

# Time-Resolved Electroluminescence of Dye Sensitized Solar Cells

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The electroluminescence of dye sensitized solar cells is measured under forward bias as a function of time after the cells are connected to and disconnected from an external voltage source. At low applied voltages, which correspond to forward currents smaller than the short circuit current under AM1.5 illumination, the electroluminescence intensity reaches its steady state within a few hundred milliseconds. The observed signals are very similar to time dependent photocurrents measured after the illumination is switched on. In this voltage range the electroluminescence intensity increases exponentially with the applied voltage in accordance with the predictions of the generalized Planck equation. Surprisingly, at larger applied voltages the electroluminescence intensity exhibits a maximum as a function of time and its steady-state value decreases with increasing applied voltage. A simple numerical model and measurements with cells containing different electrolytes suggest that this unexpected feature of the dye sensitized solar cell can be assigned to the depletion of the oxidizing species of the redox couple in the electrolyte. Energy transfer reactions from the excited state of the dye to TiO<sub>2</sub> conduction band electrons, which have been proposed for this observation, are rather improbable.

## Introduction

Recently it has been demonstrated<sup>1</sup> that the application of the generalized Planck equation<sup>2–4</sup> to measurements of the electroluminescence of dye molecules adsorbed on a nanocrystalline TiO<sub>2</sub> electrode in a dye sensitized solar cell (DSC, Figure 1) can be used to calculate  $\Delta\mu$ , the difference of the chemical potentials of adsorbed dye molecules in an excited-state D\* and in the ground-state D

$$\Delta\mu = \mu_{D^*} - \mu_D \quad (1)$$

Assuming electrochemical equilibria between the TiO<sub>2</sub> conduction band and the LUMO (lowest unoccupied molecular orbital) of the dye and between the redox couple in the electrolyte and the HOMO (highest occupied molecular orbital), it can be shown that

$$\Delta\mu = E_{F,TiO_2} - E_{Red/Ox} \quad (2)$$

where  $E_{F,TiO_2}$  is the Fermi energy of the TiO<sub>2</sub> conduction band and  $E_{Red/Ox}$  is the redox potential of the electrolyte.

The assumption of the above-mentioned equilibria is reasonable because the dyes used in DSCs are chosen such that there is good electronic coupling and consequently a large electron exchange rate between the TiO<sub>2</sub> and the LUMO on the one side and between the electrolyte and the HOMO on the other side.

The voltage of the cell is given by the difference between the Fermi energy at the front contact and the redox potential at the back contact,<sup>5</sup> if voltage drops over the TCO (transparent conducting oxide) contacts due to current flow can be neglected.

As all the potentials in eq 2 are taken at the location of the adsorbed dye molecules,  $\Delta\mu$  calculated from the electrolumi-

nescence, can be identified with the voltage at the location of the dye molecules.

In ref 1 it has been shown that a quantitative analysis of the electroluminescence of a DSC yields

$$\Delta\mu = e(U - IR_s) = eU_{int} \quad (3)$$

i.e., the voltage at the location of the dye molecules equals the applied voltage minus the voltage over a series resistance  $R_s$ . This series resistance can be assigned to the TCO sheet resistance and to contact resistances.

The equality of  $\Delta\mu$  and the internal voltage  $U_{int} = U - IR_s$  indicates that no further voltage losses occur inside the cell.

In this work, contrary to the investigation in ref 1, we investigate the electroluminescence intensity up to large voltages, which correspond to current densities which are larger than the short circuit current densities of the cells under AM1.5 ( $\sim 5$  mA/cm<sup>2</sup>).

