

Projet Photolyse de l'eau et production d'hydrogène et d'oxygène au moyen de l'énergie solaire Projektteil Universität Genf

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Abstract

We pursued studies of solar-light-driven photo-electrolysis cell employing semi-transparent WO_3 photoanode. The stability of the photoanode in different electrolytes has been evaluated. Long term photo-electrolysis runs allowed us to identify solutions of sodium chloride as being the optimum electrolytes for water cleavage in hydrogen and oxygen, with some amount of chlorine formed as a by-product. In particular, the photo-electrolysis of a 0.5 M solution of sodium chloride, which is a composition close to sea water, results in the formation of *ca* 20% of chlorine at the WO_3 photoanode with oxygen remaining the main product. Thus, the sea water appears as an abundant, non-toxic electrolyte suitable for massive hydrogen production via photo-electrolysis.

Charge and mass transport are among the main factors determining the efficiency of nanostructured semiconducting photo-electrodes. In contrast with the prevailing current opinion, our results show that it is the migrational/diffusional transport within electrolyte filling the pores of the photo-electrode and not the electron diffusion across the semiconductor matrix which controls the photocurrent-voltage behaviour. Apparently, the only restrictions to the use of relatively thick nanostructured electrodes are the penetration depth of the incident light, the rate of diffusion/migration of the electroactive species within the electrode and the conductivity of the electrolyte.

2. The goal of the project

This project aims at achieving photo-electrochemical cleavage of water using solar light. The photo-electrochemical cell (PEC) comprises a semiconducting mesoporous WO_3 film photoanode and a metallic cathode. A photovoltaic (PV) cell associated with the PEC form a tandem device represented in Figure 1. The PV cell provides here an extra bias required to split water.

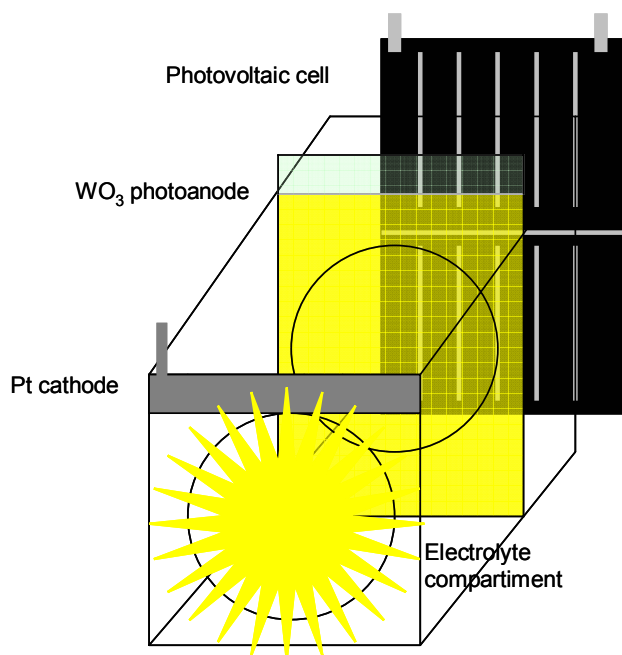
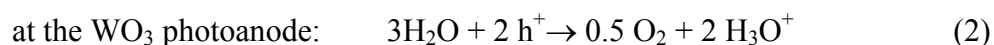
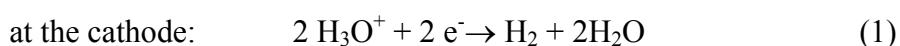


Fig.1 Tandem PEC device used in water splitting under simulated solar light illumination

4-5. Results and Discussion

(i). The search for an optimum electrolyte for a photo-electrochemical cell employing WO_3 photoanode

Semi-transparent, mesoporous WO_3 electrodes developed in our laboratory find utility in a photo-electrochemical cell (PEC) as a part of a tandem device for the cleavage of water into hydrogen and oxygen by visible light.



The device typically consists of a photo-electrolyser, comprising a photoactive WO₃ anode and a Pt cathode (a platinum sheet or, alternatively, a thin film of platinum deposited onto conducting glass), and a photovoltaic (PV) cell. In early experiments we used dye-sensitised liquid-junction PV cell and more recently an amorphous silicon PV cell. In both cases the PV cell was placed behind the back face of the WO₃ electrode; as it is depicted in Figure 1.

