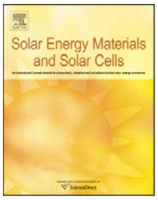
Solar Energy Materials & Solar Cells 96 (2012) 86–92

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

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



“Partly covered” photoelectrochromic devices with enhanced coloration speed and efficiency

G. Leftheriotis*, G. Syrrokostas, P. Yianoulis

Energy and Environment Lab, Physics Department, University of Patras, Rion 26500, Greece

A R T I C L E I N F O

Article history:
Received 22 July 2011
Accepted 8 September 2011
Available online 1 October 2011

Keywords:
Photoelectrochromics
Tungsten oxide
Titanium oxide
Solar control

A B S T R A C T

This work comprises an experimental study of photoelectrochromic (PEC) devices for dynamic solar control in buildings. In an effort to overcome the performance limitations of “fully covered” PEC devices in which a thin, transparent TiO_2 layer covers the entire device area, we have developed the “partly covered” PEC type, with an opaque 5 μm thick TiO_2 film covering only a fraction of WO_3 area on one end of the device. It was found that the partly covered devices are transparent in the visible (with luminous transmittance up to 51%), exhibit rapid coloration (~3 min) upon solar irradiation in open circuit conditions and achieve a considerable transmittance modulation (up to 10.2:1). Various TiO_2 to WO_3 area ratios were tried ranging from 0.23 to 0.48. Reduction of the area ratio decreases the speed of coloration but it does not affect neither the coloration homogeneity nor the end coloration result. Use of the N3 Ruthenium dye has led to substantial photo-coloration efficiencies (up to 4 times more than those achieved with Rhodamine B) and improved the durability of the devices.

1. Introduction

Photoelectrochromic devices (PEC) are hybrids of electrochromics (EC) and dye-sensitized solar cells (DSSC). They are intended for use in buildings in order to combine dynamic control of daylight through windows with solar energy production.

They were first presented in [1–4], as electrochemical cells consisting of two electrodes separated by a redox electrolyte, an electrochromic and a dye-sensitized photovoltaic one, the latter powering the coloration of the former, in response to the incoming solar radiation. A different configuration with both electrochromic and photovoltaic layers on one electrode (as shown in Fig. 1) has been proposed as a better alternative [5,6].

Since then, modified designs and novel material combinations have been used in order to enhance device performance and stability [7–10].

A typical PEC device layout is shown in Fig. 1. It consists of

1. A glass coated with a transparent conductive oxide (such as SnO_2:F or Indium Tin Oxide).
2. An electrochromic (EC thereafter) layer of optical quality (usually WO_3).
3. A nano-structured wide band gap semiconductor film (usually TiO_2) sensitized by an appropriate dye.
4. An electrolyte with high ionic and low electronic conductivity that contains a redox couple (such as I^-/I^{3-}) and Li ions.
5. A counter electrode consisting of a transparent conductive oxide with a thin Pt layer.

Parts 1, 3, 4 and 5 of the above device comprise a dye-sensitized solar cell [24] that provides the electrical potential for the coloration of the EC layer. The PEC device operation involves six different processes shown (in parentheses) in Fig. 1. They are: absorption of photons by the dye (1), injection of electrons into TiO_2 (2) and diffusion into WO_3, intercalation of Li^+ into the WO_3 layer (3) for charge equilibration, causing coloration of the WO_3 film [12] under open circuit. Under short circuit in the dark, electrons reduce I^{3-} at the counter electrode (4). Then, I^- reduces the dye molecules (5), Li^+ is transferred back to the electrolyte (6) and the WO_3 film is bleached.

In our earlier work, [11] we have developed “fully covered” PEC devices in which a thin, transparent TiO_2 layer covers the entire device area. In this type, each layer has to be designed for maximizing the device transparency without hampering its functionality, as described in [11]. The requirement for high transmittance in the bleached state, imposes limitations on the device performance: The thin (~300 nm) TiO_2 layer cannot absorb neither sufficient amounts of dye, nor sufficient photons when sensitized, thus resulting in a solar cell with a modest open circuit voltage that limits the WO_3 speed and depth of coloration. Furthermore, the mesoporous TiO_2 film causes a decrease of

---

* Corresponding author. Tel.: +30 2610 996793; fax: +30 2610 997476.
E-mail address: glefther@physics.upatras.gr (G. Leftheriotis).

