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Journal of Photochemistry and Photobiology A: Chemistry 159 (2003) 33–39

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Performance and stability of TiO_2/dye solar cells assembled with flexible electrodes and a polymer electrolyte

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Received 23 January 2003; received in revised form 12 February 2003; accepted 24 February 2003

Abstract

Solid-state, flexible TiO_2/dye solar cells were assembled using flexible electrodes, a polymer electrolyte with I^-/I_3^- and a Pt coated counter-electrode. The efficiency of the cells was enhanced when the plastic electrodes coated with TiO_2 were exposed to UV radiation, followed by heating at 140 °C in dry conditions. For comparison, a similar cell was prepared by the same procedure but using glass electrodes. The performance of these cells was investigated during a period of 50 days by current–potential and electrochemical impedance spectroscopy measurements. The flexible, solid-state TiO_2/dye solar cells ($1\,cm^2$) presented an open circuit potential of 0.72 V, short-circuit current of $60\,\mu A\,cm^{-2}$ and an efficiency of 0.32% under a light intensity of $10\,mW\,cm^{-2}$. This efficiency was maintained until the fourth day after assembling and decayed to 0.17% on the 14th day, remaining constant until the 40th day and decreasing to 0.13% on the 50th day. Impedance spectroscopy revealed that the series resistance increased with time, lowering the cell efficiency. This effect was not so evident for cells assembled with glass electrodes. Therefore, the flexible electrode limits the preparation of the porous TiO_2 photoelectrode and creates a large series resistance in the solar cell. However, these results are very promising for developing solar cells with lower costs and broader applicabilities.

Keywords: TiO_2/dye solar cell; Polymer electrolyte; Electrochemical impedance spectroscopy

1. Introduction

The TiO_2/dye solar cell consists of a dye-sensitized nanoparticulated TiO_2 film, which is usually deposited onto a transparent glass electrode, an electrolyte containing the I^-/I_3^- redox couple and a Pt coated counter electrode (Grätzel's solar cell) [1]. The energy conversion results from the injection of electrons from the photoexcited state of the sensitizer into the conduction band of the semiconductor. The redox couple in the electrolyte, after rereducing the oxidized dye, can be renewed in the counter-electrode, making the photoelectrochemical cell regenerative [1,2].

Several attempts have been made to replace the liquid electrolyte in these systems, since leakage or evaporation of the solvent limits the long-term stability of the cells. In most studies, solid-state TiO_2/dye solar cells were assembled using the I^-/I_3^- redox couple dissolved in a polymer gel medium [3–14]. In our Laboratory, we have been investigating solar cells assembled with a polymer electrolyte based on poly(ethylene oxide-co-epichlorohydrin), poly(EO-EPI). The best efficiency for energy conversion (global efficiency, η_{global}) that we have obtained for an all solid-state TiO_2/dye solar cell (with an active area of $1\,cm^2$) was $\eta_{global} = 2.6\%$ under $10\,mW\,cm^{-2}$. Thus, its efficiency was lower than that obtained for cells assembled with a liquid electrolyte, probably due to the low conductivity of the polymer electrolyte and the reduced mobility of I_3^- in such a media. However, this polymer electrolyte makes the assembly of the cell much easier, since it also acts as an adhesive between the electrodes and no sealing is required, providing a possible application of these cells for low illumination conditions [13,14].

In parallel with the studies concerning the electrolyte, the use of plastic electrodes for assembling flexible TiO_2/dye solar cells is also under investigation [15–20]. Flexible electrodes, like poly(ethylene terephthalate) coated with tin-doped indium oxide (PET-ITO), present lower costs and technological advantages relative to glass-ITO electrodes, e.g. lower weight, impact resistance and less form and shape limitations. However, deposition of nanoparticulated TiO_2 on PET-ITO is difficult, because the thermal treatment must be limited to 150 °C, decreasing adhesion, electrical contact between the particles and adsorption of the dye. This affects the efficiency of the cell, particularly when using a polymer electrolyte [19,20].

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doi:10.1016/S1010-6030(03)00106-0

In an earlier study, we investigated a flexible, solid-state TiO_2/dye solar cell assembled with the polymer electrolyte poly (EO-EPI) and PET-ITO electrodes [20]. Its efficiency was $\eta_{global} = 0.22\%$ under 10 mW cm^{-2} ($\eta_{global} = 0.12\%$ under 100 mW cm^{-2}), almost 10 times lower than that obtained for solid-state solar cells assembled with the same polymer electrolyte using glass electrodes. Also, electrochemical impedance spectroscopy (EIS), measurements revealed a larger series resistance and a smaller diffusion coefficient for the ionic species for the flexible cells [20]. Both effects could be caused, to some extent, by organic residues (from the TiO_2 suspension), which cannot be eliminated using low temperatures.