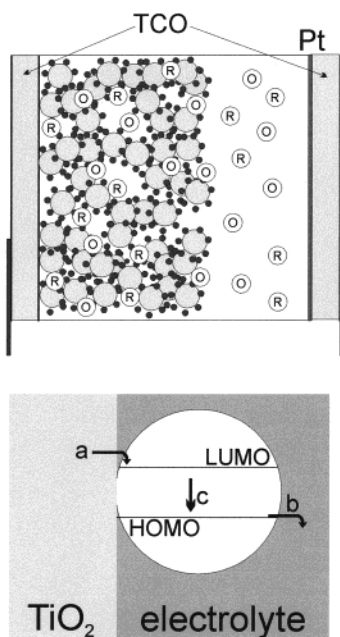
In this voltage range the electroluminescence intensity decreases with increasing forward bias, an observation which cannot be explained by a voltage drop over a constant series resistance, which must thus be interpreted in terms of an additional voltage loss inside the cell.

Energy transfer reactions from excited dye molecules to TiO<sub>2</sub> conduction band electrons have been proposed as an explanation for this observation which has already been reported for a similar system.<sup>9</sup>

An alternative explanation is that the depletion of the oxidizing ions in the electrolyte at the location of the dye molecules at large current densities is the origin of the decrease of the EL intensity with increasing applied voltage.

In the case of electroluminescence the generation of excited dye molecules takes place via two reactions. Starting with a dye molecule in the ground state, an excited molecule is generated by electron injection from the TiO<sub>2</sub> into the LUMO (Reaction *a* in Figure 1) and by electron withdrawal from the

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**Figure 1.** Upper part: Schematic representation of a dye sensitized solar cell. A nanocrystalline cluster of TiO<sub>2</sub> particles (light circles) is covered with a monolayer of a charge-transfer dye (dark circles). The liquid electrolyte containing reducing (R) and oxidizing (O) ions can interpenetrate the whole TiO<sub>2</sub>/dye network. This system is sandwiched between two conducting glass sheets, which serve as electrical contacts and as support for the cell. This geometry combines the advantages of direct contact between each dye molecule and the TiO<sub>2</sub> and of sufficient light absorption. A platinum layer on the counter electrode serves as catalyst for electron transfer from the TCO to oxidized ions in the electrolyte. Lower part: The three processes, which are involved in electroluminescence are a, electron injection from the TiO<sub>2</sub> into the LUMO of the adsorbed dye molecule; b, electron withdrawal from the HOMO of the dye molecule by an oxidizing ion in the electrolyte; c, radiative recombination of an excited dye molecule, i.e., electron transfer from the LUMO to the HOMO. Reactions a, b, and c are taking place in the opposite direction under usual working conditions of the cell, i.e., under illumination.

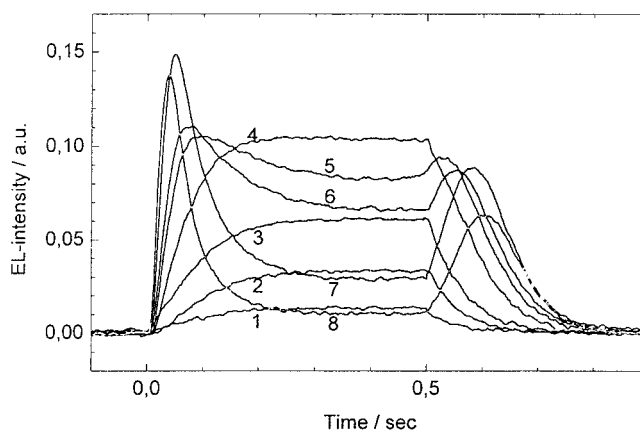
HOMO by an oxidizing ion in the electrolyte (*b* in Figure 1). No matter in which order these two reactions take place, one oxidizing ion is required for the generation of each excited dye molecule. A depletion of the oxidizing species in the electrolyte is therefore connected with a decrease of the generation rate and of the density of excited dye molecules and thus with a lower EL intensity.

As every electron contributing to the electrical current through the cell must somewhere be taken up by an oxidizing ion, the annihilation rate of oxidizing ions equals the electron current through the cell. Taking into account that in DSCs the oxidizing ion concentration in the electrolyte is usually much smaller than the concentration of the reducing ions, it is obvious that large electrical currents in the forward direction lead to a significant depletion of the oxidizing ions and thus to a lower EL intensity.

