Direct Measurement of the Recombination Losses via the Transparent Conductive Substrate in Dye Sensitized Solar Cells

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The role of the conducting glass substrate (fluorine doped tin oxide, FTO) on the performance of dye sensitized solar cells was investigated using a new technique. In most techniques used today it is impossible to isolate the source of the recombination process. This process can occur simultaneously via the nanocrystalline TiO_2 particles and via the conductive glass that are in contact with the redox electrolyte. The new technique enabled us to measure the photovoltaic performance losses of the solar cell, only via the conducting glass under stationary and working conditions at different light intensities and electrolyte concentrations. The principal idea of this new technique was to change systematically the ratio between the areas of the particle matrix and the conductive glass that are in contact with the electrolyte. The method involved gradual increment of the glass area and thereby enabled extraction of the influence of the conducting glass only. The results obtained show that, under standard cell working conditions, the losses emerging from the conducting glass to the DSSC performance are relatively minimal and occur mainly near the cell's maximum power point. These results suggest that at least in the case of cells that operate with I^-/I_3^- redox liquid electrolyte the contribution of thin underlayers covering the conductive substrate is small.

Introduction

Dye-sensitized nanocrystalline solar cells (DSSC) show promise as a potential low-cost alternative for conventional solar cells.[1] The DSSC consists of a porous semiconductor film, typically anatase TiO_2, deposited on a transparent conducting oxide substrate (TCO), and an electrolyte that permeates the porous network up to the TCO. Under photon irradiation, the electron density in the TiO_2 increases by injection from the dye molecules, giving rise to photovoltage, while the increase of negative charge in the TiO_2 is compensated by ionic species in the liquid phase.

Recombination in DSSC is an interfacial process in which photogenerated electrons are transferred to I_3^- ions (either by a direct or sequential reactions) which serve as the hole conductors in the electrolyte. In this mean, DSSC differs from conventional p-n junction solar cells where recombination occurs in the bulk of the material. The special structure of DSSC enables close proximity between the photogenerated electrons and the oxidized redox species in the electrolyte. This proximity causes the recombination process to limits the cell's performance. Recombination processes can occur at both the enormous TiO_2/electrolyte interface and via the TCO/electrolyte interface at places where the nanocrystalline TiO_2 does not cover the substrate completely. Despite this structural deficit the cell's electrons diffusion length under short circuit conditions is on the order of the film thickness which enables high collection efficiencies of more than 80% possible on a regular basis.[2] The reason for this phenomenon is the relatively slow kinetics of I_3^- reduction at the TiO_2 and TCO interfaces under short circuit conditions. Nevertheless, recombination processes may occur to a larger extent under load conditions.

The recombination process both through the conductive glass and the particle matrix depends on the system potential. It was suggested that recombination via the substrate becomes the dominant process at low photovoltages because the recombination rate via this route varies less rapidly with photovoltage in comparison with the reaction via the TiO_2 conduction band.[3] This argument was confirmed by Hore et al., who measured the effect of TiO_2 compact underlayer on functioning DSSC.[4]

Two basic approaches to overcome the recombination loss mechanism were suggested. One approach involves the glass passivation by either electro-polymerization of an isolating polymer such as poly(phenylene oxide-co-2-allylphenylene oxide)[5] or by deposition of a thin semiconductor wide gap underlayer before the particles deposition.[6] The second approach treats both the TCO and the TiO_2 in one process thus affecting the recombination reaction at the two interfaces. In practice, an energy barrier that is fabricated on the nanoporous matrix surface results in a core−shell structure.[7] This thin layer which acts as energy barrier allows electron injection from the dye to the particles matrix but on the same time slows the recombination reaction. The commonly used energy barriers are wide band gap semiconductors with conduction bands that are relatively negative to the TiO_2 conduction band enable a reduction of the recombination rate processes at the interface. This coating technique results in most cases also in substrate coverage which resembles the underlayer passivation described above. However in this case it is difficult to distinguish between the recombination contribution of the substrate and that of the TiO_2 particles.