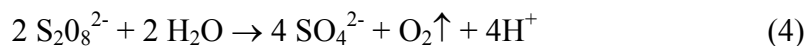
The evolution of hydrogen takes place at the platinum sheet, placed in front of WO₃ photoanode but separated from the electrolyte medium by a Nafion membrane. Such a membrane ensures the H⁺ ions entrance but preserves from the H₂ evolution to the electrolyte. The compartment between cathode and photoanode contains an aqueous electrolyte that is subjected to water photolysis. Light (simulated one sun AM 1.5) enters through the quartz window and then crosses the electrolyte and impinges upon the front face of WO₃ electrode. The WO₃ film absorbs the blue and green part of the solar spectrum, and transmits the red and yellow part to a photovoltaic cell.

To preserve tungsten trioxide from chemical dissolution, the photo-electrolysis of water must be conducted in an acidic (pH lower than 4), supporting electrolyte, insuring ionic conductivity within the cell. However, the choice of the suitable electrolyte is not evident, since careful analysis of the photo-electrolysis products showed previously that oxygen is not the only species formed at the nanostructured WO₃ photoanode. In fact, thermodynamically unstable peroxide species were detected both by means of Raman spectroscopy and of iodometric titration after photo-electrolyses conducted both in sulphuric and perchloric acids. In order to identify the exact chemical nature of the species generated at the photoanode of the PEC cell, several electrolytes subjected to the photo-electrolysis were analysed by Raman spectroscopy. In the case of 3 M aq. H₂SO₄.electrolyte, giving slowly decreasing photocurrents at the WO₃ photoanode, the analyses revealed the S₂O₈²⁻ (persulphate) species as being the principal product of the photo-electrolysis:



Measurement of the intensity ratio of the main S₂O₈²⁻ band in the difference spectrum and for the reference 0.1 M Na₂S₂O₈ solution provided an estimated concentration of ca. 0.01 M of persulphate present after prolonged photo-electrolysis in the final electrolyte. Iodometric titration of 3 M H₂SO₄ solutions photo-electrolysed at room temperature, performed in parallel with the Raman measurements, confirmed that under such conditions the persulphate formation became the main anodic process with current (faradaic) efficiencies exceeding

80%. However, with increasing temperature of the PEC cell (which can normally be expected for the real operation upon solar illumination) the persulphate species undergo accelerated decomposition to form sulphates and oxygen:



Consequently, the $\text{S}_2\text{O}_8^{2-}$ species simply store oxygen in the electrolysed solution.

In contrast with the H_2SO_4 electrolyte, in which the generation of the persulphate species only moderately affects the amount of photocurrent at the WO_3 electrode, a prolonged photo-electrolysis conducted in a HClO_4 solution results in a severe deactivation of the photoanode. Such a deactivation occurs due to the build-up of a layer of peroxo species at the WO_3 surface, accompanied by the formation of a few per cent of hydrogen peroxide in the solution, which has been identified by Raman spectroscopy. It is worth mentioning, that the WO_3 electrode does not suffer any irreversible damage during photo-electrolysis run in sulphuric or perchloric acid and its initial performance can be restored by an additional short annealing step in oxygen atmosphere or by a short reduction current pulse or by an exposure of the deactivated WO_3 surface to an intense UV illumination, since it is known that the tungsten peroxides undergo photodecomposition under UV light.

To avoid the formation of a kind of ‘passivating layer’ and to ensure an acidic medium for good operation of a tungsten oxide film in PEC device, alternative electrolytes have been identified. One of such electrolytes might be simply a solution of sodium chloride. Inspection of photocurrent-voltage curves, recorded under simulated AM 1.5 solar illumination, shows that large and stable photocurrents can be attained. in a 0.5 M solution of sodium chloride. The latter solution, which is a composition close to sea water, does not require any preliminary acidification as the formation of chlorine locally sets the solution pH to *ca.* 2. There is ~ 20% of chlorine formed at WO_3 photoanode in 0.5 M NaCl:



oxygen remaining the main photo-electrolysis product. Prolonged electrolysis experiments, lasting six days, demonstrated perfect stability of the WO_3 photoanode under conditions of chlorine evolution which allows to anticipate its suitability for the sea-water photo-electrolysis. The sea water is an abundant, non-toxic electrolyte suitable for massive hydrogen production via photo-electrolysis.