We present time-resolved measurements of the electroluminescence intensity in relative units on cells containing different electrolytes and a simple numerical model, which are used to identify the origin of the additional voltage loss at large applied voltages.

## Experimental Section

**Cell Preparation.** The TiO<sub>2</sub> layers were made by spreading a TiO<sub>2</sub> paste from Solaronix (Ti-Nanoxide D, colloidal anatase particle size 13 nm; 120 m<sup>2</sup>/g (BET)) onto a transparent conductive oxide coated glass (TCO) (Libbey-Owens-Ford, Tec-



**Figure 2.** EL-intensity of a dye sensitized solar cell (cell A) as a function of time for different current densities. At  $t = 0$  the cell is connected to an external voltage source; at  $t = 0.5$  s the cell is disconnected from the voltage source and left under open circuit conditions. The stationary values of the current density in mA/cm<sup>2</sup> are 1, 5.5; 2, 7.8; 3, 10.2; 4, 12.5; 5, 23.9; 6, 27; 7, 38.9; 8, 46.9.

glass, 8 ohm/square) by a doctor blading technique as described elsewhere.<sup>6</sup> After drying the layers were sintered in air for 30 min at 450 °C. While still hot they were then immersed into a  $3 \times 10^{-4}$  M solution of cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (N3) in ethanol and kept there overnight. The layer thickness was determined afterward to be 4  $\mu$ m with a profilometer (TENCOR, Alpha Step).

The counter electrode was platinized by depositing a small amount of a 0.05 M solution of H<sub>2</sub> PtCl<sub>6</sub> in 2-propanol onto a TCO glass, into which two holes had been drilled beforehand, and sintering at 380 °C for 20 min.<sup>7</sup> A Surlyn foil (Du Pont) mask was fitted around the TiO<sub>2</sub>-layer, and the counter electrode was placed onto it. The cell was clamped and heated until the foil was melted and the electrodes stuck together.

The electrolyte solution, (0.5 M LiI, 0.5 or 0.05 M or  $5 \times 10^{-4}$  M I<sub>2</sub>, 0.68 M 4-*tert*-butylpyridine in acetonitrile) was filled in and the cell was sealed.

**Experimental Setup.** The EL of the DSCs was measured by placing the cells at a defined distance of 1 cm from the detector, which was a calibrated silicon diode with an area of 1 cm<sup>2</sup>. As no optical instruments were placed between the cell and the detector the measured signal is proportional to the integral EL intensity  $j_{v,int}$ . The signal was observed with a current voltage converter with a transimpedance of  $10^8$  V/A and a digital oscilloscope which could directly be read out by a PC. An external voltage source was used to apply the desired forward bias. After disconnection from the external voltage source the cells were left under open circuit conditions. Either the current through the cell or the voltage between the contacts could be measured simultaneously with the EL intensity.

## Results and Discussion

Figure 2 shows the EL intensity of a DSC (cell A) containing the usual electrolyte concentration (0.05M I<sub>2</sub>) as a function of time for different applied voltages corresponding to different current densities. At  $t = 0$  the cell is connected to and at  $t = 0.5$  s the cell is disconnected from the external voltage source.

At low current densities the EL intensity initially rises slowly to its stationary value, which is reached within a few hundred milliseconds. We find that with increasing current density the initial rise of the EL intensity gets faster.

Similar observations were also made for the time dependence of the photocurrent of the cell after an illumination is switched

on. The photocurrent is found to reach its steady state value quite slowly within a few 10 to a few hundred milliseconds, the rise getting faster with increasing incident light intensity.

The observations regarding the time dependence of the photocurrent have already been described by Schwarzburg and Willig,<sup>8</sup> who interpreted their results in terms of trap filling in the TiO<sub>2</sub>. The traps are due to surface states, which are present at high concentrations in nanocrystalline materials due to the large internal surface.

