

Optimization of dye-sensitized solar cells prepared by compression method

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Received 24 July 2001; received in revised form 11 September 2001; accepted 11 September 2001

Abstract

Nanostructured TiO₂ films have been deposited onto conducting glass and on flexible conducting plastic substrates using a compression technique. Dye-sensitized solar cells prepared from Degussa P25 TiO₂ powder, red dye (Ru(dcbpy)₂(SCN)₂) or black dye (Ru(tcterpy)(SCN)₃) and an electrolyte containing LiI and I₂ in 3-methoxypropionitrile were tested using standard photoelectrochemical techniques. The average overall efficiency of small open cells sensitized with the red dye on plastic substrates was 4.5% (100 W m⁻²). In a direct comparison, red and black dye gave about the same efficiencies. For both dyes, addition of 4-*tert*-butylpyridine to the electrolyte resulted in a decreased IPCE response in the whole spectral range, with a specific decrease in the red region, which is attributed to a shift in the conduction band edge of the nanostructured TiO₂. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nanostructured; TiO₂; Dye-sensitization; Solar cell; Press

1. Introduction

We have recently introduced a new method for the preparation of nanostructured TiO₂ films at room temperature [1,2]. This method involves the compression of a TiO₂ powder film at pressures exceeding 200 kg cm⁻². The resulting films are porous and mechanically stable, even without heat treatment. Compressed nanostructured TiO₂ films on conducting plastic and glass substrates have been tested for use in dye-sensitized solar cells. Efficiencies of 4–5% were obtained under simulated solar light illumination [1,2].

Many groups have studied dye-sensitized solar cells (DSCs) since the introduction of efficient nanostructured TiO₂ films by O'Regan and Grätzel [3]. The current record efficiency for dye-sensitized solar cells stands at 10.4% (AM 1.5 G, 1000 W m⁻²), for a small cell sensitized with the 'black' dye Ru(tcterpy)(SCN)₃ [4]. Efficiencies of about half this value are found for cells which are made in larger series using techniques such as screen-printing, which use the red dye Ru(dcbpy)₂(SCN)₂ as sensitizer. This lower efficiency and problems associated with sealing and stability make that, with the current state of technology, DSCs cannot compete with solid state solar cells on the market of large scale energy production.

Under low light intensity illumination, however, DSCs perform well and can compete with solid state solar cells in terms of efficiency [5]. For many smaller niche applications such as consumer electronics a lifetime of 5 years is sufficient. This can be achieved using DSCs [6]. Only if the production costs of DSCs are significantly lower than that of their solid state equivalents, large scale introduction of DSCs can be foreseen. Production methods such as repeated screen-printing and firing steps appear to be too costly and time consuming. The recently developed press method on the other hand, is very quick. The pressure needs to be applied for only a very short period of time (~1 s) and can even be applied using a roller mill in a continuous production line [2]. As firing steps are omitted, flexible polymer substrates can be used.

This paper presents an update of the current state of the DSCs prepared by the compression method. First, recent results of DSCs on flexible substrates are discussed, then the performance DSCs with the red dye Ru(dcbpy)₂(SCN)₂ and the black dye Ru(tcterpy)(SCN)₃ will be compared, and finally a more general discussion on the possibilities of improvement in solar cell efficiencies of DSCs is presented.

2. Experimental

TiO₂ powder (Degussa P25) was added to ethanol to a concentration of 20 wt.%, followed by stirring. The resulting suspension was applied onto a substrate by doctor

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blading using scotch tape as frame and spacer. Two types of substrate were used: TEC 8 conducting glass, supplied by Hartford Glass (F-doped SnO₂, sheet resistance: 8 Ω/square) and ITO-60 conducting plastic, supplied by IST (ITO on poly(ethylene terephthalate), 60 Ω/square). After evaporation of the ethanol, the substrate with the attached powder film was put between two planar steel press plates and pressure was applied by using a hydraulic press (600 kg cm⁻² for glass substrates and 1500 kg cm⁻² for plastic substrates). Dye adsorption took place in a 0.5 mM solution of *cis*-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis-tetrabutylammonium (purchased from Solaronix S.A., Switzerland) in ethanol. The counter electrode consisted of a thermally platinized conducting glass, or platinized SnO₂ powder pressed on a conducting plastic. The electrolyte was LiI and I₂ (Aldrich) in 3-methoxypropionitrile (Fluka). 4-*tert*-Butylpyridine or 1-methylbenzimidazole (both Aldrich) were used as additives to the electrolyte. The black dye Ru(H₃tcterpy)(SCN)₃((C₂H₅)₃NH) (Solaronix S.A.) was converted to its monoprotonated version [4], and adsorbed from a 0.2 mM ethanolic solution.