A study of the recombination processes at the TCO/electrolyte interface in an operating DSSC requires the ability to modify this interface without changing the other parts of the cell. Conceptually the simplest approach involves variation of the ratio between the TiO_2 and the TCO surface areas which are in contact with the redox solution. One can envision two ways of achieving this goal: keeping the TCO substrate area constant while the surface area of the TiO_2 film is changed by variation

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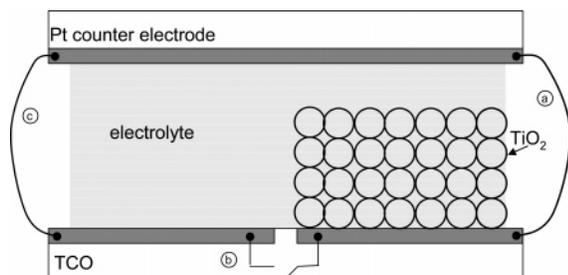
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Figure 1. Schematic description of the gap electrode setup. The electrode's TCO is separated by a narrow nonconducting gap into two parts: one part was covered with sensitized TiO_2 particles while the second was kept uncovered. This setup enabled separate measurements of both sides of the gap against Pt counter electrode (TiO_2 only (a) and FTO only (c)) or together (TiO_2 + FTO (b)) against the same counter electrode when both parts were short-circuited.

of its thickness, or vice versa changing the TCO area for a given TiO_2 surface.

In this work, we focused on changing the TCO surface area using two different setups. In the first setup, we used a gap electrode that allowed the addition of one constant glass area inside the illuminated cell, while the second setup provided the opportunity to change the exposed glass area gradually and systematically in an adjacent compartment. These new techniques allow measurements of physical quantities such as the losses to the open circuit voltage and the recombination currents in the DSSC emerging from the TCO/electrolyte interface under steady state and working conditions of liquid DSSC.

The results obtained in this work are important for the understanding of the TCO/electrolyte interface in liquid (I^-/I_3^- redox) based DSSC. With this understanding, we can answer the question whether a barrier underlayer for preventing recombination processes is needed in these cells.

Experimental Section

A. Gap Electrode Configuration. The TCO (Libby Owens Ford, 15 ohm/square F-doped SnO_2) used in this study was patterned with a 200 μm nonconducting gap by means of laser etching at Israel Aircraft Industries. The patterned TCO was cleaned with soap, rinsed with deionized water, and dried in a nitrogen stream. TiO_2 particles were deposited only on one part of the substrate using electrophoretic deposition under a constant current deposition mode resulting in 2 μm thin film. The second part of the conducting gaped TCO was covered with adhesive glue during the EPD in order to keep it clean from particles. The electrode was fired at 450 °C for 30 min in air without influencing the film thickness.

For all DSSC electrodes prepared in this work, the dye (*cis*-di(isothiocyanat)-*N*-bis(4,4′-dicarboxy-2,2′-bipyridine) ruthenium(II)) was adsorbed on the TiO_2 film using overnight immersion in a 0.5 mM ethanol solution of the dye. Pt sputtered F-doped SnO_2 film was used as a counter electrode and standard electrolyte of 0.5M LiI/ 0.05M I_2 in 1:1 acetonitrile:NMO was used to close the circuit ($I_3^- \leftrightarrow I_2 + I^-$, $K \approx 10^{-7}$ mol/dm^{-3} [8]). The DSSC measured in this study had the regular sandwich-type configuration (as shown in Figure 1 and for the DSSC in Figure 2). Cell illumination was performed using a calibrated Xe lamp and an Eco Chemie potentiostat was used to measure the I−V characteristics of the cell.

For the gap electrode measurement, the gap was placed in the middle of the illumination area so both parts of the gap were equally illuminated.
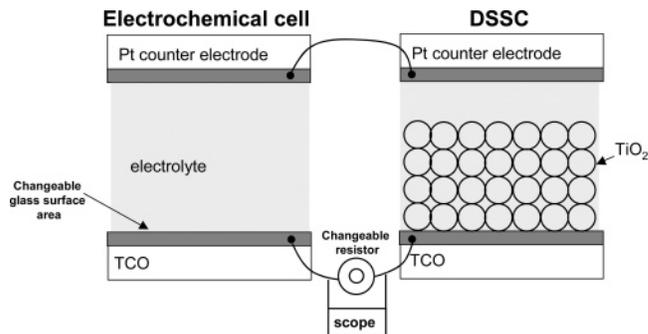

Figure 2. Schematic presentation of the system for measuring the influence of addition glass surface on the DSSC performance. The system is composed of two cells connected in serial: regular sandwich-type configuration of DSSC (right), and electrochemical cell composed of TCO and Pt counter electrode separated by electrolyte (left). The tunable resistor was connected between the cells to allow the measurement of the recombination current due to the increased interface surface area TCO/electrolyte.