In this work we demonstrate that UV radiation is a suitable method for removing organic residues from the TiO_2 film, considering the well-known activity of TiO_2 toward photodegradation of organic compounds [21]. This study also reports on the stability of flexible and solid-state TiO_2/dye solar cells, investigated by current–potential and EIS measurements by irradiating for 50 days.

2. Experimental section

Photoelectrochemical cells were assembled using transparent flexible PET-ITO electrodes (*Innovative Sputtering Technology*, 60 Ω cm) and glass-ITO electrodes (*Delta Technology*, 20 Ω cm) as substrates for the photoelectrode and counter-electrode. All solutions were prepared using p.a. grade reagents. Counter electrodes (CE) were prepared by sputter depositing a thin Pt film on plastic or rigid electrodes. For preparation of photoelectrodes, a small aliquot of TiO_2 suspension (Ti nanoxide-T, *Solaronix*) was spread onto the transparent electrodes using a glass rod with an adhesive tape as spacer (thickness ∼42 μm). The electrodes with TiO_2 films were UV irradiated in a merry-go-round for different time intervals, 10 cm from the internal bulb of a 125 W high pressure Hg lamp (HPL-N Philips) [22]. At this distance, the intensity of the lamp was 1.3 mW at 254 nm and 2.2 mW at 366 nm. After the UV treatment, the electrodes were heated at 140 °C for 2 h in an oven placed inside a MBraun dry box filled with argon (humidity $<$ 1 ppm). The electrodes were then immersed for 16 h in a 1.5×10^{-4} mol l^{-1} solution of the sensitizer dye, cis-bis-(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II), (ruthenium-535, *Solaronix*) in absolute ethanol, rinsed with ethanol and dried. Afterwards, a film of the polymer electrolyte was deposited onto the sensitized electrodes by casting, using a solution of 0.3 g of poly(EO-EPI, 84:16) (Daiso Co. Ltd.,Osaka), 27 mg of NaI, 3 mg of LiI and 7 mg of I_2 in 25 ml of acetone (the ionic conductivity of this electrolyte is 5×10^{-6} S cm^{-1} at 50% relative humidity [23]). The assembly of the solid solar cells was done by pressing the CE against the sensitized electrodes coated with the polymer electrolyte. An adhesive tape (42 μm) was placed between the two electrodes, to control electrolyte film thickness and to avoid short-circuiting of the cell. The active area of the cells was 1.0 cm^2.

The efficiency of the devices was investigated on an optical bench having an Oriel Xe (Hg) 250 W lamp. Water and cut off filters were used to avoid IR and UV radiation and the light intensity was varied using neutral density filters. Light intensity was measured with a Newport Optical Power Meter. *I–V* and EIS measurements were performed with the Eco-Chimie Autolab PGSTAT 10 with FRA module. The device was connected in a two-electrode configuration: the sensitized porous electrode was connected as working electrode and the Pt CE was used as pseudo-reference (circuited with the counter-electrode). *I–V* curves were obtained using linear sweep voltammetry at 0.8 mV s^{-1}. EIS spectra were obtained by applying sinusoidal perturbations of ±10 mV over the V_{OC}, at frequencies from 5×10^{-3} to 10^5 Hz, in the dark and under illumination. The EIS results were analyzed using Boukamp software [24]. Each cell was irradiated for 2 h at 100 mW cm^{-1} in short-circuit conditions and then characterized by *I–V* and EIS measurements. After that, the measurements were taken under 10 mW cm^{-1}. This procedure was performed every 2 days in the first week after assembling the cells and, afterwards, twice a week.

The surface of the different TiO_2 films was examined after thermal treatment using a Jeol Scanning Electron Microscope (JSM). The TiO_2 films, as well as the PET-ITO substrate were also analyzed by ATR-FTIR (from 4000 to 650 cm^{-1}), using a Nicolet FTIR-520. Adsorption of the dye in sensitized TiO_2 electrodes was evaluated from Vis absorption spectra performed with a Hewlett-Packard UV-Vis spectrophotometer model 8453. The spectrum of each sensitized electrode was recorded using a similar non-sensitized ITO-TiO_2 electrode as reference (blank).