Interestingly, even the addition of small amounts of chloride and also bromide ions (as NaCl or NaBr) to an acidic electrolyte (such as for example a HClO₄ solution) allows to maintain large and stable photocurrents. Figure 2 shows that only minor changes in the photoanodic current occur during initial stages of prolonged photo-electrolysis of a 1 M HClO₄/0.01 M NaCl solution. The addition of only 0.01 M of Cl⁻ ions to the electrolyte allows, in fact, to stabilize the photocurrent after a few hours of electrolysis which contrasts with a severe drop of the photocurrent occurring in the HClO₄ solution alone. Similar result has been obtained for an addition of 0.01 M of bromide ions to a HClO₄ solution, which like chloride ions counterbalance deactivation of the WO₃ photoanode whilst maintaining oxygen as the main photo-electrolysis product.

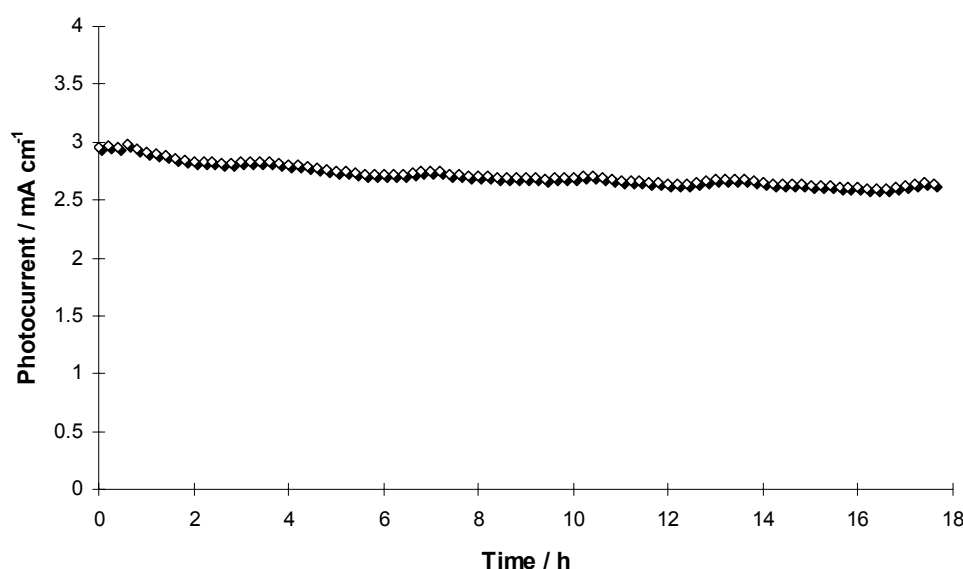


Fig.2 Stabilization of the anodic photocurrent during prolonged photoelectrolysis at WO₃ of a 1 M HClO₄/0.01 M NaCl solution upon simulated solar AM 1.5 irradiation.

Given small amounts of either chlorine or bromine generated from 1 M HClO₄ / 0.01 M NaCl or 0.01 M NaBr solutions, corresponding to current efficiencies of a few percent, the observed stabilization of the photocurrent can only be explained by considering Cl⁻ and Br⁻ ions acting as promoters of the photo-oxidation of water at WO₃. In fact, a direct parallel can be drawn between the activating effect of halide ions upon the WO₃ photoanode and their reactivity towards peroxo complexes of tungsten (VI) in solution [1].

These observations open an attractive possibility to adapt the concentration of chloride ions added to the electrolyte to fit the desired O₂ / Cl₂ ratio formed at the WO₃ photoanode,

especially that relatively small amount of chlorine present in the gas evolved at the photoanode can be easily eliminated by washing the gases with water: $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^-$. The formed hypochloric solution can be used as disinfectant for water, for swimming pools or others.

In Figure 3 are depicted photocurrent-voltage curves for water splitting at the WO_3 electrode recorded in 0.5 M NaCl, respectively 3 M $\text{CH}_3\text{SO}_3\text{H}$ (methane sulphonic acid) solution. In both electrolytes the WO_3 photoanode maintains comparable, essentially stable currents over prolonged photo-electrolysis runs. Due to its less acidic character, sodium chloride solution (sea water) will be preferred provided that one accepts or finds useful the generation of minor amount of chlorine (together with oxygen) at the photoanode.