B. Separate Electrochemical Cell Configuration. In this study, 6 different electrochemical cells (EC) were made using Teflon. Each cell had 2 round openings. The openings were sealed using TCO and Pt coated TCO and O-rings before they were filled with standard DSSC electrolyte. The TCO and the Pt electrode were respectively connected to the dyed TiO_2 electrode and to the Pt counter electrode of regular DSSC as shown in Figure 2. This measurement configuration enabled monitoring the effect of additional TCO/electrolyte area which emerged by the addition of ECs. A tunable resistor was connected between the DSSC and the EC, which enabled measurements of the recombination currents flowing from the DSSC to the EC due to addition of TCO/electrolyte areas in the EC. The recombination current was calculated using Ohm's law from the resistance maintaining constant of 10mV drop across the tunable resistor.

The exposed TCO area varied through the EC series enabling measurements for a variety of TCO/electrolyte interface areas. The additional TCO areas in the EC were 0.3, 0.95, 2, 3, and 7.8 cm^2. The addition of areas was also available upon serial connection of several ECs. These combinations allowed increments of the interface areas TCO/electrolyte even up to a factor of 30 with respect to the original exposed TCO area in the DSSC.

Results and Discussion

Gap Electrode Measurements. Gap electrode configuration allowed 3 different I−V measurements. The first option was measurement of the TiO_2 coated part of the gap electrode (Figure 1a). Connecting the second half of the gap electrode allowed us to measure the influence of addition TCO area on the performance of the TiO_2 part (Figure 1b). The addition of the bare TCO in the second part increased the TCO exposed area by a factor of 3, if one assumes that 50% of the glass in the deposited part is covered by TiO_2. Prior to the connection of the bare side, this side was measured separately both under illumination and in the dark to ensure a lack of photoactivity contribution from this side. Figure 3 shows I−V characteristics of the 3 measurements of the gap electrode. The TCO by itself did not show any photoactivity characteristics, thus, illumination of this part cannot contribute to the overall performance of the cell. However, this part of the gap electrode can serve as an additional recombination route upon connection. The Jsc obtained by the connected parts was exactly the same as for the TiO_2 when it was measured alone, because under short

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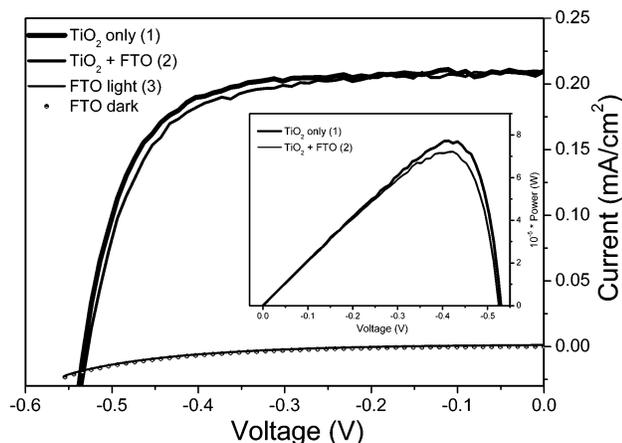*J. Phys. Chem. C, Vol. 112, No. 7, 2008* **2781**

Figure 3. IV characteristics for the three measurement options of the gap electrode under one sun illumination. The inset shows that the difference in the extracted power as a function of the voltage for the TiO$_2$ only (a) and when both parts of the electrode are connected (b). The difference is more pronounced near the maximum power point.