3. Results and discussion

3.1. Pressed films on flexible substrates

Pressed TiO₂ films on ITO-PET substrates were tested in a sandwich configuration with a counterelectrode consisting of platinized SnO₂ on ITO-PET. The TiO₂ electrodes were sensitized with the red dye Ru(dcbpy)₂(SCN)₂, which can be considered as the standard sensitizer in DSC-research. An average efficiency of 4.5% is found for a series of samples (~20) under 100 W m⁻² simulated sunlight. 1-Methylbenzimidazole was used as an additive to the electrolyte. Like 4-*tert*-butylpyridine, this additive increases the voltage output of the cell, but unlike 4-*tert*-butylpyridine it does not seriously decrease the current. The IV characteristics of two good plastic DSCs are shown in Fig. 1. The solar cell efficiency is about 5.5% for both cells, with an open circuit voltage of about 0.63 V, short circuit current of 1.4 mA cm⁻² and a fill factor of about 0.6, see Table 1. The two cells were made under identical conditions. To get more insight into the observed differences of these cells, the IV curves were fitted using a 1-diode model including resistive losses (drawn lines in Fig. 1):

$$V = \frac{mkT}{e} \ln \left(\frac{I_{inj} - I}{I_0} - \frac{V + IR_s}{I_0 R_p} + 1 \right) - IR_s, \quad (1)$$

where V is the voltage, m the diode quality factor, I the current, I_{inj} the injected electron current, I_0 the exchange current, R_s the series resistance and R_p the parallel (or shunt) resistance. The fitted parameters are listed in Table 1. Lower R_p and higher R_s of cell A gives rise to the lower fill factor observed for this cell. The series resistance is mainly due to the resistivity of the ITO substrates, but also solu-

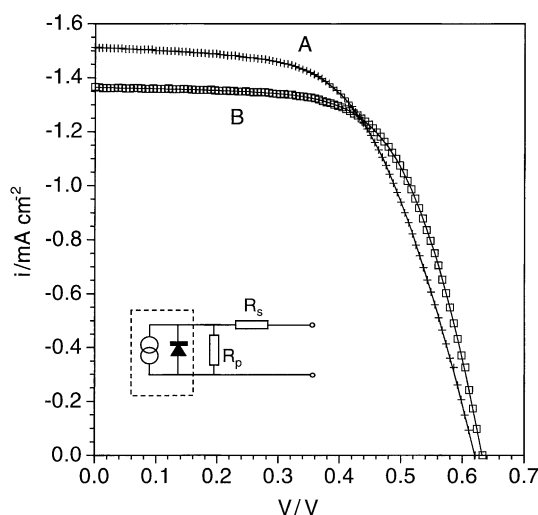


Fig. 1. IV characteristics of two plastic Ru(dcbpy)₂(SCN)₂-sensitized solar cells in 100 W m⁻² simulated sunlight. The electrolyte was 0.5 M LiI, 0.05 M I₂ and 0.5 M 1-methylbenzimidazole in 3-methoxypropionitrile. Symbols: experimental data, drawn line: fit according to the electric circuit shown in the inset.

tion resistance can give some contribution. The parallel resistance can be attributed to losses such as contacts between the TiO₂-covered electrode and the counter electrode.

Sealed modules on conducting ITO-PET were made using Surlyn as a sealant. The initial results were promising: the modules gave reasonable efficiencies and could be bent to a certain extent (for instance 45° over a length of 3 cm) without loss of efficiency. The stability was poor however. One of the reasons is permeability of the ITO-PET substrate to water and other small molecules. High concentrations of water are a problem in Ru(dcbpy)₂(SCN)₂ sensitized solar cells, because of dye desorption and ligand exchange. Extended stability tests are currently under way.