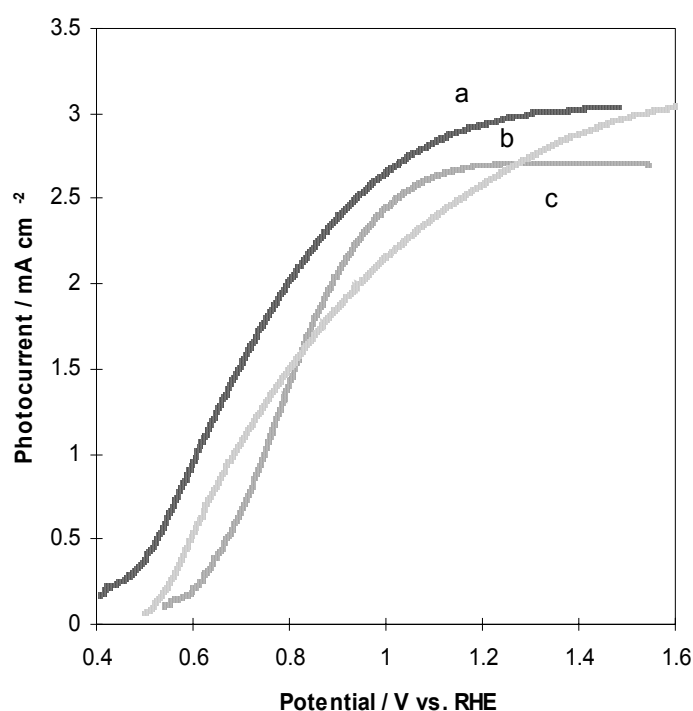


Fig.3 Steady-state photocurrent-voltage curves for a *ca.* 3 μm -thick mesoporous WO_3 photo-electrode recorded in 3 M $\text{CH}_3\text{SO}_3\text{H}$ (curve *a*), 0.5 M NaCl (curve *b*) and in 3 M H_2SO_4 (curve *c*) under simulated solar AM 1.5 irradiation.

Given the restricted domain of visible light absorption – up to 500 nm, one can consider the water photo-oxidation currents exhibited by mesoporous WO_3 electrodes under solar illumination as fairly large. Important is the excellent stability of the WO_3 films in moderately and/or highly acidic aqueous solutions. Besides application for solar water and sea-water splitting, the WO_3 photoanodes appear particularly well suited to the

photodegradation of industrial wastewater containing organic chemicals [2]. In such cases, the generation of the persulphate species, occurring in sulphate-based supporting electrolytes, allows an almost complete removal of organic carbon from water. Moreover, due to the frequent occurrence of the photocurrent doubling during photo-oxidation of organic species, hydrogen is usually generated at the cathode with higher solar efficiency than during simple photo-electrolysis of water.

(ii) Effect of charge and mass transfer upon photocurrent-voltage behaviour of nanostructured semiconductor films.

Significant part of the work has also been devoted to the evaluation of the mass and charge fluxes within the nanostructured semiconductor films. For this purpose, we used as a model system a series of TiO₂ films of different thickness formed by deposition onto conducting glass substrates and sintering of 25-30 nm in diameter P25 particles consisting of a mixture of anatase (*ca* 80%) and rutile. The main features of such photo-electrodes are: (i) significant thickness to allow effective absorption of incident light: the films consist typically of 100-1000 superimposed layers of individual nanoparticles; (ii) large porosity: *ca* 50 % of the film volume is normally filled with electrolyte; (iii) particularly large surface-to-volume ratio resulting from the small size of TiO₂ nanoparticles forming the film.

It is to be recalled, in this connection, that the charge and mass transport within the nanocrystalline mesoporous network are among the major factors affecting the efficiency of TiO₂-based dye-sensitised solar cells and photocatalytic devices. Over more than a decade the prevailing view was that the electron transport across the nanocrystalline TiO₂ films must be dominated by diffusion, driven by the electron-concentration gradient [3]. In particular, the "electron diffusion model" has been largely used as the basis for the interpretation of transient photocurrent and intensity-modulated photocurrent spectral (IMPS) measurements aimed at describing quantitatively the charge transport through the dye-sensitised nanocrystalline TiO₂ films. Interpretation of the time-resolved photocurrent and IMPS measurements, assuming slow electron diffusion in nanostructured TiO₂ films, allowed determination of the effective diffusion coefficient of photoinjected electrons, D_e . Interestingly, the values of D_e inferred from the IMPS data changed over almost 4 orders of magnitude as a function of illumination intensity [3,4]. It is also noticeable that the values of D_e obtained at solar illumination levels were in the range of diffusion coefficients expected for ionic species in solution (*ca.* 10^{-5} cm² s⁻¹) and two to three orders of magnitude lower than

the diffusion coefficients derived from electron mobilities in a single crystal of rutile or anatase [3,4].