Figure 4. Losses to open circuit potential in the DSSC as a function of the added glass areas in the EC at different light intensities. The I$_3^-$ concentration in EC was 0.05 M, identical to the I$_3^-$ concentration in the connected DSSC and in the standard dye cell.

circuit conditions recombination processes are negligible especially from the TCO. However, the Voc of the connected parts was 5 mV lower than that of the TiO$_2$ coated part when this side was measured alone due to the additional recombination route. Note, that the obtained I−V characteristics values for the gap electrode presented in this paper are relatively low with comparison to standard performance of DSSC electrode. The reason for this stems from the relatively thin TiO$_2$ layer. This thin layer ensures that exposure of an extra TCO area will dominantly affect and change the ratio TiO$_2$/TCO areas that are in contact with the electrolyte.

The power that can be extracted from the cell in these two measurement options is shown in the inset of Figure 3. The influence of the additional extra glass upon connection of the bare half is pronounced mainly near the maximum power point (MPP). As mentioned above, it is commonly agreed that recombination at short circuit conditions is negligible anywhere in the system, thus, it is almost not affected by the addition of extra glass. Under open circuit conditions, the more dominant route for recombination is through the high surface area TiO$_2$ particles, therefore, the glass addition affected this parameter only slightly. However, when the current begins to flow, losses via the TCO become more dominant. These losses, increase to maximal values near the system's maximum power point, as was also shown by theoretical modeling.[9] The gap electrode configuration measurement indicates that the addition to the TCO/electrolyte interface even by a factor of 3 has minimal effect on the Voc and slightly more on the power, even though this affects the extracted power by not more than 5% of its original value.

Since the gap electrode configuration measurement permits addition of only one constant TCO area, it provides only limited insight of the recombination via the TCO/electrolyte interface. For better understanding of this process a second method of changing of the ratio between the TiO$_2$/TCO areas is used.

Separated Electrochemical Cells Measurements. In order to improve our understanding on the TCO influence on DSSC parameters, we developed a second technique that enables a gradual systematic decrease of the ratio TiO$_2$/TCO surface area. This decrease in ratio was achieved using serial connection of ECs (electrochemical cells) with varying TCO/electrolyte interfaces areas to a standard sandwich type DSSC (Figure 2).

In the first stage, we measured the losses to the DSSC photovoltage upon connection of different ECs with various
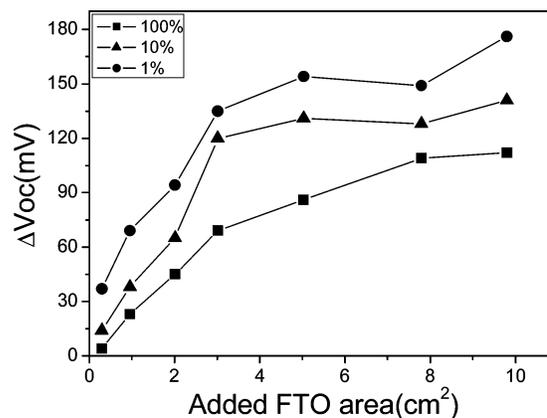
areas of TCO under different light intensities. The losses to the DSSC photovoltage upon the connections are shown in Figure 4. The initial Voc values for the DSSC before the EC connection were 763, 660, and 540 mV for illumination under 100%, 10%, and 1% respectively, where 100% illumination is equivalent to one sun illumination intensity. Figure 4 indicates that the losses to the photovoltage due to the addition of TCO (in the EC) are higher for low light intensities despite their initial lower Voc. We note that small deviations of the electrolyte concentration may occur in the DSSC upon illumination. These are not represented in the EC but as shown below have negligible effect on the results. Extrapolations for the curves in Figure 4 can help to extract quantitative data for the voltage losses occurring due to the TCO addition. These extrapolations were drawn for small TCO area addition where the voltage losses have linear dependence with the added areas. By definition, the extrapolations cut the origin because no external voltage losses occur without TCO addition in the EC. The extrapolations reveal that for 0.6 cm^2 DSSC, under one sun illumination, the loss to the voltage emerging from the exposed TCO is 22.8 mV per cm^2 exposed TCO. These losses are relatively higher for illumination with intensities of 10% and 1% of one sun illumination and are 37.7 and 47.6 mV per cm^2 TCO addition, respectively. Hence, in our case where the illuminated area of the DSSC is 0.6 cm,^{2} if we assume TiO$_2$ coverage of 0.5, the exposed TCO in the dye cell is in the range of 0.3 cm.^{2} These obtained results suggest that using an underlayer that prevents any TCO/electrolyte contact will only result in the gain of 6.8, 11.3, and 14.3 mV for illumination with 100%, 10%, and 1% of one sun illumination. These losses are without a doubt minor in comparison to an initial Voc of 763, 660, and 540 mV for the respective illumination intensity without the addition of glass. Even in an extreme situation, in which the TiO$_2$ coverage is only 20% of the geometrical DSSC area, the voltage losses will increase only up to 11.4, 18.8, and 23.8 mV for these illumination intensities.