0927-0248/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2011.09.014

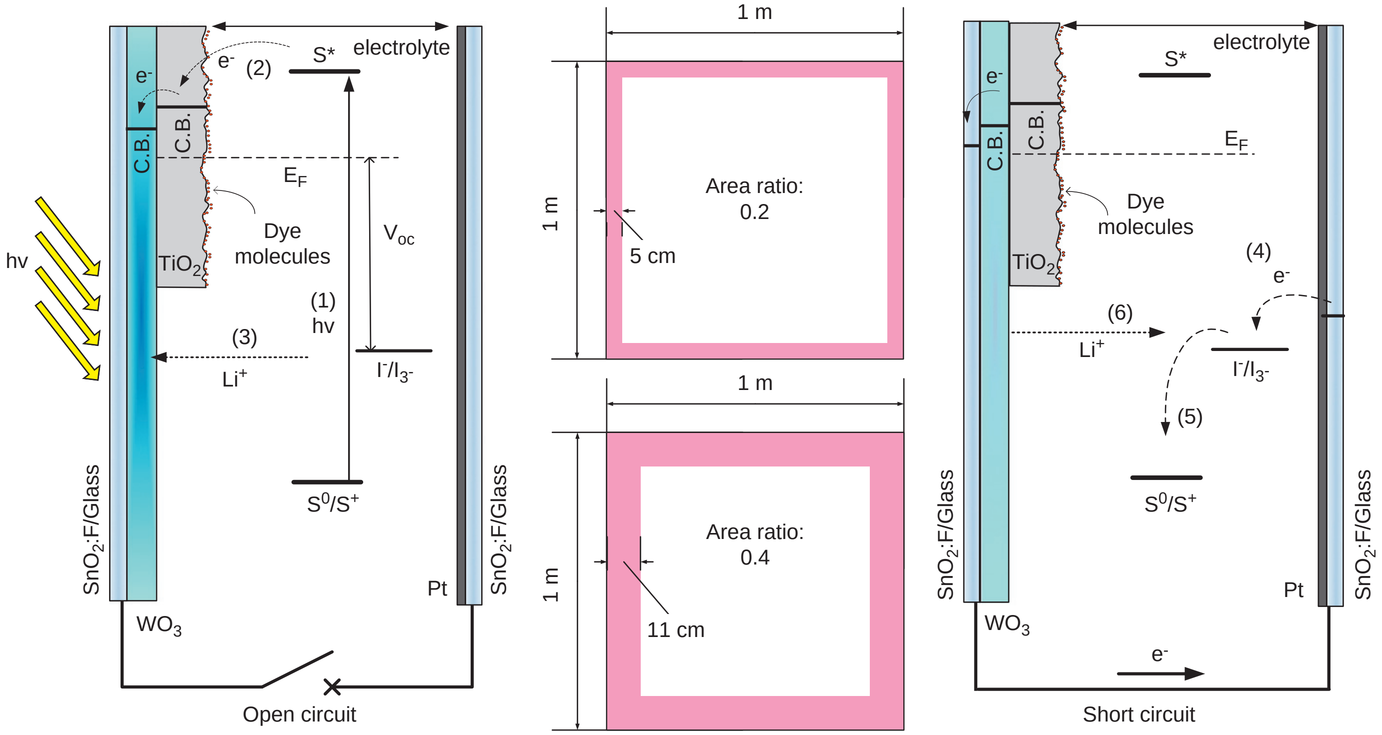


Fig. 1. Layout and operation of a partly covered photoelectrochromic device.

specular transmittance at short wavelengths (below 500 nm) due to scattering losses at the oxide grains.

One way round these problems is the spatial "decoupling" of photovoltaic and electrochromic elements in the device, and thus the "partly covered" type comes about. Instead of a thin transparent solar cell, the "partly covered" device employs a thick, opaque TiO_2 film, that covers only a fraction of the WO_3 film, on one end of the device. In that way, the requirement for a thin PV film is alleviated. The high electron mobility within the WO_3 film (e^- diffusion coefficient in the order of 10^{-3} cm^2/s, [13]) is believed to ensure that covering a small percentage of the total device area should be enough for the device to function. In a practical situation the opaque titania film could be placed along the perimeter of the PEC window, as shown in Fig. 1. In these regions WO_3 and TiO_2 overlap to ensure fast and efficient electron transfer.

In order to validate the "partly covered" principle, PEC cells of small dimensions have been fabricated and tested. Their properties (optical and electrical) have been assessed and compared with similar "fully covered" devices developed by others.

2. Experimental methods and development of materials

2.1. Instrumentation and characterization techniques

The thicknesses of the films were measured by an Ambios XP-1 profilometer. Scanning electron microscopy (SEM) pictures of the films were taken using a JEOL 6300 microscope. The transmittance spectra in the visible at normal incidence, $T(\lambda)$, of the PEC devices during different coloration stages were recorded with use of a Perkin Elmer Lambda 650 UV/VIS Spectrometer. Characteristic *I–V* curves of the PEC devices were taken with use of a potensiostat–galvanostat (AMEL, model 2053), a function generator (AMEL, model 586) and noise reducer (AMEL NR 2000). These instruments were also used to assess the electrochemical properties of the WO_3 films by the Galvanostatic Intermittent Titration Technique (GITT). The electrochemical cell used for these experiments incorporates two transparent conductive oxide glass sheets (K-glass), one coated with a WO_3 layer, the other being a plain K-glass sheet, serving as the working and the counter electrode respectively. A Pt foil placed 1 mm away from the WO_3 film has been used as the reference electrode. A detailed description of the cell can be found in [14]. During the GITT experiments, a series of 120 square current pulses with amplitude 0.2 mA and duration 5 s was fed into the electrochemical cell, each followed by an equilibration period of 30 s. The potential between working and reference electrodes (corresponding to the EMF of the WO_3 film) versus the inserted charge density has been measured. The "intercalation parameter" x in the resulting Li_xWO_3 films and the Li ion diffusion coefficient has been calculated as described in our previous work [15]. In both experiments, a computer has been used to store and manipulate the data. The incident solar radiation was measured with a Kipp & Zonen CM6B pyranometer.

2.2. WO_3 films

WO_3 films were prepared by electron beam gun evaporation at room temperature, at pressures at about 10^{-5} mbar, in a vacuum chamber evacuated by a turbo-molecular and a mechanical pump. The starting material was 99.99% pure WO_3 powder. As substrate we have used 4 mm thick glass coated with a transparent conducting oxide (SnO_2:F sheet resistance of 16.7 Ω/sq, 80% transmittance in the visible, trade name: K-glass). The evaporated tungsten oxide films are of optical quality, highly transparent in the visible with a thickness of 400 nm. The electrochemical properties of the films were assessed by GITT. The results appear in Fig. 2 as plots of EMF and Li^+ diffusion coefficient (D_{Li}^+) versus the Li^+ intercalation parameter (-*x*- in the Li_xWO_3 tungsten bronze). The monotonous EMF curve reveals the amorphous nature of the films [16]. The average value of D_{Li}^+ was found to