Electroluminescence of the Dye-Sensitized Solar Cell

T. Trupke and P. Würfel*

Institut für Angewandte Physik, Universität Karlsruhe, Kaiserstrasse 12, D-76128 Karlsruhe, Germany

I. Uhlendorf and I. Lauermann

Institut für Angewandte Photovoltaik, Munscheidstrasse 14, D-45886 Gelsenkirchen, Germany Received: June 9, 1998; In Final Form: December 8, 1998

Measurements of the electroluminescence of dye-sensitized solar cells are presented for the first time. Forward biasing of a dye-sensitized solar cell leads to electron injection into the dye which is adsorbed on a nanocrystalline TiO_2 film. Application of the generalized Planck equation yields $\Delta\mu_D$, the difference of chemical potentials of dye molecules in an excited state and in the ground state, which are involved in the optical transition. We find that $\Delta\mu_D$ is equal to the voltage between the contacts of the cell, after the latter is corrected for a voltage drop over a series resistance.

1. Introduction

Since energy conversion yields of 7.9% in simulated solar light and 12% in diffuse daylight could be demonstrated for solar cells based on dye-sensitized colloidal TiO₂ films,¹ research on this system has been expanding rapidly. Meanwhile, energy conversion yields up to 11% for AM 1.5 have been demonstrated². These films consist of nanometer-sized TiO₂ particles covered with a monolayer of a charge-transfer dye which was *cis*-(SCN⁻)₂bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium-(II) (also called N3) in the investigated solar cells, a dye which has proved to have outstanding properties as a sensitizer in regenerative solar cells.³

To our knowledge electroluminescence (EL) of a finished dye-sensitized solar cell (DSC) has not been observed so far. This might be due to the fact that the EL is expected to be suppressed by ultrafast electron injection from the excited state of the dye into the TiO₂ conduction band. This is the process that occurs predominantly under illumination and is the basis of the functioning of the DSC, because in the excited state of the dye the electron is located in one of the 4,4'-dicarboxy-2,2'-ligands which serve to attach the dye molecules to the surface of the TiO₂.⁴

Measurements of electroluminescence from dye molecules adsorbed on a rotating TiO₂ rod have recently been published.⁵ These measurements have been carried out with an electrolyte containing peroxodisulfate, which facilitates electron injection and thus luminescence.

We show in this paper that finished DSCs emit EL under forward bias with a spectral distribution of the emitted photons indicating that the emission arises from the adsorbed dye molecules. The question, which transitions in the dye contribute to the emission and to the absorption of light, will be discussed in the following section.

Under forward bias the processes giving rise to the electrical current and to the emission of EL are the same that cause losses in an illuminated DSC. As the cells in our investigation contain the usual iodide electrolyte and have not particularly been

A high open circuit voltage under illumination indicates, that a high forward bias can be applied with a comparatively low current flowing through the cell. As the latter limits the maximum voltage, which can be applied to the cell without causing irreversible damage, measurable emission of EL can be expected from DSCs with a high open circuit voltage $U_{\rm OC}$ under illumination. The $U_{\rm OC}$ of the cells investigated in this study were slightly above 0.75 V under 1000 W/m² AM 1.5. Cells with open circuit voltages in the range of 0.65 V did not emit measurable EL.

We have optimized our cells for large $U_{\rm OC}$ with respect to the thickness of the TiO₂ layer and the purity of the dye, which were found to affect the open circuit voltage and the EL of the cells.

2. Theory

In the DSC the application of a forward bias leads to the generation of excited dye molecules and hence to the emission of electroluminescence via electron injection from the TiO_2 conduction band and hole injection from the electrolyte into the adsorbed dye molecules. The reactions leading to excited dye molecules (D*) involve D, the ground state, and D⁺, the oxidized state of the dye.

$$D \leftrightarrow D^+ + e_{al} \tag{1}$$

$$D^* \leftrightarrow D^+ + e_{TiO_2} \tag{2}$$

where $e_{\rm TiO_2}$ and $e_{\rm el}$ stand for an electron in the TiO₂ conduction band and for an electron in the electrolyte, respectively. If these reactions are in chemical equilibrium, i.e., if the rates of these reactions in both directions are equal, the minimum of the free energy yields the following relations between the electrochemical potentials

$$\mu_{\rm D} = \eta_{\rm D^+} + \eta_{\rm el\,dve} \tag{3}$$

modified for our purposes the results are more suitable to yield information about the functioning of the DSC than the investigations in ref 5.

 $[\]mbox{*}$ Author to whom correspondence should be addressed. Peter.Wuerfel@phys.uni-karlsruhe.de.

$$\mu_{\mathrm{D}^*} = \eta_{\mathrm{D}^+} + \eta_{\mathrm{TiO}_2,\mathrm{dye}} \tag{4}$$

where $\eta_{TiO_2,dye}$ and $\eta_{el,dye}$ stand for the electrochemical potentials of electrons in the TiO_2 conduction band and in the electrolyte, both values taken at the location of the adsorbed dye molecules. Assuming equilibrium of the reactions in eqs 1 and 2, even if a voltage is applied, is justified if the relativ change of the transition rates due to the current is small.