3. Results and discussion

The suspension used to prepare the TiO_2 films contains different organic ingredients, which must be removed to improve the photoactivity. When using glass electrodes, these impurities are removed by firing the electrode at 400–500 °C. With PET substrates this is not possible. Thus, our strategy was to use the ability of anatase TiO_2 to degrade organic compounds to remove such contaminants. Exposition to UV radiation can act upon the properties of TiO_2 films deposited onto flexible PET-ITO electrodes, affecting adherence to the substrate and adsorption of the dye sensitizer. Several periods of time of UV radiation were tested. TiO_2 films irradiated for intervals longer than 30 min presented lower adhesion to the substrate and have not retained their integrity during the assembly of the solar cell. The best results were observed for TiO_2 films exposed for only 15 min to UV radiation, followed by heating at 140 °C for 2 h in a dry box, called TiO_2 ($UV_{15\,min} + 140\,°C_{2\,h}$) film. Such films were mechanically stable, presented an intense adsorption of the dye and a good performance in flexible TiO_2/dye solar cells.

FTIR spectroscopy was used to evaluate the effect of 15 min of UV irradiation on the composition of the TiO_2 films deposited on PET-ITO electrodes. The analyses were performed for the TiO_2 ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$) film and, for comparison, for a film prepared using just the thermal treatment, TiO_2 ($140\,^{\circ}C_{2\,h}$) film. The FTIR spectra of both films presented an absorption band at 1100 cm^{-1} and a broad band between 800 and 650 cm^{-1} that can be attributed to the Ti–O–Ti linkage [25,26]. The spectrum of the TiO_2 ($140\,^{\circ}C_{2\,h}$) film also presented a broad absorption band in the region 3600–3000 cm^{-1}, which can be related to OH stretching vibrations [25]; bands at 2925, 2865 and a band at 1080 cm^{-1}, which can be caused by stretching of aliphatic C–H and of the C–O bond in primary alcohols [25], and other bands with lower intensities at 1650, 1410, and 1340 cm^{-1}, which can be related to the surfactants present in the TiO_2 suspension. These bands were not observed in the spectrum of the sample treated by UV radiation, TiO_2 ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$) film. In addition to the absorption at 800–650 cm^{-1}, only bands with very low intensity at 1710, 1340 and 1200 cm^{-1} were observed. Thus, only 15 min of UV radiation can eliminate most of the organic residues originating from the suspension used to deposit the TiO_2 films. Moreover, this procedure practically did not affect the morphology of the TiO_2 films as comparison of SEM images revealed that the surface of the TiO_2 ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$) film was just slightly rougher than the surface of the TiO_2 ($140\,^{\circ}C_{2\,h}$) film.

Exposition to UV radiation also enhanced the dye adsorption in TiO_2 films. After sensitization, the TiO_2 ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$) films were more intensely colored than the TiO_2 ($140\,^{\circ}C_{2\,h}$) electrodes. The visual observation was consistent with the absorption spectra, presented in Fig. 1. Probably, after elimination of organic residues, there are more active sites available for dye adsorption on the TiO_2 surface. The absorption spectrum of a glass-ITO|TiO_2 ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$) is also included in Fig. 1 and reveals that the sensitization of the TiO_2 film was slightly affected by the type of substrate (glass-ITO or PET-ITO).

The efficiency of three solar cells prepared using TiO_2 ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$) films deposited on flexible PET-ITO electrodes and, for comparison, a cell prepared by the same procedure using glass-ITO electrodes, was investigated by *I–V* and EIS measurements for 50 days using a laboratory light source. The results presented by the three flexible cells were quite reproducible; 7 days after assembling the photocurrents and the efficiencies differed by less than 20%. From the first week until almost 2 months, the differences in the performances of the flexible cells were lower than 10%. However, during all this period, the cell assembled with glass electrodes, using the same procedure, exhibited a better performance. Fig. 2 shows some of the *I–V* curves registered under 10 and 100 $mW\,cm^{-2}$ over 50 days, to investigate the stability of the solid-state and flexible solar cells prepared with the UV irradiated TiO_2 ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$) photoelectrodes. The *I–V* curve for the cell prepared by the same procedure using glass electrodes (50 days after assembly) was also included.

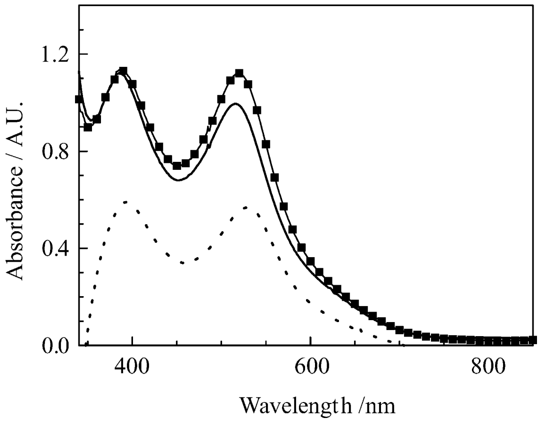

Fig. 1. Absorption spectra of dye-sensitized TiO_2 films deposited on flexible or rigid electrodes: (---) PET-ITO|TiO_2 ($140\,^{\circ}C_{2\,h}$), (—) PET-ITO|TiO_2 ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$), and (■) glass-ITO|$TiO_2$ ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$).