As the transport of electrons through the TiO<sub>2</sub> is also involved in the process of EL we believe that the model for the time dependence of the photocurrent presented in ref 8 can also be applied to the time dependence of the EL intensity.

At larger current densities,  $j > 20 \text{ mA/cm}^2$ , the EL intensity as a function of time reaches a maximum after the initial rise, then decreases and reaches its stationary value. All curves in Figure 2 are plotted on the same scale for the EL intensity, and it can thus be seen that the stationary value of the EL intensity decreases with increasing current density.

A further surprising observation, which has not been found for the photocurrent, is that at  $t = 0.5 \text{ s}$  when the cell is disconnected from the external voltage source and left under open circuit conditions the EL intensity rises again and has a second maximum. These observations cannot be explained by trap filling.

A decrease of the EL intensity with increasing applied voltage has already been observed for a Ru-dye adsorbed on a rotating nanocrystalline TiO<sub>2</sub> rod in an oxidizing electrolyte by Athanassov et al.<sup>9</sup> They explain this observation by so-called energy transfer reactions (ETR) from excited dye molecules to TiO<sub>2</sub> conduction band electrons. These reactions are thought to become the dominant recombination channel for excited dye molecules with increasing electron density in the TiO<sub>2</sub> conduction band at large applied voltages.

This explanation implies that the density of excited dye molecules decreases while at the same time the electron density in the TiO<sub>2</sub> increases. We will briefly discuss whether such a behavior can be expected.

The electrochemical equilibrium between the TiO<sub>2</sub> conduction band and the LUMO of the adsorbed dye molecules is not disturbed significantly if the rate of energy transfer reactions is small compared to the electron-transfer rates between the TiO<sub>2</sub> and the LUMO.

As one electron is transported from the TiO<sub>2</sub> into the electrolyte during each energy transfer reaction, the electron current through the cell is an upper limit for the rate of ETR. On the other hand the time constant for electron injection from photoexcited dye molecules into the TiO<sub>2</sub> has been measured to be on the order of femtoseconds,<sup>10</sup> which indicates a very large equilibrium exchange rate between the TiO<sub>2</sub> and the LUMO.

A quantitative estimate of the exchange rates assuming a time constant for electron injection in the femtosecond range shows that the exchange rate is at least 1 order of magnitude larger than that of the electron current through the cell.

Taking into account that a large portion of the electrical current is transported directly from the TiO<sub>2</sub> into the electrolyte, it is obvious that ETR do not disturb the electrochemical equilibrium between the TiO<sub>2</sub> and the LUMO significantly.

According to these considerations a decrease of the density of excited dye molecules with increasing electron density and thus ETR as an explanation for the decreasing EL intensity with increasing forward bias are rather improbable.

As mentioned above the increasing annihilation rate of oxidizing ions in the electrolyte with increasing current density through the cell provides an explanation for the observed decrease of the EL intensity with increasing applied voltage.

Using a very simple model, which will be described below, we made numerical calculations for the time dependence of the density of excited dye molecules, which are used to check whether the above explanation is consistent with the measured time dependence of the EL intensity shown in Figure 2.

In this model the cell is divided into two parts. One part of the cell is modeled as an effective medium containing the redox system and the TiO<sub>2</sub> with the adsorbed dye molecules. In this part the concentration of all particles is constant throughout the thickness. Any effects of spatial inhomogeneities and of the nanocrystalline geometry of the TiO<sub>2</sub> electrode are thus not included in our model. The second part only contains the electrolyte with a reducing and an oxidizing species with their respective concentrations  $C_{\text{ox}}$  and  $C_{\text{red}}$ . This part is subdivided into 20 segments with a thickness of  $0.2 \mu\text{m}$ . The initial concentration of the ions is equal in each segment.

The concentration of the ions in the effective medium is equal to the concentration in the first segment  $C_{\text{ox}}^0$ . The concentration in the last segment, i.e., at the counter electrode is held constant.