3.2. Comparison of red and black dye on compressed films

Fig. 2a shows the incident photon to current conversion efficiency (IPCE) as a function of illumination wavelength for pressed TiO₂ films on conducting glass sensitized with

Table 1
Characteristics and fitted parameters of the plastic dye-sensitized solar cells of Fig. 1

	Cell A ^a	Cell B
Efficiency (%)	5.43	5.51
V _{oc} (V)	0.62	0.63
I _{sc} (mA cm ⁻²)	1.51	1.36
Fill factor	0.58	0.64
I _{inj} (mA)	0.489 (0.0002)	0.437 (0.0001)
I ₀ (nA)	15.3 (0.2)	29.9 (0.4)
m	1.92 (0.23)	2.08 (0.22)
R _p (Ω)	2.57 × 10 ⁴ (5 × 10 ²)	6.10 × 10 ⁴ (2.2 × 10 ³)
R _s (Ω)	235 (4)	142 (4)

^a Standard deviations of fitted parameters are in parentheses. The active cell area is 0.32 cm².

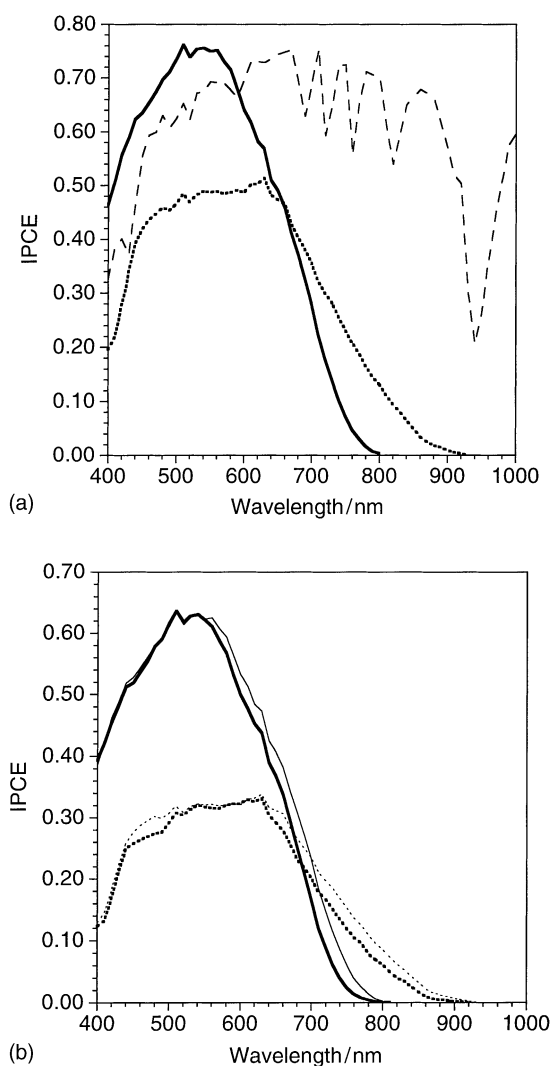


Fig. 2. (a) IPCE spectra of $\text{Ru}(\text{H}_2\text{dcbpy})_2(\text{SCN})_2(\text{TBA})_2$ (red dye, drawn line) and $\text{Ru}(\text{Htcterpy})(\text{SCN})_3(\text{TBA})_3$ (black dye, dotted line) sensitizers on $12\ \mu\text{m}$ thick pressed TiO_2 film. Electrolyte was 1.0 M LiI and 0.1 M I_2 in 3-methoxypropionitrile. Striped line: relative photon flux of sunlight (AM 1.5 G). (b) IPCE spectra of the same sensitized electrodes in electrolyte containing additionally 0.5 M 4-*tert*-butylpyridine. Thin lines are the IPCE traces of (a) scaled down to match in the IPCE maxima of the respective dyes.

two different dyes: the red dye $\text{Ru}(\text{dcbpy})_2(\text{SCN})_2$ and the black dye $\text{Ru}(\text{tcterpy})(\text{SCN})_3$. The highest IPCE values (up to 76%) are obtained for the red dye. The black dye on the other hand, shows a much broader wavelength response. Also shown in the same figure is the spectral distribution of the photons in the AM 1.5 G solar spectrum. Due to the better overlap with the solar spectrum, the calculated AM 1.5 G ($1000\ \text{W m}^{-2}$) short-circuit current is higher for the black than for the red dye at 13.2 and $12.3\ \text{mA cm}^{-2}$, respectively.