The recombination currents at Voc emerging from the TCO addition at different light intensities are shown in a logarithmic scale in Figure 5a. These currents, measured with the tunable resistor, increase both by increasing the TCO areas exposure in the EC and also with increasing light intensity. Since the measurement is performed at Voc, where the injection current equals the overall recombination current, it is possible to reveal the ratio between the recombination via the glass in comparison with the overall recombination. One can assume that the injection current can be taken as the value of the DSSC short circuit current, because under these conditions recombination
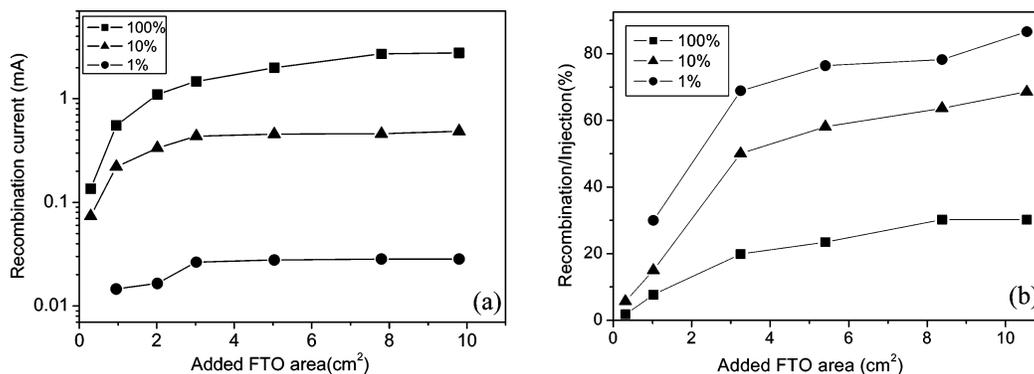
Figure 5. Absolute recombination currents (a) and normalized to the injected current (b) emerging due to addition of various glass surface areas under different light intensities. The recombination current was calculated using Ohm's law from the resistance on the changing resistor when constant 10mV were dropped for each glass addition. The injection current in (b) is the short circuit current measured under illumination for each light intensity.
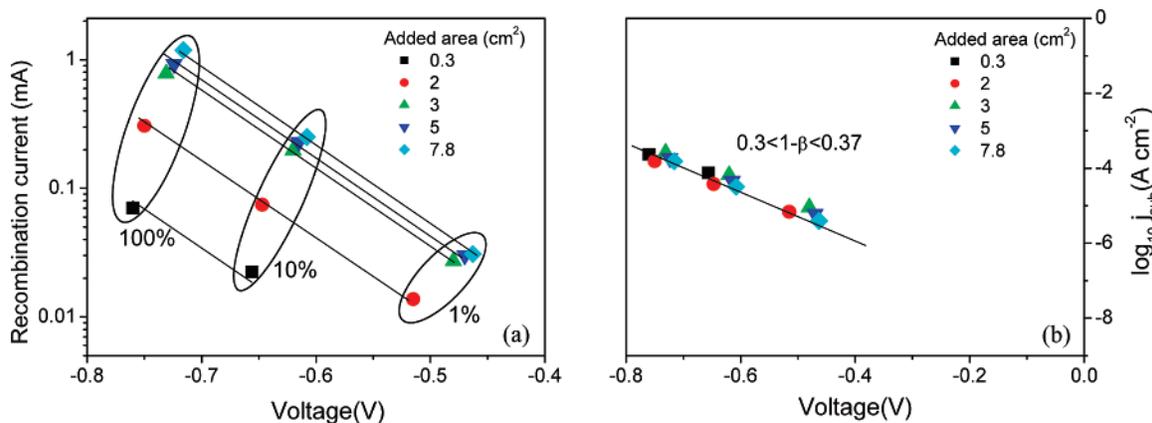