The motion of the ions in the part of the cell which only contains the electrolyte is described by the diffusion equation

$$j_{\text{ox}} = -D_{\text{ox}} \frac{dC_{\text{ox}}(x)}{dx} \quad (4)$$

where  $D_{\text{ox}}$  is the diffusion constant for the oxidizing ions in the electrolyte. As we are only interested in a qualitative description, we neglect the complications arising from the fact that the  $\text{I}^-/\text{I}_3^-$  redox system is used in the cells and assume a simple  $\text{I}^-/\text{I}^\cdot$  redox system.

At  $t = 0$  a homogeneous electron generation rate  $g$ , which is proportional to the current through the cell, is switched on in the effective medium and the evolution of the system as a function of time is calculated numerically.

In the calculation the following processes are taken into account. A single trap level in the TiO<sub>2</sub> is considered, which can exchange electrons with the TiO<sub>2</sub> conduction band and with the electrolyte. The change of the density of filled traps  $n_t$  is given by

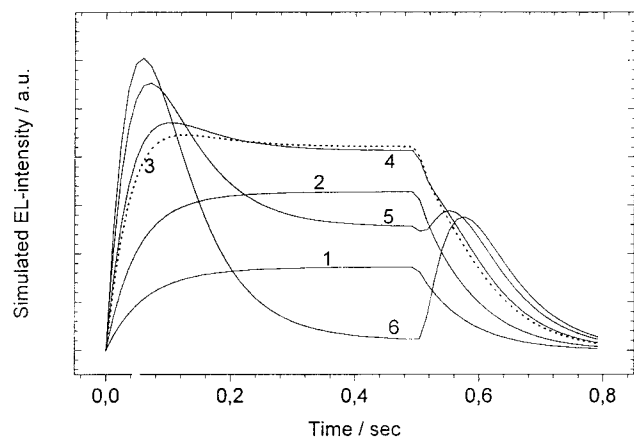
$$\frac{dn_t}{dt} = k_t(N_t - n_t)n_e - k_d n_t - k_1 n_t C_{\text{ox}}^0 \quad (5)$$

where  $N_t$  is the density of traps,  $n_e$  is the density of TiO<sub>2</sub> conduction band electrons,  $k_t$  and  $k_d$  are the rate constants for trapping and detrapping,  $k_1$  is the rate constant for electron transfer from a filled trap into the electrolyte, and  $C_{\text{ox}}^0$  is the concentration of oxidizing ions in the electrolyte at the interface between the two parts of the cell. The time evolution of the electron concentration is given by

$$\frac{dn_e}{dt} = g - k_t(N_t - n_t)n_e + k_d n_t \quad (6)$$

Equations 5 and 6 are found in ref 8 except for the term  $-k_1 n_t C_{\text{ox}}^0$ , which allows for the electron transfer from an occupied trap state into the electrolyte.

The luminescence intensity is proportional to the number of excited dye molecules. As described above, in the case of EL, the generation of excited dye molecules involves electron injection from the TiO<sub>2</sub> into the LUMO and withdrawal of an



**Figure 3.** Calculated time dependence of the EL-intensity according to a simple numerical model (see text for details). The parameters used for these calculations are  $D_1 = 7 \times 10^{-6} \text{ cm}^2/\text{s}$ ;  $C_{\text{ox}} = 3 \times 10^{19} \text{ cm}^{-3}$  (corresponding to 0.05M);  $N_t = 7 \times 10^{19} \text{ cm}^{-3}$ ,  $k_d = 1/\text{s}$ ,  $k_t = 2 \times 10^{-19} \text{ cm}^{-3}/\text{s}$ ;  $k_i = 10^{-14} \text{ cm}^{-3}/\text{s}$ ; thickness of the effective medium  $d = 4 \mu\text{m}$ . The part of the cell, which only contains the electrolyte, is subdivided into 20 segments with a thickness of  $0.2 \mu\text{m}$ . The generation rates (in units of  $10^{19}/\text{cm}^3/\text{sec}$ ) 1, 8.6; 2, 19.5; 3, 37; 4, 42; 5, 60; 6, 73 correspond to electrical current densities of 5.5, 12.5, 23.9, 27, 38.9, 46.9  $\text{mA}/\text{cm}^2$  for a homogeneous generation rate and for a cell thickness of  $4 \mu\text{m}$ .