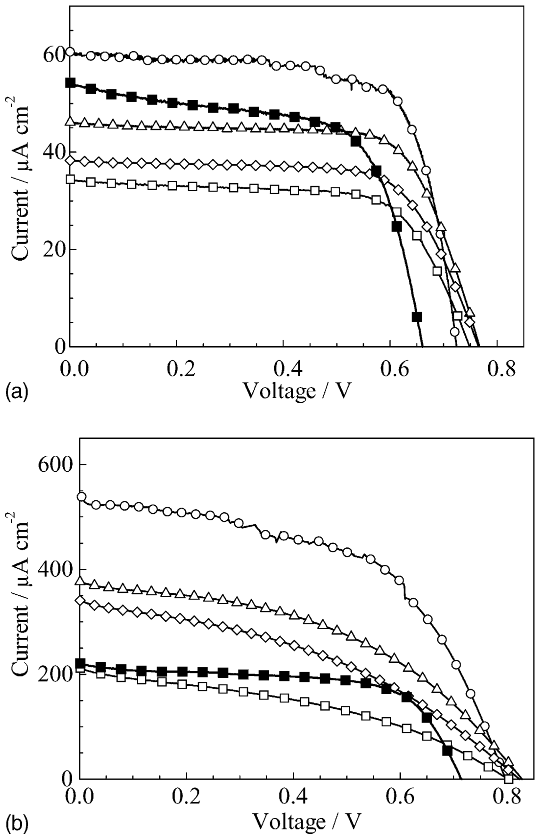

Fig. 2. Current–potential curves for a solid-state, flexible solar cell prepared with a polymer electrolyte and PET-ITO|TiO_2 ($UV_{15\,min}+140\,^{\circ}C_{2\,h}$) film: after the 1st (○), 6th (△), 9th (◇) and 50th (□) day of irradiation under (a) 10 $mW\,cm^{-2}$ and (b) 100 $mW\,cm^{-2}$. The *I–V* curve for a rigid cell prepared by the same procedure using glass-ITO electrodes in its 50th day (■) is also presented.

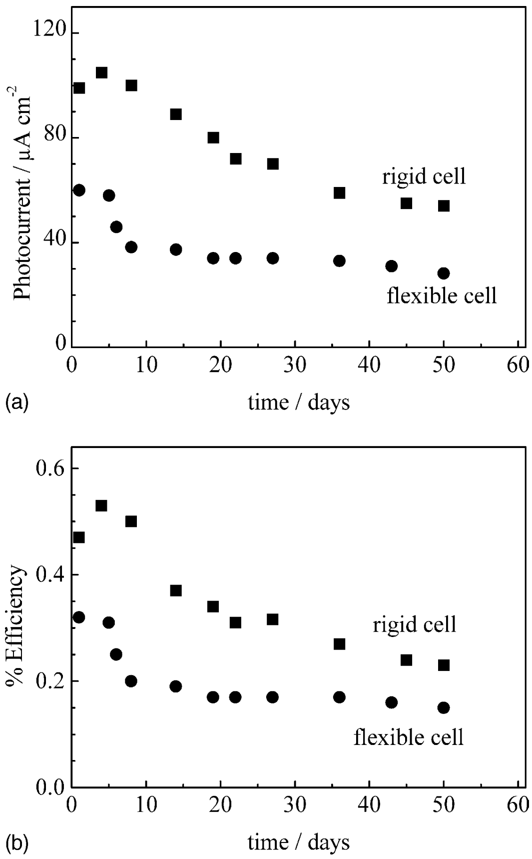

Fig. 3. Performances and stabilities for solar cells prepared with a polymer electrolyte and TiO_2 ($UV_{15\,min} + 140\,^{\circ}C_{2\,h}$) films deposited on PET-ITO ((●), flexible cell) or glass-ITO electrodes ((■), rigid cell). Variation of (a) short-circuit current and (b) efficiency as a function of time (under $10\,mW\,cm^{-2}$).

