Experimental evidence of trap-limited electron transport in dye-sensitized solar cells : A Study by Intensity Modulated Photocurrent Spectroscopy.

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Porous networks consist of an insulating or semiconducting solid forming a promising basis for several electrical and optical devices. Electron flow in a porous nanostructured network interpenetrated with an ionic conductor occurs by diffusion since there is, a priori, no microscopical electrical field. It has been shown that electron transport in assemblies of nanometer-size TiO_2 particles is controlled by extremely slow diffusion of ion-screened charge carriers.

Intensity Modulated Photocurrent Spectroscopy (IMPS), is an optical modulation technique that proves to be a powerful characterization tool for elucidating the dynamic response of photoelectrochemical modules [1]. In this study, electron transport, dominated by trapping and detrapping processes in bandgap states, present at high density, distributed in energy, is investigated by Optoelectrical admittance spectroscopy as otherwise IMPS is referred.

Experimental

IMPS measurements were carried out on the dye sensitized TiO_2 cells using a combination of low-intensity modulated illumination from a blue (λ = 460 nm) LED and constant white light illumination from a quartz halogen lamp providing 80 mW cm^{-2} in the spectral region 400-700 nm. The voltage across the cell was controlled by a fast operational potentiostat Solartron 1286 operating in two electrode mode. IMPS measurements were performed using a Solartron 1250 frequency response analyzer to drive the LED and to analyze the photocurrent response. Typically the modulated intensity was at least 10^3 times smaller than the *dc* illumination level.

Results

Here, interesting values of incident photon to current efficiencies (shown in Figure 1) were obtained from dye sensitized solar cells using a new Ru(II)-polypyridyl complex grafted on TiO_2 photoanodes: Ru1 [Ru(II)(bdmpp)(bpy)Cl](PF$_6$).
In Figure 2, characteristic plots of the optoelectronic admittance $\Phi(\omega)$ in the complex plane are presented, obtained at different points along the I-V curve. The photoelectrode is polarised negatively with respect to the Pt counter-electrode. If the RC-time constant of the porous electrode is shorter than the transit time (the time it takes the electron to reach the substrate) of the photogenerated charge carriers through the porous network, the externally measured photocurrent response corresponds to the internal photocurrent flow in the porous electrode. In such a case, the transit time of photogenerated charge carriers through the porous network can be obtained from the optoelectrical admittance. The plots are mainly located in the (real=positive, imaginary=negative) 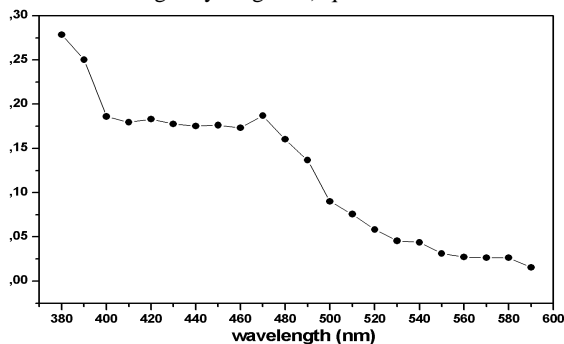quadrant because the diffusion of electrons from any point to the substrate contact introduces a time delay. At high frequencies $\Phi(\omega)$ is close to zero, indicating that electrons injected into the TiO_2 film cannot reach the back contact, and as a result, a modulated photocurrent is not observed in the external circuit. At sufficiently low frequencies, the intercept with the real axis corresponds to the steady-state photocurrent quantum yield ($\Phi(\omega)$=19%). At intermediate frequencies, a distorted semicircle is present under short-circuit conditions. When polarizing closer to open circuit potential, Nyquist diagrams are resolved into two contributions. All the IMPS diagrams in fig.2 cannot be correctly simulated if just Nernst diffusion and electron recombinations are considered. An agreement is only obtained if trapping-detrapping effects are taken into account too. Experimental data are well fitted using a
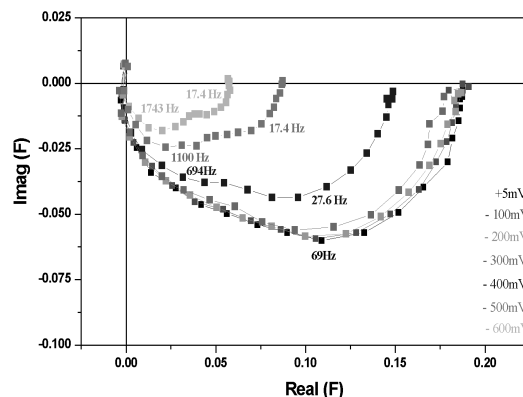
Fig. 2 Experimental IMPS spectra of a Ru1 sensitized TiO_2 cell when varying the potential from short-circuit to open-circuit conditions. Illumination from the substrate side giving 0.26 mAcm^{-2} short circuit *dc* current.

non-linear least square procedure applied to the analytical expression provided by Dloczik et al. [2]. Mean values of 10^{-4} cm^2.s^{-1} and 10^3 cm^{-1} are found for the effective diffusion coefficient and the absorption coefficient respectively. The relative importance of trapping effects in determinig the IMPS response may be due to the unexpected low value of the transfer rate constant at the rear contact for the cell under test, found to be around 0.15 cm.s^{-1}, without significant potential dependence.

Frequency analysis of IMPS spectra is currently in progress for a number of dye-sensitized photoelectrochemical cells, changing the dc illumination level, the electrolyte (liquid or solid) and the couple dye-TiO_2.

References
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Fig. 1 IPCE spectrum of Ru1 sensitized TiO_2 cell