electron from the HOMO by an oxidizing ion. Therefore we assume the density of excited dye molecules to be proportional to the electron density in the  $\text{TiO}_2$  and to the density of oxidizing ions  $C_{\text{ox}}^0$ . This assumption is reasonable at low electron densities.

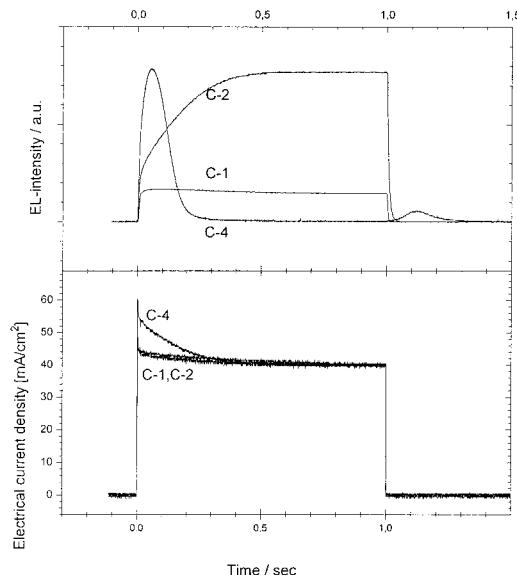
We tried to reproduce the experimental results with the above-described model and with realistic parameters (the numerical values of the parameters for the calculations presented in Figure 3 are given in the caption) but we want to emphasize that the numerical calculations are rather intended to check whether the observed time dependence of the EL intensity can be reproduced qualitatively.

It should be mentioned that in our calculations the value of the trapping rate  $k_d$  has no significant influence on the results. Therefore, an estimation of the position of the trap level with respect to the conduction band using the ratio  $k_d/k_t$  is not meaningful.

The result of the numerical calculations is shown in Figure 3. The time dependence of the product  $n_e C_{\text{ox}}^0$  for different generation rates is very similar to the observed time dependence of the EL intensity. The slow increase of the signal, the faster rise with increasing current density, the maximum as a function of time, the decreasing stationary value, and even the maximum after switching off the generation rate are reproduced with our model. According to these calculations the decrease of the EL intensity occurs simultaneously with the depletion of the oxidizing ions. The slow initial rise of the EL is mainly determined by the filling of the trap states.

The maximum after the generation rate is switched off is due to the fact that the electron density in the  $\text{TiO}_2$  decreases more slowly, than the concentration of the oxidizing ions increases by diffusion. An experimental evidence for the slow decrease of the electron density in the  $\text{TiO}_2$  is obtained from the observation that the open circuit voltage of the cell decreases within a few hundred milliseconds to zero after the cell is disconnected from the external voltage source.<sup>1</sup>

To find a further indication for our explanation we investigated three cells ( $C_1, C_2, C_3$ ) which were identical except for the concentration of oxidizing ions in the electrolyte (0.5, 0.05, and



**Figure 4.** EL intensity and electrical current density of three cells as a function of time for an equal stationary value of the current density. The cells C-4, C-2 and C-1 only differ in the concentration of  $I_2$  in the electrolyte (0.0005, 0.05, and 0.5 M, respectively). The decrease of the EL-intensity after an initial peak is only observed for the cell C-4, with the lowest concentration of oxidizing ions.

0.0005 M, respectively). If the decrease of the EL intensity is related to the depletion of the oxidizing ions, it is expected that the effect is most pronounced for a cell containing a low concentration of oxidizing ions.

In Figure 4 the electrical current and the EL-intensity of these three cells are plotted as a function of time. For an equal stationary value of the current density, the steady-state value of the EL intensity is larger for the cell C-2 than that for the cell C-1.