Figure 6. (a) Recombination currents emerging from the addition of various glass surface areas as a function of the cell photovoltage under different light intensities. In (b), the cathodic branch of Tafel plot is presented. In this plot, the recombination current was normalized to the TCO area. The slope of the trend line reveals β values of approximately 0.7, while the it is intersect presents exchange current density of 10^{-8} A cm^{-2}.

processes in the system are negligible. The recombination (via TCO)/injection currents for the different light intensities are shown in Figure 5b. The results reveal that the ratio between the recombination and injection currents is relatively higher at low light intensities. These results are in qualitative agreement with previous reports showing that a back reaction via the conducting glass affects the DSSC performance mainly at low light intensities and low photovoltages.[3] We note however that quantitatively we find the effect to be minor, as shown below.

A better understanding can be gained by plotting the measured recombination currents under different light intensities against the resulting system voltage, and not as a function of the added TCO area. This approach when adapted (Figure 6a) indicates that the slopes of the lines describing the recombination currents at different light intensities as a function of the system voltage are identical for all the added TCO areas. Consequently if the recombination current is plotted in the form of current density we obtain a master "recombination Tafel plot" for an operating cell (Figure 6b).

The TCO layer behaves essentially as a noncatalytic metal.[10] In the absence of diffusion limitations, the total current density over the TCO/electrolyte interface is described by the Butler-Vollmer equation. In general, the Butler-Vollmer equation describes the charge transfer over a metal/electrolyte interface which is not determined by diffusion limitation in the electrolyte.

In this case, the charge transfer only depends on the applied potential

$$j_{sub} = -j_0 \left[\exp\left(\beta \frac{e}{k_b T} U_{photo}\right) - \exp\left(-(1-\beta) \frac{e}{k_b T} U_{photo}\right) \right] \quad (1)$$

where j_0 represents the exchange current density at the equilibrium electrode potential, n is the number of electrons participating in the electro-reduction of tri-iodide ions, and β and $(1 - \beta)$ are the anodic and cathodic transfer coefficient respectively. The magnitude of the exchange current determines the electron's ability to exchange with solution, while β determines how the current is affected by the photovoltage. When plotting the overpotential (in our case, the photovoltage) against the logarithm of the absolute value of the current density, we obtained the so-called Tafel plot. Both branches of the curve, indicating eq 1, approach asymptotes for $U_{photo} \gg k_b T/e$, when either the first or the second term on the right-hand side of eq 1 can be neglected. In our case, even the minimal intensity illumination (1% of one sun) results in system photovoltage of more than 500mV. This is much higher than the 25mV of $k_b T/e$ at room temperature, thus, it is possible to consider this range of photovoltages as asymptote of Tafel plot. In addition, under DSSC operation, U_{photo} is negative, therefore, the relevant part of eq 1 is only the left term in the right side of the equation which corresponds to the reduction of I_3^- in solution. These
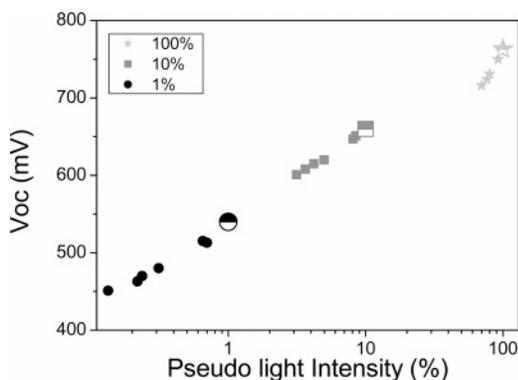
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Figure 7. The *Y* axis presents measured open circuit voltage for DSSC under 3 light intensities, with (small shapes) and without (big semi-transparent shapes) an increment to the origin glass surface. The *X* axis shows the pseudo light intensities of each point that were calculated by subtracting the recombination current, flow through the resistor, from the injection current which was taken as the DSSC short circuit current measured without any additional EC.

