

Limiting Processes in Photoelectrochromic Devices with a Pt layer

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We prepared photoelectrochromic devices, which can be switched from transparent to dark, by adding an electrochromic layer (WO_3) to a dye-sensitised solar cell. They consist of several components (fig.1): 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: $3\text{I}^- \rightarrow \text{I}_3^- + 2\text{e}^-$. 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 over 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 the WO_3 , and the WO_3 is bleached. This process happens also during illumination.

In contrast to electrochromic devices, the colouring is induced by illumination and no external voltage source is necessary. The transmittance can be decreased under illumination and can be increased again in the dark. Furthermore, in contrast to photochromic devices, the system is externally switchable.

In contrast to an alternative configuration reported by Bechinger [1], this device allows not only rapid colouring and bleaching but also a high contrast ratio [2]. Also, the kinetics of the colouring is independent of the area of the device.

Applications of these devices include, for example, switchable sunroofs in cars or smart windows in buildings.

Using a liquid electrolyte under 1sun of illumination, the visual transmittance changes from 51% to 5% with switching times of about 3 minutes (fig.2, 3)

In this paper we discuss variations of the light intensity, the concentrations of Li^+ , I^- , and I_3^- ions in the electrolyte and of the solvent. By this, we can define the limiting processes of the device. For the colouring with open circuit it is the electron excitation at the dye by the incident light. The electron transfer from the WO_3 to the I_3^- in the electrolyte is the dominating loss reaction and the phase change of the WO_3 during charge injection is also of importance. Transport processes in the TiO_2 or WO_3 or loss reactions at the TiO_2 are less significant. For open-circuit bleaching, electron transfer from the WO_3 to the I_3^- is the dominating process. Short-circuit bleaching is limited by the Li^+ diffusion in the WO_3 .

Acknowledgements:

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References:

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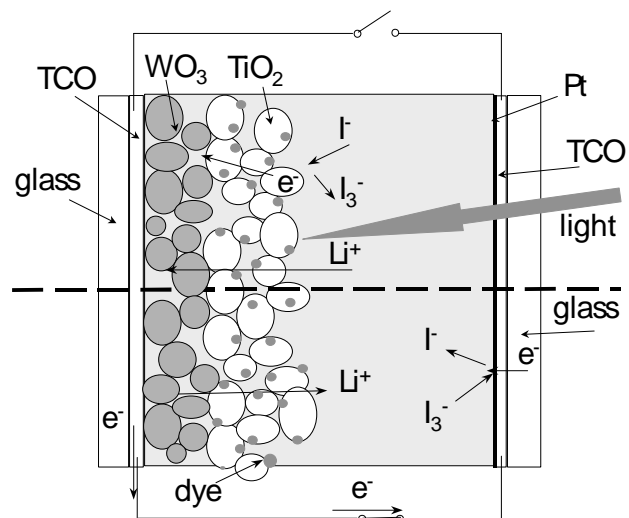


Fig. 1: Construction and operating principle of a photoelectrochromic device. The upper part shows the coloration in open circuit (switch open) and the lower part the bleaching in short circuit (switch closed).

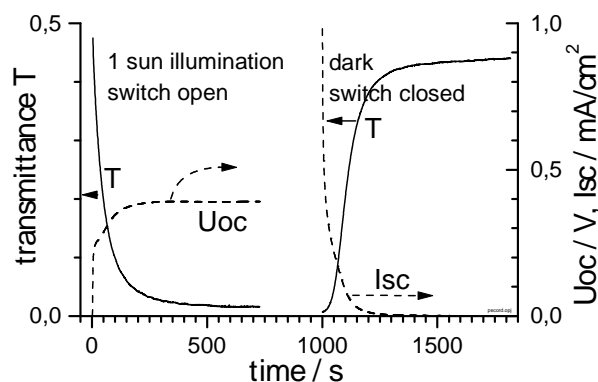


Fig. 2: Typical kinetics of the transmittance T and voltage U_{oc} during open-circuit colouring and transmittance and current density I_{sc} during short-circuit bleaching.

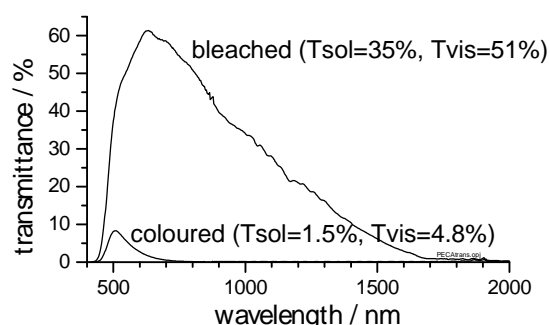


Fig. 3: Typical spectra of the photoelectrochromic device with a liquid electrolyte in the bleached and coloured states.