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Photoelectrochromic window with Pt catalyst

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Abstract

Photoelectrochromic windows represent a special kind of switching windows. The energy for colouring is provided by sunlight, so that a voltage supply is not required. The transmittance can be decreased on illumination and can be increased again in the dark. In contrast to photochromic devices, the system is externally switchable under illumination. Our photoelectrochromic window consists of several components: a dye-covered nanoporous TiO_2 layer, which is situated on a nanoporous electrochromic layer, such as WO_3, two glass substrates coated with a transparent conductive oxide, of which one is coated with Pt, an iodide/tri-iodide redox couple and Li^+ ions in a solid ion conductor. All the layers can be kept quite thin, so that they are transparent. The pores of the TiO_2 and WO_3 layers are filled with the electrolyte. This configuration is a particularly advantageous combination of the dye solar cell and an electrochromic element. The colouring time is independent of the area, the transmittance can be varied also in the illuminated state, and the system can also be switched by an auxiliary external voltage. Initial samples with solid electrolyte change their visible transmittance from 62% to 1.6%, their solar transmittance from 41% to 0.8%. The time for colouring and bleaching is about 15 min.

Keywords: Smart windows; Photoelectrochromic

1. Introduction

Photoelectrochromic systems combine electrochromic layers [1,2] and dye solar cells [3,4]. Electrochromic layers change their transmittance reversibly when electrons and cations are injected. In photoelectrochromic systems, the dye solar cell provides the energy for the coloration of the electrochromic layer. Thus, the transmittance of the photoelectrochromic device can be decreased under illumination and can be increased again when illuminated or in the dark. An external voltage supply is not required. Applications of these devices include, for example, switchable sunroofs in cars or smart windows in buildings.

We developed the photoelectrochromic configuration illustrated in Fig. 1, which is a particularly advantageous device. It consists of several components: a dye-covered nanoporous TiO_2 layer, a porous electrochromic layer, such as WO_3, two glass substrates coated with a transparent conductive oxide (TCO), of which one is coated with Pt, an iodide/triiodide redox couple and Li^+ ions in an organic solvent. Both the TiO_2 and the Pt layers can be kept quite thin, so that they are transparent. The pores of the TiO_2 and WO_3 layers are filled with the electrolyte.

During illumination (upper part of Fig. 1), a dye molecule absorbs a photon of the incident light. Then an electron is rapidly injected from the excited state of the dye into the conduction band of the TiO_2 and diffuses to the WO_3. Ionised dye molecules are reduced by I^- in the electrolyte according to the reaction: $3I^- \rightarrow I_3^- + 2e^-$. Li^+ ions intercalate into the WO_3 and keep the charges balanced. Because of the injection of electrons, the WO_3 changes its colour from transparent to blue.

If electrons are allowed to flow via an external circuit from the WO_3 via a TCO layer to the Pt electrode (lower part of Fig. 1, external switch closed), then the Pt catalyses the reverse reaction, i.e., the reduction of I_3^- to I^-. Li^+ leaves

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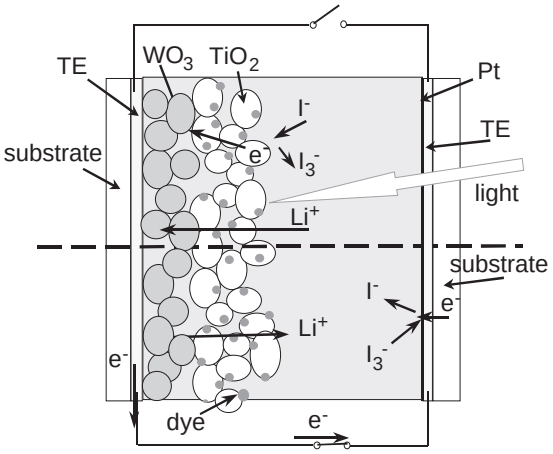

Fig. 1. Construction and operating principle of the photoelectrochromic device. The upper part shows the coloration in open circuit (switch open) and the lower part shows the bleaching in short circuit (switch closed).

the WO_3, and the WO_3 is bleached fast. This process occurs also during illumination. If the external switch is open, electrons can leave the WO_3 only by loss reactions. This process is very slow.