One of the common assumptions of the electron diffusion model is that, since the charges of photoinjected electrons diffusing through the nanoparticulate TiO_2 network are screened by the electrolyte ions (cations), the effect of electrolyte on the charge transport can be simply regarded as just affecting the effective electron diffusion coefficient [3]. The role of the electrolyte is considered in an essentially similar way in the “effective medium” picture treating the nanoporous semiconductor/electrolyte ensemble as a highly polarisable medium with electron transport coupled to solvent and ion rearrangement [5]. The mutual interactions between diffusing electrons and ions of the electrolyte are included in the description of the charge transport across the nanoporous TiO_2 photo-electrode in a more elaborated way by employing the concept of ambipolar diffusion [3].

Within our study we compared directly the impact of the electron transport across the TiO_2 matrix and that of the ionic transport in the electrolyte upon photocurrent-voltage characteristics of the photo-electrode. The electronic and ionic fluxes are conveniently displayed on the following scheme representing the nanostructured TiO_2 film as a three-dimensional electrode (*cf.* Figure 4). In this representation the photo-electrode includes two coincidental superimposed continua; an electronically conducting solid matrix (the network of interconnected TiO_2 nanoparticles) and an ionic conductor (the electrolyte filling the pores of the nanocrystalline TiO_2 film).

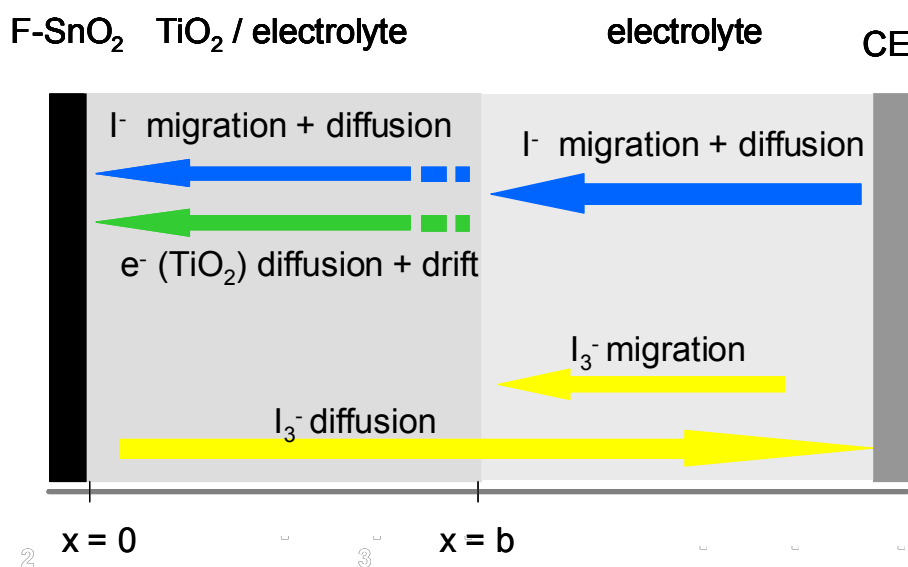


Fig. 4 Schematic representation of main ionic and electronic fluxes involved in the operation of the dye-sensitised liquid-junction photovoltaic cell, employing an electrolyte composed

principally of an iodide salt (such as LiI), under steady-state conditions. To simplify the scheme, the diffusion/drift of Li^+ cations is not shown.

The adopted experimental approach was to use TiO_2 films of different thickness, either comparable or much larger than the penetration depth of the incident light. Electrolytes with conductivities varying over several orders of magnitude have been employed. We used incident light intensities ranging from less than a mW cm^{-2} (where the photocurrents are mainly controlled by the photon flux) to several hundreds mW cm^{-2} (where the mass- and charge-transport control of the photocurrent largely prevails) [4].