Combining eqs 1 and 2 yields the difference between the chemical potentials of the molecules in the excited state and of the molecules in the ground state

$$\Delta\mu_{\rm D} = \mu_{\rm D^*} - \mu_{\rm D} = \eta_{\rm TiO_2, dye} - \eta_{\rm el, dye}$$
 (5)

Similar equations could also be used for the generation of excited dye molecules involving reduced molecules, also yielding eq 5, as the electrochemical potential of the reduced molecules cancels as well as the one for the oxidized molecules in the above equations.

The electrochemical potential of electrons in the TiO_2 is the Fermi-energy, while the electrochemical potential in the electrolyte is called redox-potential. According to eq 5, the difference between the Fermi-energy in the semiconductor and the redox-potential (both values taken at the location of the adsorbed dye molecule) equals $\Delta\mu_D$. As the voltage which is measured between the contacts of the cell equals the difference between the Fermi-energy at the front contact and the redox-potential at the back contact, $\Delta\mu_D$ is expected to be equal to the applied voltage if no voltage losses on the way from the dye molecules to the contacts are present.

 $\Delta\mu_D$ can be determined experimentally from the luminescence as it is contained in the generalized Planck equation (GPE),

$$\mathrm{d}r_{\mathrm{sp}}(\hbar\omega) = \alpha(\hbar\omega) \frac{\frac{c_0}{n(\hbar\omega)} D_{\gamma}(\hbar\omega)}{\exp\left(\frac{\hbar\omega - \Delta\mu_{\mathrm{D}}}{kT}\right) - 1} \mathrm{d}(\hbar\omega)\mathrm{d}\Omega \quad (6)$$

which relates the rate of non-thermal, spontaneous emission $\mathrm{d} r_{\mathrm{sp}}(\hbar\omega)$ in the photon energy interval $\mathrm{d}(\hbar\omega)$ and in the solid angle interval $\mathrm{d}\Omega$ to the absorption coefficient $\mathrm{d}(\hbar\omega)$. In this formula, $D_{\gamma}=n^3(\hbar\omega)^2/4\pi^3\hbar^3c_0^3$ is the density of states for photons with energy $\hbar\omega$, where c_0 is the velocity of light in vacuum and $n(\hbar\omega)$ is the refractive index of the material involved.

Thus our investigation consists of using the luminescence as an indicator for the difference of chemical potentials $\Delta\mu_D$ in the adsorbed dye molecules, which we compare to the applied voltage. Similar investigations on DSCs have been made by Smestad,⁶ who showed that the maximum open circuit voltage which can be expected from a solar cell can be predicted from the luminescent properties of the absorbing medium.

The GPE has explicitly been derived for direct semiconductors in ref 7 and in ref 8 and for indirect semiconductors in ref 9 and has been confirmed experimentally by measurements of the emission by direct transitions in GaAs LEDs¹⁰ and by indirect transitions in silicon solar cells.¹¹ It was also applied to the luminescent emission of molecules.¹²

The chemical potential difference $\Delta\mu_{\rm D}$ is related to the densities of molecules in the excited state and in the ground state (N^* and N, respectively) by 12

$$\frac{N^*}{N} \frac{N^0}{N^{*,0}} = \exp\left(\frac{\Delta \mu_{\rm D}}{kT}\right) \tag{7}$$

where N^0 and $N^{*,0}$ are the densities of molecules in the ground state and in the excited state at complete thermal and chemical equilibrium, i.e., without an applied voltage.

This formula is valid if there are two sets of states which are occupied according to separate thermal distributions with different chemical potentials for the upper and for the lower set of states.

Assuming that by absorption of light or by any other excitation the number of molecules in the ground state is not substantially changed with respect to N^0 , eq 7 can be simplified to

$$\frac{N^*}{N^{*,0}} = \exp\left(\frac{\Delta\mu_{\rm D}}{kT}\right) \tag{8}$$

which shows that the determination of $\Delta\mu_D$ corresponds to the determination of the ratio $N^*/N^{*,0}$.

The emission of luminescence depends on the number of molecules in the excited state and on their distribution over the vibrational and rotational sublevels. The major assumption, which is crucial for the applicability of the GPE is that all excited molecules participating in the emission of luminescence must occupy the vibrational and rotational levels according to a thermal distribution with a defined temperature, which implies that the time for the thermalization within all sublevels must be substantially shorter than the radiative lifetime of the molecules.

In this case the ratio $N^*/N^{*,0}$ equals the ratio between the emitted luminescence intensity and the thermal emission of the molecules. Hence we obtain $\Delta\mu_{\rm D}$ by measuring the luminescence intensity and dividing it by the thermal emission, which is given by Planck's law in eq 6 for $\Delta\mu_{\rm D}=0$.

The assumption that the number of molecules in the ground state does not change is by no means necessary. In a general case, eq 7 must be used instead of eq 8, which shows that the difference of chemical potentials is due to a shift of both chemical potentials.