In general, the performance of the cells remained relatively constant until the fourth day after assembling, with a subsequent decay. The cells presented a high V_{OC}, comparable or even higher than the values reported for the V_{OC} of TiO_2/dye cells assembled with liquid electrolytes [2]. This effect was previously discussed in details [13,14]. Briefly, using the polymer electrolyte, the ether oxygen of the ethylene oxide, a Lewis base, can interact with the acid sites of the TiO_2. This interaction can shift the Fermi level and affects the electron occupancy of trap states of the TiO_2 film, as observed when the base *tert*-butylpyridine was added in cells assembled with liquid electrolyte, which resulted in higher values of photovoltage and suppression of the dark current [2]. For 50 days, the values of V_{OC} slowly decayed with time. Under $10\,mW\,cm^{-2}$, V_{OC} varied from 0.72 to 0.69 V for the flexible cell, and from 0.71 to 0.66 V for the cell assembled with the glass-ITO electrodes. The cells presented a similar tendency under $100\,mW\,cm^{-2}$.

The evolution of I_{SC} and efficiency (η_{global}) with time, under $10\,mW\,cm^{-2}$, for cells assembled with PET-ITO and glass-ITO electrodes, using the same procedure, is represented in Fig. 3. For the flexible cells, until the fourth day after assembling, $I_{SC} = 60\,\mu A\,cm^{-2}$ and $\eta_{global} = 0.32\%$ under $10\,mW\,cm^{-2}$ ($I_{SC} = 0.54\,mA\,cm^{-2}$ and $\eta_{global} = 0.23\%$ under $100\,mW\,cm^{-2}$). This performance was better than that previously obtained for flexible cells assembled with the same polymer electrolyte and non-irradiated TiO_2 ($130\,^{\circ}C_{4\,h}$) films, which presented overall efficiencies of 0.22% and 0.12% under 10 and $100\,mW\,cm^{-2}$, respectively [20]. Comparison of this result with other studies reported in the literature is not easy because most of the TiO_2/dye flexible cells were assembled with liquid electrolytes. For instance, an efficiency of 4.5% was obtained under $10\,mW\,cm^{-2}$ for a smaller cell ($0.32\,cm^2$) prepared with TiO_2 film deposited on PET-ITO by the compression method, but the cell was assembled using a liquid electrolyte, LiI and I_2 in 3-methoxypropionitrile instead of the polymer electrolyte used here [18].

During the same period of time, i.e. until the fourth day after assembling, the photocurrent and efficiency for the cell prepared using the glass-ITO electrodes were $I_{SC} = 0.11\,mA\,cm^{-2}$ and $\eta_{global} = 0.53\%$ under $10\,mW\,cm^{-2}$ ($I_{SC} = 0.92\,mA\,cm^{-2}$ and $\eta_{global} = 0.45\%$ under 100 mW cm^{-2}). Thus, for flexible photoelectrodes prepared using the low temperature thermal treatment, the exposure to UV irradiation allowed a better sensitization of the TiO_2 film and enhanced the performance of the flexible solar cells.

The overall efficiency of the flexible cells decreased considerably with time from the 4th to the 10th day and then remained almost constant at 0.17% until the 40th day, decreasing to $\eta_{global} = 0.13\%$ at the 50th day. During all this period of this investigation, the values of photocurrent and efficiency of the cell assembled with the glass-ITO electrodes also decayed with time, but the values were always higher than those exhibited by the flexible cell. On the 50th day, $\eta_{global} = 0.23\%$ for the rigid cell (under $10\,mW\,cm^{-2}$). The same behavior was observed under $100\,mW\,cm^{-2}$ (results not shown): on the 50th day, the overall efficiencies exhibited by the flexible and rigid cells were 0.07 and 0.10%, respectively. Considering the general form of the I–V curves registered on the 50th day after cell assembly (Fig. 2b), especially under high light intensity, it can be concluded that the series resistance of the rigid cell was lower than that of flexible cells. This effect was also observed from EIS measurements.

Fig. 4 presents some of the Nyquist diagrams registered under $10\,mW\,cm^{-2}$ for a flexible solar cell prepared with the TiO_2 ($UV_{15\,min}+140\,^{\circ}C_{2\,h}$) photoelectrode. For comparison, the impedance spectrum obtained 50 days after assembling the cell prepared by the same procedure using the glass electrodes is also included. In Fig. 4, experimental data are represented by symbols while the solid lines correspond to the fit obtained with Boukamp software using the equivalent circuit $R_S\,[C_1\,(R_1O_1)]\,(R_2Q_2)$, as previously discussed [20]. In this circuit, the symbols R and C describe resistance and capacitance, respectively; O, which depends on the parameters $Y_{o,1}$ and B, accounts for a finite-length Warburg diffusion (Z_{Dif}), and Q is the symbol for the constant phase element, CPE (its parameters were $Y_{o,2}$ and n) [24,27]. For the TiO_2/dye solar