In Figure 5 are displayed photocurrent-voltage curves for two TiO_2 films of largely different thicknesses ($2.5\ \mu\text{m}$ and $25\ \mu\text{m}$) irradiated with high intensity argon-ion laser UV light having an absorption depth comparable with the former film thickness. Consequently, in this experiment the major part (*ca.* 90%) of the thicker film remained electrochemically inactive and functioned just as an electronic lead to the conducting glass substrate.

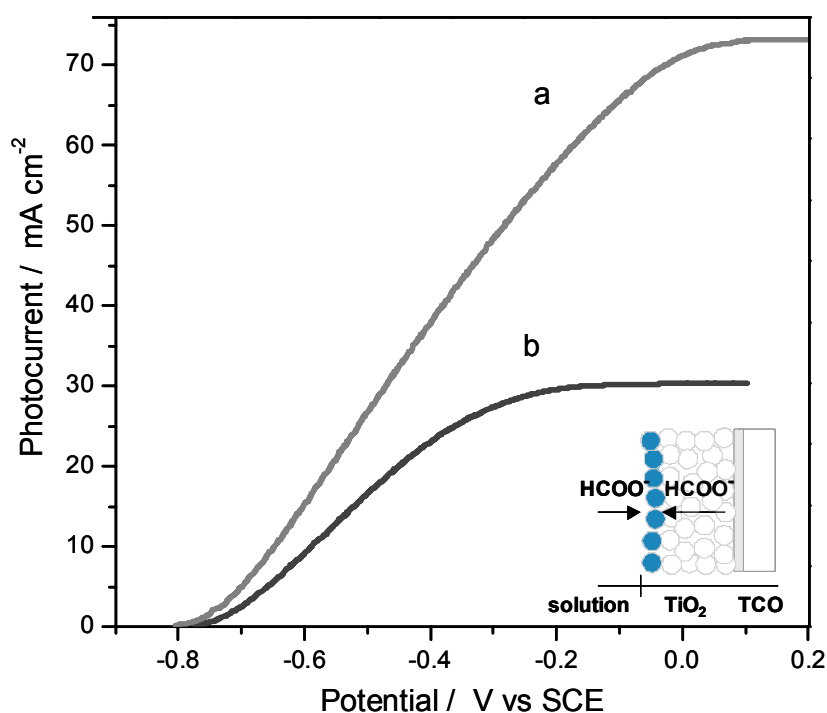


Fig. 5 Photocurrent-voltage curves for two nanocrystalline TiO_2 photo-electrodes, a *ca.* $25\ \mu\text{m}$ -thick (curve *a*) and a *ca.* $2.5\ \mu\text{m}$ -thick (curve *b*), polarised in a $1.5\ \text{M NaClO}_4/1.5\ \text{M HCOONa}/1.5\ \text{M HCOOH}$ solution under argon-ion laser illumination ($700\ \text{mW cm}^{-2}$) incident from the side of the film| solution boundary.

Much steeper rise of the i vs. E curve for the 25 μm -thick photo-electrode indicates clearly that it is the mass transport in the electrolyte and not the electron transport across the network of TiO_2 particles which controls the electrode resistance and the amount of the photocurrent. Importantly, these diffusional/migrational limitations arise despite large concentration of the electroactive formate species in the electrolyte and the overall ionic concentration on the order of $2 \times 10^{21} \text{ cm}^{-3}$. In no case, the steady-state behaviour of the nanocrystalline TiO_2 photo-electrodes was affected by the electron transport.

Similar behaviour was observed over an extended range of incident light intensities, from a few mW cm^{-2} (where the mass-transport control of the photocurrent starts) to several hundreds mW cm^{-2} . Given that the dark resistivity of nanocrystalline anatase films is of the order of 10^7 - $10^{10} \Omega \text{ cm}$ [3], the observed behaviour of the 25 μm -thick photo-electrode is consistent with large self-doping of the unilluminated portions of the film, occurring at the initial stages of the film illumination, leading to a substantial rise in conductivity of the nanoparticulate TiO_2 network [6]. These results question the current interpretation of transient photocurrent and IMPS measurements assuming electron diffusion within the TiO_2 matrix as determining the photocurrent-voltage behaviour at medium and high illumination levels.