The addition of 0.5 M 4-*tert*-butylpyridine to the electrolyte led to a significant decrease in the IPCE, see Fig. 2b. The integrated AM 1.5 G short circuit current decreased by 22 and 33% for the red and black dye, respectively. The IPCE does not decrease proportionally over the whole spec-

tral range, as can be seen by comparing the IPCE spectra in the presence of 4-*tert*-butylpyridine with those without the additive. For ease of comparison, the IPCE spectra of Fig. 2a are also plotted in b, where they are scaled to match the maximum values. It is obvious that the decrease in IPCE is stronger on the red side of the spectra after addition of 4-*tert*-butylpyridine. A possible explanation is that the additive, which is an organic base, causes some additional deprotonation of the dyes, which is known to result in a blue shifted absorption spectrum [4,7]. However, no significant changes in the absorption spectra of the adsorbed dyes on TiO_2 were observed. We therefore believe that the blue shift in the IPCE spectra is due to a negative shift in the conduction band edge energy of TiO_2 . As will be discussed later, a decreased injection efficiency for red light excitation can then be expected. By decreasing the number of adsorbed protons at the TiO_2 surface or by adsorbing at the surface itself, 4-*tert*-butylpyridine can cause such a shift. It is well known that the addition of 4-*tert*-butylpyridine to the redox electrolyte of DSCs leads to an improved photovoltage [8]. Under low-intensity monochromatic illumination the open circuit voltage increased in our experiment from 0.40 to 0.50 V for the red dye (530 nm light, $0.77\ \text{mW cm}^{-2}$), and from 0.28 to 0.43 V for the black dye (600 nm, $0.72\ \text{mW cm}^{-2}$).

The IV-characteristics were recorded under white light illumination for 40 samples of pressed TiO_2 sensitized with the red or the black dye. No significant improvement in the solar cell efficiency was found by using the black dye, because of the low voltage in absence of 4-*tert*-butylpyridine and the low photocurrent in the presence of this additive.

3.3. Improvement of DSC performance

An energy scheme of the $\text{Ru}(\text{dcbpy})_2(\text{SCN})_2$ -sensitized TiO_2 solar cell is shown in Fig. 3. The electrolyte is as-

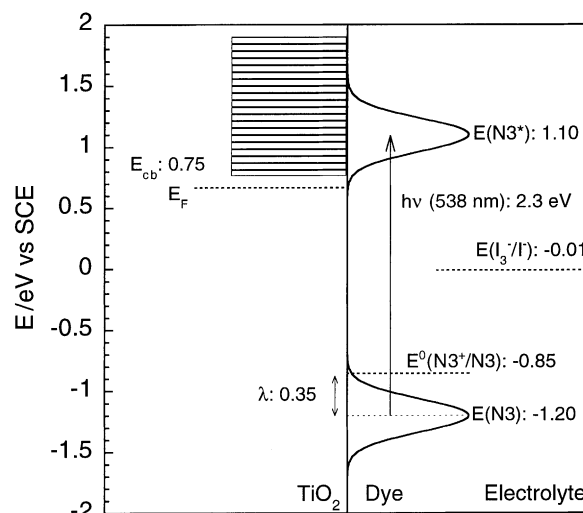


Fig. 3. Energy scheme of a $\text{Ru}(\text{dcbpy})_2(\text{SCN})_2$ -sensitized TiO_2 solar cell. Electrolyte: 0.5 M LiI and 0.05 M I_2 in acetonitrile.