According to the predictions of the generalized Planck equation and to the investigation in ref 1, the absolute intensity of the EL is determined by the applied voltage if no voltage losses occur inside the cell.

But due to the different composition of the electrolyte, the three cells have different  $I(V)$  characteristics and therefore the same current density corresponds to different applied voltages. Thus a comparison of the absolute intensities for equal current densities is not meaningful. We rather want to emphasize the different relative time evolution of the EL intensity of the three cells.

It can be seen that the drastic decrease of the EL intensity only occurs for the cell C-4 with the lowest oxidizing ion concentration, in accordance with our prediction. This can be interpreted in the way that only for the cell C-4 the current density of  $40 \text{ mA}/\text{cm}^2$  results in a significant depletion of the oxidizing ion concentration. Also the time evolution of the current density of the cell C-4 in Figure 4 suggests that at  $40 \text{ mA}/\text{cm}^2$  the diffusion limitation is reached. The fact that after the initial increase the current density and the EL intensity reach their stationary value more or less simultaneously is a further indication that the decrease of both quantities has the same origin, namely, the depletion of the oxidizing ions.

Comparing the time dependence of the EL intensity of the cell A in Figure 2 and of the cell C-2 in Figure 4 it is obvious that the decrease of the EL intensity occurs at much lower current densities for the cell A although the same ion concentration is used in both cells.

We find that cells from different series which are actually produced under equal conditions sometimes differ substantially



in their electronic properties, e.g., in the  $I(V)$  characteristic. One explanation for these variations in the cell quality might be variations in the quality and in the purity of the employed materials. But the ultimate cause for these variations has not been found so far.

As the cells A and C-2 were produced in different series the measurements presented in Figure 2 and in Figure 4 are not comparable.

The measurements presented in Figure 4 were obtained on cells from the same series. Up to the filling of the cells with electrolyte all production steps were carried out identically and with the same materials. The only difference between the cells is the variation in the  $I_2$  concentration in the electrolyte. Different electronic properties must therefore be due to the influence of the  $I_2$  concentration.

In addition the measurements in Figure 4 were repeated with several cells from the same series containing the same ion concentrations such as the cells C-1, C-2, and C-4. Apart from slight deviations between measurements on identically produced cells, the qualitative trend, the decrease of the EL intensity occurring at lower current densities for cells with a lower oxidizing ion concentration, could unambiguously be confirmed.

If a depletion of the oxidizing ions is the origin of the decrease of the EL intensity, one might also expect a strong decrease of the current density, which is obviously in contradiction to the experimental observations (Figure 4).

We think that the oxidizing ions which are regenerated at the counter electrode and which reach the nanocrystalline  $TiO_2$  electrode via diffusion are consumed directly at the interface  $TiO_2$ /electrolyte, giving rise to the electrical current. The consumption of the oxidizing ions prevents them from entering the nanocrystalline electrode and consequently from contributing to the generation of excited dye molecules throughout the thickness of the  $TiO_2$  layer. This would explain why the current density only shows a small decrease as a function of time, while the EL intensity decreases by orders of magnitude.

## Conclusions

The time dependence of the electroluminescence of dye sensitized solar cells could be measured for different applied voltages.

With increasing applied voltage we observe a decrease of the EL intensity, which is connected with a characteristic time dependence of the signal. The decreasing EL intensity with increasing applied voltage indicates that at large current densities there is an additional voltage loss inside the cell.

Numerical calculations using a simple model for the DSC and measurements on cells containing different electrolytes revealed that this additional voltage loss can be assigned to the depletion of the oxidizing ions in the electrolyte.

This is in contrast to the explanation given by Athanasov et al.<sup>9</sup> who interpreted similar observations in terms of energy transfer reactions, which we believe to be improbable due to the electrochemical equilibrium between the  $TiO_2$  and the LUMO of the dye, which is not expected to be significantly disturbed by the current through the cell.

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