arguments suggest that the slope of the asymptote (Tafel slope) is $2.3K_bT/(1 - \beta)e$, and that the asymptote crosses the line $U_{photo} = 0$ (axis *Y*) at the point log j_0.[11] Hence, it is possible to determine β and j_0 of the operating cell from a line received from logarithmic scale of the recombination current density (j_{sub}) as a function of the cell photovoltage. For this case, the recombination currents that were measured with the tunable resistor were normalized to the TCO area through which they flow. Figure 6b presents the normalized recombination current as a function of the system's photovoltage. Assuming one electron transfer, Figure 6b shows that $1 - \beta$ is in the range of $0.3 < 1 - \beta < 0.37$ hence $0.63 < \beta < 0.7$. This β value which was measured under an operating cell conditions should be compared with β values measured by standard electrochemical methods.[12] The β measured in this study indicates that a back reaction via substrate is indeed varying less rapidly with photovoltage than reaction via the conduction band but not for such a substantial amount, as thought previously ($\beta n = 0.5$).[13]

The trend line intersects the *Y* axis ($U_{photo} = 0$) giving j_0 value of 10^{-8} A/cm². This value is also lower in comparison to values of $10^{-5}-10^{-6}$ A/cm² reported by Cameron et al.[3] Consequently, while confirming the general understanding regarding the role of the TCO in the overall recombination described by Cameron et al. we find that the actual effect of the TCO in the liquid based DSSC is relatively low.

One of the possibilities to explain the differences between our measured values and the results obtained by Cameron et al. is related to the type of FTO used in the experiment.[12] While our TCO was Libby Owens Ford FTO, the FTO used by Cameron et al. was supplied by Asahi. The difference in the glass cleaning procedure can also affect the glass electrochemical activity. The ultracleaned glass used by Cameron et al. may result in higher j_0 in comparison to a regular cleaning procedure. Therefore, the electrochemical activity of the FTO substrate used by Cameron et al. could be much higher than that of the one used by us. Our relatively small exchange current density (10^{-8} A cm⁻²) is a good clue for this behavior and may explain the small losses occurred upon TCO exposure in our measurements.

Figure 7 demonstrates the validity of the measurements presented herein. In this figure, measured photovoltages (*Y* axis) are plotted vs "pseudo light intensity": the measured photo-voltage is taken from Figure 4. Here, they are presented as full Voc measured with the EC addition rather than the ΔVoc used above. The "pseudo light intensity" (*X* axis) is a value calculated based on the linear relation between the injection current and the I_0. Therefore, by subtracting the recombination current measured upon exposure of additional TCO, from Jsc (which represents the injection current) we obtain a value that represents the photoactive injection current. Variations in this value are similar to variations in I_0. When the photovoltages are plotted as a function of the "pseudo light intensity" logarithm, a straight line with a slope of 120 mV/decade is obtained. This behavior is a typical DSSC characteristic.

Another confirmation of the validity of our measurements was obtained when different iodine concentrations were used in the EC electrolyte, while keeping a standard iodine concentration in the DSSC. In this case, reducing the I_3^- concentration decreased the voltage losses of the DSSC upon additional TCO exposure.

Conclusions

New technique for the study of TCO which affect the performance of DSSC is presented. The technique allows measurements of the Voc losses and the recombination currents under stationary conditions occurred due to exposure of added TCO areas. The gap electrode configuration also allows measurements of the losses to the extracted power under working cell conditions. Light dependent measurements, conducted with an additional ECs, showed that a back reaction via the substrate is more pronounced under low light intensities. Neverthe less, j_0 is relatively small (in the range of 10^{-8} Acm⁻²) and the value of β is close to 0.7. These findings indicate that the electrochemical activity of the FTO used in this experiment is low. We found that under regular DSSC working conditions with one sun illumination, the cell's voltage loss which originates from the TCO is less than 3% of the Voc for each cm² of uncoated TCO that is in contact with the redox solution.

In conclusion, the back reaction of electrons from the fluoride-doped tin oxide conducting glass substrate can be neglected during the operation of DSSC at least when iodide/tri-iodide ions are used as redox electrolytes.

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