sumed to be 0.5 M LiI and 0.05 M I₂ in acetonitrile. The standard potential for the reaction $I_3^- + 2e^- = 3I^-$ is +0.017 V vs. SCE in acetonitrile [9]. The redox potential of the electrolyte is calculated to be +0.01 V vs. SCE. The position of the conduction band edge of nanostructured TiO₂ (anatase) was estimated from the data presented by Redmond and Fitzmaurice [10]. It is noted, however, that they used bare TiO₂ electrodes, that is without any adsorbed dye. Adsorption of the dye will probably affect the position of the conduction band edge. There is to our knowledge no data available on the shift of the conduction band edge upon dye adsorption. There is, however, some indirect evidence. Nazeeruddin et al. [7] showed that the degree of protonation of Ru(dcbpy)₂(SCN)₂ affects both the short-circuit current and the open-circuit voltage in nanostructured TiO₂ solar cells. This is possibly due to shifts in the conduction band edge of TiO₂ due to protonation of the surface.

The reversible Ru(dcbpy)₂(SCN)₂⁺/Ru(dcbpy)₂(SCN)₂-potential has been well studied for the dye dissolved in various solvents [8,11]. The precise potential of the adsorbed dye may, however, be different. In absence of reliable data for dye adsorbed at TiO₂, the solution value for the fully protonated Ru(dcbpy)₂(SCN)₂ dye was used in Fig. 3. Thermal fluctuations in the interactions with surrounding solvent molecules and fluctuations in the internal vibrations and rotations in the dye give rise to a Gaussian distribution of the HOMO energies. The average HOMO level is lower in energy than the reversible oxidation energy, the difference being the reorganization energy λ . For a comparable ruthenium complex, Ru(bpy)₃²⁺, λ has been determined to be 0.56 eV in aqueous solution [12]. Taking into account a correction for the solvent acetonitrile and the fact that the dye is bound onto a semiconductor [13], λ is estimated to be 0.35 eV for Ru(dcbpy)₂(SCN)₂ bound to TiO₂.

The energy of the injecting state of the dye is obtained by adding the energy of the absorbed photon to the HOMO distribution. This is valid, as it has been determined that most of the electron injection occurs on a femtosecond time scale [14,15], before relaxation to the lowest excited state and solvent reorganization takes place. It is clear from Fig. 3 that there is a good overlap between the energy levels of the excited Ru(dcbpy)₂(SCN)₂ dye and the conduction band of TiO₂, when the dye is excited in the absorption maximum (538 nm). The figure suggests that when the dye is excited with 636 nm light (1.95 eV), only half of the excited state levels would overlap with the conduction band and would be able to inject. From Fig. 2a it can be seen that the IPCE of the red dye is still about 0.55 at this wavelength, suggesting that the relative energies of the TiO₂ conduction band and the Ru(dcbpy)₂(SCN)₂ dye are not entirely accurate in Fig. 3. The suggestion of a decreased injection efficiency in the red part of the IPCE spectrum, due to poor overlap of excited state and conduction band levels, seems to be valid.

The open circuit voltage (V_{oc}) is given by the difference between the redox potential and the Fermi level in the TiO₂. The position of the Fermi level in nanostructured TiO₂ de-

pends on the concentration of conduction band electrons, and will be close to the conduction band edge under open circuit conditions. Hence, the maximum V_{oc} is estimated to be 0.75 V, in good agreement with the results of the best DSCs [4,8]. An increase in the V_{oc} is possible by heightening the conduction band edge energy level. This can be done by (base) additives to the electrolyte or by replacing Li⁺ ions with other cations such as Na⁺, TBA⁺, etc., which have less affinity for the TiO₂ surface. Alternatively, TiO₂ can be replaced by Nb₂O₅, SrTiO₃, etc., which have a higher conduction band position. A problem with both these approaches is that the injection of electrons in the red part of the spectrum will decrease due to less energetic overlap (see Fig. 3). On the other hand, the energy of the redox electrolyte can be brought down to increase the V_{oc} . Unfortunately, to date no promising alternatives for the I⁻/I₃⁻ system have been identified. The I⁻/I₃⁻ couple provides rapid regeneration of the oxidized dye combined with very low dark currents (slow reaction of electrons in TiO₂ and the back contact with I₃⁻).