In addition to diffusional/migrational limitations associated with the transport of the electroactive species, operation of the nanocrystalline TiO_2 electrodes is also clearly affected by the conductivity of the electrolyte. As shown in Figure 6, the use of low conductivity electrolytes causes dramatic decrease of the slope of i vs. E curves for the TiO_2 photo-electrodes working in an ample volume of electrolyte both because of an extra series resistance and also due to a less even current distribution. The conductivity of the chosen electrolyte has also been shown to affect in the same way the fill factor of the TiO_2 -based dye-sensitised solar cells [4]. In fact, the excessively low conductivity of the electrolyte will impede penetration of the photocurrent inside the mesoporous electrode regardless the actual value of the diffusion coefficient of the electroactive species.

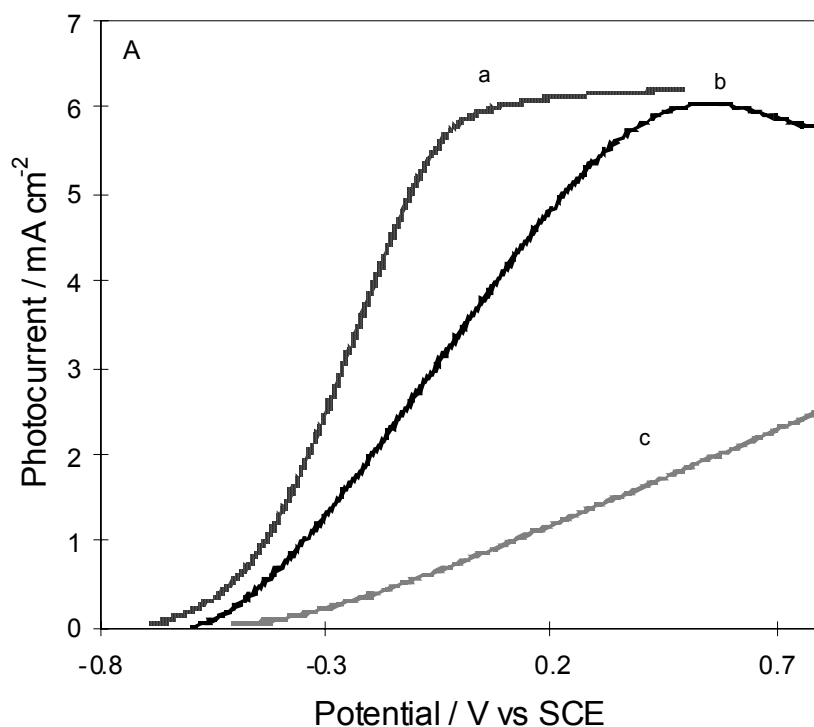


Fig. 6. Effect of the electrolyte conductivity upon photocurrent-voltage plots for a *ca.* 2.5 μm thick nanocrystalline TiO_2 electrode irradiated with argon-ion laser light of 600 mW cm^{-2} from the side of the film|solution boundary. Curves *a* were obtained in 0.1 M LiClO_4 /1 M CH_3OH aqueous solution (conductivity, $\sigma = 8 \text{ mS cm}^{-1}$), curves *b* in a 0.1 M LiClO_4 solution in $\text{C}_2\text{H}_5\text{OH}$ ($\sigma = 2.6 \text{ mS cm}^{-1}$) and curves *c* in a 0.1 M LiClO_4 /1 M CH_3OH solution in THF ($\sigma = 0.2 \text{ mS cm}^{-1}$)

The relative contributions of migration and diffusion to the transport of electroactive species within mesoporous semiconductor photo-electrodes were also modeled in our recent work [7].

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Collaborations

International:

Collaboration with Dr Kazuhiro Sayama - group leader at Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan resulted recently in a joint publication (*cf.* Ref. 4). Dr Sayama constructed and characterized a series of TiO₂-based dye-sensitised solar cells filled with electrolytes of different conductivities. His results complemented our work performed with similar nanostructured TiO₂ electrodes illuminated with the band-gap UV light.

There is equally a current collaboration with our American partners within the framework of Annexe 20 IEA:

Dr John Turner of NREL (National Renewable Energy Laboratory) Colorado

Dr Clovis Linkous of the Florida Solar Energy Center.

National:

Dr Radovan Cerny, Laboratoire de cristallographie, Université de Genève.

Prof. Michael Grätzel, Institut de photonique et interfaces, EPFL.