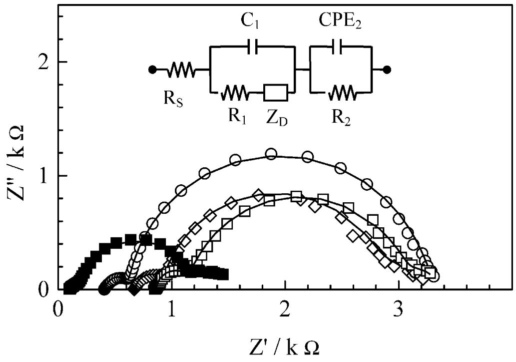

Fig. 4. Time evolution of Nyquist diagrams of the impedance spectra obtained for a solid-state, flexible solar cell prepared with a polymer electrolyte and TiO_2 ($UV_{15\,min}+140\,^{\circ}C_{2\,h}$) film deposited on PET-ITO electrode after the 1st (○), 9th (◇) and 50th (□) day of irradiation under $10\,mW\,cm^{-2}$. The Nyquist diagram obtained for a cell prepared by the same procedure using glass-ITO electrodes on the 50th day, is also presented (■). Experimental data are represented by symbols and solid lines correspond to fits obtained with Boukamp software using the equivalent circuit presented in the insert.

cells, R_S would describe the series resistance, and the elements with subscripts 1 and 2 are related, respectively, to the contribution of the interfaces of counter-electrode|electrolyte and porous electrode|electrolyte [20]. Time evolution of parameters obtained by fitting the experimental spectra obtained under $10\,mW\,cm^{-2}$ with this equivalent circuit, in the frequency ranging from 7.0×10^{-3} to 8.0×10^{4} Hz, are shown in Table 1.

The general behavior of the impedance spectra exhibited by the flexible TiO_2/dye solar cell in Fig. 4 was similar to that observed for cells assembled with the polymer electrolyte poly(EO-EPI) and different TiO_2 photoelectrodes, discussed in detail in previous studies [20]. Briefly, in the dark, the solar cells presented high impedance and the time constants were not well defined; under illumination, three semicircles could be identified in the Nyquist diagrams of the EIS spectra. The medium frequency response, which exhibited a strong dependence on the light intensity, was correlated to the TiO_2|electrolyte interface (R_2Q_2 elements). The small semicircle observed at high frequency was associated to the capacitance and charge transfer resistance at the Pt|electrolyte interface (C_1 and R_1 elements). This sub-circuit also accounts for the contribution of the diffusion of electroactive species in the polymer electrolyte, associated with the low frequency response. Such behavior may be related to the low ionic conductivity of the polymer electrolyte and the reduced mobility of I_3^-/I^- species in such a medium. Finally, the series resistance of the system (R_S), can account for the resistance of the polymer electrolyte, the resistance within the TiO_2 film and the PET-ITO electrode, as well as the contacts [20].

Considering, initially, the results obtained by fitting the impedance spectra presented by the freshly prepared cells (first and fourth day after assembling, Table 1), a correlation can be made with the results previously reported for a cell assembled with the same polymer electrolyte and a non-irradiated TiO_2 ($130\,^{\circ}C_{4\,h}$) film [20]. In that study, under $10\,mW\,cm^{-2}$, we obtained $R_S=0.38\,k\Omega$; $C_1=6.6\,\mu F$, $R_1=0.18\,k\Omega$, $Y_{o,1}=50\,mS$, $B=3.7\,s^{1/2}$; $R_2=0.87\,k\Omega$, $Y_{o,2}=0.08\,mF\,s^{n-1}$, and $n=0.9$. Thus, comparison of the parameters obtained in both studies reveals that the values of most of the parameters differed by less than 10%, except for the parameters associated with the TiO_2|electrolyte interface and with the diffusion of electroactive species in the polymer electrolyte, which presented considerable differences. Since the only difference between the cells investigated in both studies was related to the methodology of preparation of the TiO_2 films, such results confirm that the equivalent circuit used for fitting the impedance spectra is suitable to represent the TiO_2/dye solar cells assembled with the polymer electrolyte.