With a liquid electrolyte, the device's visible (solar) transmittance under 1000 W/m^2 of illumination changes from 51% to 5% (35% to 1.5%) with switching times of about 3 min. Using a solid electrolyte, a visible transmittance change from 62% to 1.6% and a solar transmittance change from 41% to 0.8% are achieved with switching times of about 15 min. The colouring time is independent of the area.

An alternative photoelectrochromic configuration was first published in [5]. The colouring and the bleaching are competing processes, because the bleaching is possible only via loss reactions. Therefore, either fast colouring and bleaching with a small transmittance change [5] or a large transmittance change with slow bleaching is achievable [6], or an external voltage is used for bleaching [7]. In our new device, the materials can be optimised for colouring and bleaching independently, so it simultaneously allows fast colouring and bleaching and high contrast [8].

In [8], we introduced this new device and discussed the differences to the alternative photoelectrochromic system and the advantages of our new system.

Experiments with different layer configurations of photoelectrochromic devices were reported in [9]. From these experiments, we concluded that the loss reactions of electrons from the TiO_2 can be neglected compared to the loss reactions of electrons from the WO_3.

We investigated both liquid electrolytes [8,9] and solid electrolytes [10,14]. Liquid electrolytes allow a faster switching, but need good sealing to be stable on the long term, whereas solid electrolytes, especially polymer electrolytes, show slower switching properties but are more suitable for most window applications.

2. Experimental

Samples with solid electrolyte were prepared as described in detail in [14], with liquid electrolyte in [9]. Peroxopolytungstic (P-PTA) sols were made by dissolving tungsten powder in hydrogen peroxide followed by thermal condensation in ethanol. Ormosil was made by an acylation reaction between isocianatopropyltriethoxy silane and diaminopolypropylene glycol 4000 in tetrahydrofurane. 1 mol% of ormosil diluted in ethanol (1 g of ormosil/10 ml of ethanol) was added to the P-PTA sol. The solution was slowly stirred for 30 min. Films were formed by dip-coating the transparent conductive glass substrate (TCO). After drying in air, the films were heat treated for 30 min at 450 °C. To make TiO_2 layers, Ti(IV) isopropoxide was added to 10 ml of ethanol solution containing 2.6 g of ethyl acetoacetate. Separately, 1 g of ormosil (see above) was dissolved in 10 ml of ethanol and a hydrolyzation/condensation reaction was catalysed with 0.1 ml 0.1 M HCl. After 30 min of stirring, the Ti solution was added and the solution was further stirred for 30 min. Thin layers were deposited using the dip-coating technique and annealed for 30 min at 450 °C.

Tungsten oxide and TiO_2 layers were successively dip-coated onto the TCO-coated glass substrates. As TCO, we used F:SnO_2-coated glass substrates from Flabeg with 8 Ω/square. The thickness of WO_3 and TiO_2 layers was about 600 and 150 nm, respectively. The layers were left for 2 h in 0.001 M ethanol solution of dye [*cis*-bis(isothiocyanato)bis(2,20-bipyridyl-4,40-dicarboxylato) ruthenium(II) dye (by Solaronix). Dye solution was heated up to 60 °C. The Pt layers were sputtered with a thickness of about 2 nm.

As a liquid electrolyte, 0.5 M LiI and 0.005 M I_2 dissolved in propylene carbonate (PC) was used. The distance of the electrodes was about 1 mm.

As a solid electrolyte, an ormosilane network was synthesised. Equimolar amounts of 3-isocyanatopropyltriethoxysilane and *O*,*O*bis(2-Aminopropylpolyethyleneglycol) (ME 4000 g/mol) were reacted to form a precursor composed of poly(propylene)oxide bis-endcapped with triethoxysilane groups.

Hydrolyzation/condensation reactions were catalysed with acetic acid. The concentration of LiI in the electrolyte was 0.5 M and an appropriate amount of I_2 was added to obtain 0.005 M concentration. In addition, a cationic surfactant based on dodecyl acid was added to the ormosil in a mass ratio (surfactant/ormosil) of 1:3. A polymer foil (Surlyn from Dupont) on each electrode with a thickness of 25 μm served as a spacer and a glue between both electrodes. Electrolyte was doctor-blade printed onto the electrodes. The electrodes were then pressed together and heated up to 90 °C for few min. The size of the PEC samples was 5×5 cm^2 or 10×10 cm^2.