As discussed above, it will be difficult to increase the voltage output of DSCs significantly without sacrificing the photocurrent. Improvement of the photocurrent is probably a more promising way to increase the efficiency of DSCs. There are several ways to achieve this. First, the thickness of the TiO₂ films can be increased, so that more dye is adsorbed and more light is absorbed. This has the disadvantage that the voltage will go down due to the increase in the dark current, which is proportional to the surface area. Furthermore, transport problems, both for redox species in the electrolyte and electrons in the nanostructured film may be encountered. A better approach is to optimize the light absorption characteristics of the DSC by adding light-scattering particles to the TiO₂ film, adding a light-scattering film on top of the TiO₂ film, or by using a reflecting counterelectrode. Second, a dye with a broader absorption spectrum can be used, for instance the black dye Ru(tcterpy)(SCN)₃. The black dye has a more positive oxidation energy (closer to that of the redox couple), so that the injection into TiO₂ is still good, even with (near-infra)red excitation. Disadvantages of the black dye are the low extinction coefficient and the lower coverage, so that thicker films are needed to absorb sufficient light, which makes it more difficult to make high efficiency cells.

The photocurrent of compressed films of TiO₂ sensitized by Ru(dcbpy)₂(SCN)₂ are quite good, but can certainly be improved. The integrated AM 1.5 G (1000 W m⁻²) photocurrent density of the IPCE spectrum in Fig. 2a is 12.3 mA cm⁻². Using the same approach, a photocurrent density of 16.6 mA cm⁻² has been calculated for optimized TiO₂ films with the same dye (which gave 18.2 mA cm⁻² under simulated sunlight) [8]. The lower photocurrent found here may be caused by the low purity of the TiO₂ powder (Degussa P25), which is known to contain some Fe₂O₃ (100 ppm). The IPCE found in this study (76% in the maximum at 530 nm) is, however, better than the IPCE maxima

of 50–65% for Ru(dcbpy)₂(SCN)₂-sensitized P25 films that have been prepared in the conventional way (grinding of the powder/paste followed by spreading and firing at temperatures exceeding 400 °C) [16,17]. Taking into account that reflection losses are about 10%, a maximum IPCE of 90% can be achieved. As we have found a maximum of 76%, recombination losses are about 14% under short circuit conditions. The highest published IPCE value for the same system is 85%, which was obtained after a TiCl₄ after-treatment of a nanostructured TiO₂ (P25) electrode [8]. The IPCE-values were consistently higher in the whole spectral range, compared to our results. This suggests that the TiCl₄ treatment suppresses recombination reactions. Unfortunately, the TiCl₄ treatment requires time (overnight soaking) and another heat treatment, and is therefore not suitable for rapid DSC production processes. Pretreatment of the powder, or using a powder of higher purity are possible ways to increase the photocurrent for pressed films.

For long-term stability of flexible dye-sensitized solar cell, replacement of the water-sensitive Ru(dcbpy)₂(SCN)₂ dye appears to be necessary. The water permeability of the polymers normally used for flexible conducting films is too high to be used in combination with this dye. We are currently looking into alternative dyes which have a better water tolerance.

4. Conclusions

Good overall efficiencies have been obtained for flexible dye-sensitized solar cells prepared by pressing (up to 5.5% under 100 W m⁻² solar illumination). The stability of these cells is poor, which is mainly attributed to an increase of water concentration in the electrolyte and the water-sensitive Ru(dcbpy)₂(SCN)₂ dye that was used. In a direct comparison, the performance of the red dye Ru(dcbpy)₂(SCN)₂ dye and the black dye Ru(tcterpy)(SCN)₃ on pressed TiO₂ was tested and found to be approximately equal. The broader absorption spectrum of the black dye is counterbalanced by its lower IPCE and voltage output. Addition of 4-*tert*-butylpyridine to the electrolyte resulted in a overall decreased IPCE spectral response and a specific

decrease in the red region, attributed to an increase in the conduction band edge energy of the TiO₂.

Acknowledgements

This work has been financed by the Swedish Foundation for Strategic Research and the Swedish National Energy Administration. Viviane Aranyos is thanked for preparation of the monoprotonated black dye.

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