Examination of the time evolution of values presented in Table 1 reveals that the series resistance of the flexible cell increased with time. This effect can also be clearly observed from the Nyquist diagrams in Fig. 4. A similar behaviour was observed for the spectra obtained for the flexible cell under $100\,mW\,cm^{-2}$, as well as for the rigid cell. Under $10\,mW\,cm^{-2}$, R_S increased from $0.42\,k\Omega$ (first day) to $0.87\,k\Omega$ (50th day) for the flexible cell. On the other hand, for the same period of time, the R_S of the cell assembled

Table 1
Characterization of a solid-state, flexible TiO_2/dye solar cell assembled with PET-ITO electrodes and a polymer electrolyte under illumination at $10\,mW\,cm^{-2}$

Time days	V_{OC}/V	I_{SC} ($\mu A\,cm^{-2}$)	η (%)	R_S ($k\Omega$)	C_1 (μF)	R_1 ($k\Omega$)	$Y_{o,1}$ (mS)	B ($s^{1/2}$)	R_2 ($k\Omega$)	$Y_{o,2}$ ($mF\,s^{n-1}$)	n
1st	0.72	60	0.32	0.42	5.5	0.19	79	4.3	2.7	0.17	0.92
4th	0.76	57	0.31	0.38	6.2	0.15	30	4.4	1.8	0.20	0.89
9th	0.76	40	0.20	0.68	6.0	0.23	14	4.3	1.9	0.16	0.90
14th	0.72	38	0.20	0.81	6.2	0.26	17	4.0	1.8	0.16	0.89
22nd	0.72	35	0.16	0.78	6.0	0.29	21	4.8	2.0	0.14	0.88
40th	0.78	35	0.14	0.87	6.4	0.27	21	5.7	1.9	0.14	0.88
50th	0.69	27	0.10	0.87	6.0	0.30	21	5.4	2.0	0.14	0.88

Variation with time of the parameters estimated from I–V curves and obtained by fitting the impedance spectra using the equivalent circuit $R_S[C_1(R_1O_1)](R_2Q_2)$. Fitting performed with Boukamp software. The symbols R and C account for resistance and capacitance, respectively. The symbol O, which depends on parameters $Y_{o,1}$ and B, describes the finite-length Warburg diffusion (Z_D). The symbol Q (parameters $Y_{o,2}$ and B), accounts for the constant phase element, CPE.

with the glass electrodes increased from 37 to 100 Ω. However, the time evolution of the other parameters in Table 1 is not so systematic. For the elements associated with the TiO_2|electrolyte interface, R_2 remained almost constant and $Y_{o,2}$ decreased from 0.17 to 0.14 mF s^{n-1} from the 1st to the 50th day. For the elements related with the CE|electrolyte interface, C_1 remained almost constant and R_1 increased from 0.2 to 0.3 kΩ. Finally, for the parameters related to the Warburg diffusion in a finite-length region of length l_e, B increased from 4.3 to 5.4 $s^{1/2}$ and $Y_{o,1}$ decreased from 79 to 21 mS from the 1st to the 50th day. From these parameters, the coefficient of the diffusing species (D) can be estimated from $D = l_e^2/B^2$ [27]. Considering that the diffusion length l_e can be considered as the thickness between the electrodes (from the thickness of the adhesive tape, 42 μm), then it can be roughly estimated that D decayed from 1.2×10^{-6} to 0.8×10^{-6} $cm^2\,s^{-1}$, for both flexible and rigid solar cells [20].

Thus, the lower efficiency presented by the flexible cells, in comparison with the cell assembled with glass electrodes (using the same procedure), must be related to the increase in R_S with time, as also observed from *I–V* curves (Fig. 1). Therefore, this effect must be avoided for better performance and long-term stability of flexible, solid-state solar cells, which can present lower costs and broader applicability.

4. Conclusion

The performance and the stability of solid-state, flexible solar cells assembled with flexible TiO_2 photoelectrodes treated with UV radiation were investigated over a period of 50 days. UV radiation is a fast and low energy consuming method that aided the preparation of TiO_2 films onto flexible PET-ITO electrodes, allowing degradation of the surfactants commonly used to prepare the TiO_2 suspensions. This treatment, followed by heating at 140 °C in dry conditions (2 h), resulted in mechanically stable films which presented an intense adsorption of the dye sensitizer. Solid-state, flexible solar cells (1 cm^2) were assembled using such photoelectrodes, a polymer electrolyte and a Pt counter-electrode. For comparison, a similar cell was assembled using the same procedure and glass electrodes. The flexible, solid-state dye-sensitized TiO_2 solar cells presented an open circuit potential $V_{OC} = 0.72$ V, a short-circuit photocurrent $I_{SC} = 60\,\mu A\,cm^{-2}$ and an efficiency $\eta_{global} = 0.32\%$ under 10 mW cm^{-2} illumination; $\eta_{global} = 0.23\%$ under 100 mW cm^{-2}. This performance was maintained until the fourth day after assembling and then decayed. From the fourth until the 14th day, the V_{OC} values were almost constant but photocurrent and efficiency decreased considerably. The efficiency remained almost unchanged at 0.17% from the 14th until the 40th day and then decayed to 0.13% on the 50th day (10 mW cm^{-2}). The cell prepared by the same procedure using glass-ITO electrodes presented a better performance over all the time period investigated. Electrochemical Impedance Spectroscopy revealed that the series resistance in the flexible solar cells increased with time, affecting the stability and lowering cell efficiency. This effect was not so evident for cells assembled by the same procedure using glass electrodes. Therefore, the flexible electrode limits the preparation of the porous TiO_2 photoelectrode and creates a large series resistance during long-term irradiation of the solar cell. However, these results are still very promising for developing solid-state, flexible solar cells with lower costs and broader applicability.

