist. Bechinger et al. reported that the response speed of an EC device is proportional to the coloration current, I [3]. The coloration current in an EC device can be expressed as the following equation[3]:

$$I = \frac{V_e}{R_t} = \frac{[V_a - (\phi_{\text{IS}} - \phi_{\text{EC}}) - V_b]}{R_t}$$

where V_e is the effective coloring voltage, V_a the applied voltage, V_b the sum of all of the interface barriers, and R_t is the sum of the resistances in the various layers. ϕ_{IS} and ϕ_{EC} are the internal chemical potential differences of the IS and EC layers in the EC device, respectively, and the fundamental factor. Therefore, the response time is strongly dependent on the V_b and R_t values. In this experiment, the SnO_2 TCO substrate initially had a sheet resistance of $10 \Omega \square^{-1}$, as measured by a four-point probe. However, it was significantly increased to $24 \Omega \square^{-1}$ after the sintering of the mesoporous TiO_2 layers at 450°C , leading to an increase of the R_t value. Therefore, the significantly increased sheet resistance of the substrate may act as the rate-limiting factor and increase the response time of the EC device. Detailed studies of this issue are currently underway.

4. Conclusions

Tandem DSSC-EC devices were fabricated, in which two series-connected, semitransparent DSSCs were used in order to provide a high enough driving voltage for the EC devices. Although the two series-connected, semitransparent DSSCs had low cell efficiency and I_{sc} values due to the decreased amount of absorbed dye and 4 nm-thick Pt layer, the tandem DSSC-EC device showed a ΔOD of 1.2 at 750 nm and reasonable response times of about 60 and 45 s during the coloring and bleaching processes of the EC device, respectively, indicating that the two series-connected, semitransparent DSSCs can be used as the power sources in the tandem PV-powered EC devices. Although

more detailed studies and optimization of the tandem DSSC-EC devices are required, we expect that they will be useful as tandem PV-powered EC windows with a reasonable ΔOD and response time.

Acknowledgements

This work was supported by Sol–Gel Innovation Project from the Ministry of Commerce, Industry and Energy in Korea. Yung-Eun Sung thanks Korean Science and Engineering Foundation (Grant Number R01-2004-000-10143) for the financial support.

References

- [1] F. Pichot, J.R. Pitt, B.A. Gregg, *Langmuir* 16 (2000) 5626.
- [2] D.K. Benson, H.M. Branz, *Sol. Energy Mater. Sol. Cells* 39 (1995) 203.
- [3] C. Bechinger, J.N. Bullock, J.-G. Zhang, C.E. Tracy, D.K. Benson, S.K. Deb, H.M. Branz, *J. Appl. Phys.* 80 (1996) 1226.
- [4] C. Bechinger, S. Ferrere, A. Zaban, J. Sprague, B.A. Gregg, *Nature* 383 (1996) 608.
- [5] J.N. Bullock, C. Bechinger, D.K. Benson, H.M. Branz, *J. Non-cryst. Solids* 198 (1996) 1163.
- [6] W. Gao, S.H. Lee, J. Bullock, Y. Xu, D.K. Benson, S. Morrison, H.M. Branz, *Sol. Energy Mater. Sol. Cells* 59 (1999) 243.
- [7] B. O' Regan, M. Grätzel, *Nature* 353 (1991) 737.
- [8] M.K. Nazzerruddin, A. Kay, I. Podicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* 115 (1993) 6382.
- [9] H. Kim, G.P. Kushto, C.B. Arnold, Z.H. Kafafi, A. Piqué, *Appl. Phys. Lett.* 85 (2004) 464.
- [10] L. Schmidt-Mende, S.M. Zakeeruddin, M. Grätzel, *Appl. Phys. Lett.* 86 (2005) 013504.
- [11] K.S. Ahn, Y.C. Nah, Y.-E. Sung, K.Y. Cho, S.S. Shin, J.K. Park, *Appl. Phys. Lett.* 81 (2002) 3930.
- [12] K.S. Ahn, Y.C. Nah, Y.-E. Sung, K.Y. Cho, S.S. Shin, J.K. Park, *Appl. Phys. Lett.* 82 (2003) 3379.
- [13] L.C. Chen, K.C. Ho, *Electrochim. Acta* 46 (2001) 2151.
- [14] K.S. Ahn, M.S. Kang, J.K. Lee, B.C. Shin, J.W. Lee, *Appl. Phys. Lett.* 89 (2006) 013103.
- [15] V.I. Basura, C. Chuy, P.D. Beattie, S. Holdcroft, *J. Electroanal. Chem.* 501 (2001) 77.
- [16] K.S. Ahn, Y.C. Nah, Y.-E. Sung, *Solid State Ionics* 156 (2003) 433.
- [17] K.S. Ahn, Y.C. Nah, Y.-E. Sung, *Solid State Ionics* 165 (2003) 155.
- [18] S. Ito, T. Kitamura, Y. Wada, S. Yanagida, *Sol. Energy Mater. Sol. Cells* 76 (2003) 3.
- [19] S.K. Deb, S.H. Lee, C.E. Tracy, J.R. Pitts, B.A. Gegg, H.M. Branz, *Electrochim. Acta* 46 (2001) 2125.