Acknowledgements

Authors acknowledge financial support from FAPESP (fellowships 00/03086-3 and 01/02454-1), PRONEx/CNPq, and thank Daiso Co. Ltd. Osaka, Japan, for providing the polymer electrolyte.

References

[1] B. O'Reagan, M. Grätzel, Nature 353 (1991) 737.
[2] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
[3] F. Cao, G. Oskam, P.C. Searson, J. Phys. Chem. 99 (1995) 17071.
[4] W. Kubo, K. Murakoshi, T. Kitamura, Y. Wada, K. Hanabusa, H. Shirai, S. Yanagida, Chem. Lett. (1998) 1241.
[5] K. Tennakone, G.K.R. Senadeera, V.P.S. Perera, I.R.M. Kottegoda, L.A.A. De Silva, Chem. Mater. 11 (1999) 2474.
[6] Y. Ren, Z. Zhang, S. Fang, M. Yang, S. Cai, J. Appl. Electrochem. 31 (2001) 445.
[7] M. Matsumoto, Y. Wada, T. Kitamura, K. Shigaki, T. Inoue, M. Ikeda, S. Yanagida, Bull. Chem. Soc. Jpn. 74 (2001) 387.
[8] E. Stathatos, P. Lianos, C. Krontiras, J. Phys. Chem. B 105 (2001) 3486.
[9] E. Stathatos, P. Lianos, U. Lavrencic-Stangar, B. Orel, Adv. Mater. 14 (2002) 354.
[10] G. Katsaros, T. Stergiopoulos, I.M. Arabatzis, K.G. Papadokostaki, P. Falaras, J. Photochem. Photobiol. A: Chem. 149 (2002) 191.
[11] Y. Ren, Z. Zhang, S. Fang, M. Yang, S. Cai, Sol. Energy Mater. Sol. Cells 71 (2002) 253.
[12] A.F. Nogueira, M.-A. De Paoli, Sol. Energy Mater. Sol. Cells 61 (2000) 135.
[13] A.F. Nogueira, J.R. Durrant, M.-A. De Paoli, Adv. Mater. 13 (2001) 826.
[14] A.F. Nogueira, M.-A. De Paoli, I. Montanari, R. Monkhouse, J. Nelson, J.R. Durrant, J. Phys. Chem. B 105 (2001) 7517.
[15] F. Pichot, S. Ferrere, R.J. Pitts, B.A. Gregg, J. Electrochem. Soc. 146 (1999) 4324.
[16] P.M. Sommeling, M. Späth, J. Kroon, R. Kinderman, J. van Roosmalen, in: Proceedings of the 16th European Photovoltaic Solar Energy Conference and Exhibition, Glasgow, 1–5 May 2000.
[17] H. Lindström, A. Holmberg, E. Magnusson, L. Malmqvist, A. Hagfeldt, J. Photochem. Photobiol. A: Chem. 145 (2001) 107.
[18] G. Boschloo, H. Lindström, E. Magnusson, A. Holmberg, A. Hagfeldt, J. Photochem. Photobiol. A: Chem. 148 (2002) 11.
[19] M.-A. De Paoli, D.A. Machado, A.F. Nogueira, C. Longo, Electrochim. Acta 46 (2001) 4243.
[20] C. Longo, A.F. Nogueira, M.-A. De Paoli, H. Cachet, J. Phys. Chem. 106 (2002) 5925.

[21] A. Fujishima, K. Honda, Nature 238 (1972) 37.

[22] M.-A. De Paoli, C. Feliciano, Quím. Nova 1 (1978) 16.

[23] A.F. Nogueira, M.A. Spinacé, W.A. Gazotti, E.M. Girotto, M.-A. De Paoli, Solid State Ion. 140 (2001) 327.

[24] B.A. Boukamp, EQUIVCRT, version 4.51, University of Twente, The Netherlands, 1995.

[25] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964.

[26] H. Steven, A.J. Calussi, M.R. Hoffman, J. Phys. Chem. B 104 (2000) 9842.

[27] J.R. Macdonald, in: J.R. Macdonald (Ed.), Impedance Spectroscopy, Wiley, New York, 1987.