At this point we would like to emphasize the major difference between our investigation and the determination of radiative lifetimes, ^{14,15} which also makes use of the close relation between the emission and the absorption expressed by the GPE. For the calculation of the rate constant for radiative transitions, which is the reciprocal of the radiative lifetime, the number of molecules in the excited state must be known. This is possible only if the ratio between the partition functions of the upper and of the lower set of states is known. In most applications the partition functions defined with respect to the lowest vibrational state of the respective set of states are assumed to be equal. ¹²

Our investigation involves only the ratio between different occupations of the same set of states (see eq 7). Hence, all the detailed information about the density of states contained in the partition function need not be known.

The rate of spontaneous emission in eq 6 cannot directly be observed experimentally. In ref 16, it has been shown for silicon solar cells that the integration of the rate of spontaneous emission $dr_{\rm sp}(\hbar\omega)$ yields the photon current density $dj_{\gamma}(\hbar\omega)$, which is emitted into a half sphere

$$dj_{\gamma}(\hbar\omega) = A(\hbar\omega, T) \frac{(\hbar\omega)^{2}}{4\pi^{2}\hbar^{3}c_{0}^{2}} \frac{1}{\exp\left(\frac{\hbar\omega - \Delta\mu_{D}}{kT}\right) - 1} d(\hbar\omega)$$
(9)

when multiple reflections and reabsorption of the photons on

their way to the surface of the cell are taken into account. $A(\hbar\omega,T)$ is the absorptivity, which is defined as the ratio between absorbed and incident photon current.

As the GPE, which is the basis of eq 9, is the same for a semiconductor and for molecules we will also make use of this formula in the present study. A homogeneous distribution of the excited molecules in the cell is assumed in the derivation of eq 9.

Since $\hbar\omega - \Delta\eta \gg kT$ in our investigations, eq 9 can be rewritten

$$dj_{\gamma}(\hbar\omega) = C \exp\left(\frac{\Delta\mu_{\rm D}}{kT}\right) A(\hbar\omega, T) (\hbar\omega)^2 \exp\left(\frac{-\hbar\omega}{kT}\right) d(\hbar\omega)$$
(10)

which shows that the luminescence intensity equals the thermal emission times $\exp(\Delta \mu_D/kT)$.

From eq 10 it can be seen that the only unknown quantity which determines the spectral distribution of the emitted luminescence is the absorptivity $A(\hbar\omega,T)$, while the absolute value of the luminescence is influenced by $\Delta \mu_D$ and by the absorptivity. Hence $A(\hbar\omega,T)$ in relative units can easily be calculated from the EL-spectrum which also needs to be measured in relative units only. If the absorptivity is known from other experiments or from the literature at a single energy $\hbar\omega$, which lies within the spectral range of the luminescence, the relative values obtained from the spectrum can be scaled into absolute values.

The integral photon current density $j_{\gamma,int}$ can be calculated as a function of $\Delta\mu_D$ by integrating eq 10 over $d(\hbar\omega)$. This relation between $j_{\gamma, \text{int}}$ and $\Delta \mu_D$ can be used to calculate $\Delta \mu_D$ from measured absolute values of $j_{\gamma,int}$.

This procedure, which will be applied to the investigation of DSCs in the Experiments section, has the advantage that absolute values for $j_{\gamma,int}$ can be determined much more accurately than absolute values for $dj_{\gamma}(\hbar\omega)$, because when $j_{\gamma,int}$ is measured the DSC can be placed directly in front of the detector with no other optical devices in between.

It is important to notice that the values of $\Delta \mu_D$, which are determined this way are very insensitive to the above-mentioned transformation of the absorptivity into absolute values. At room temperature, an error of a factor 3 results only in an absolute error in $\Delta\mu_D$ of about 30 meV, which is a relative error of 3–5% of the applied voltage in our investigation.

The procedure we present here is applicable only if the emission of luminescence originates from excited states, which are occupied according to a thermal distribution. Band and Heller¹⁷ already showed that the general relationship between the absorption and the emission in multilevel systems requires as the only assumption the internal thermal equlibrium within the initial states involved in the transition.

It is known that the dye molecules used in the investigated cells (N3) have an excited singlet state and an energetically lower-lying excited triplet state. While optical transitions between the ground state (which is also a singlet state) and the excited singlet state are spin allowed, the transitions between the ground state and the triplet state are spin forbidden. Therefore the absorption coefficient at the energy difference between the two singlet states is much larger than the absorption coefficient at the energy difference between the ground state and the excited triplet state, $\alpha(\hbar\omega_{SS}) \gg \alpha(\hbar\omega_{ST})$.

Under illumination the much larger absorption coefficient α- $(\hbar\omega_{SS})$ leads to a high generation rate of excited singlet states,

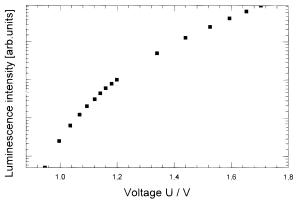


Figure 1. Luminescence intensity on a logarithmic scale as a function of the applied voltage.

which is followed by a very rapid thermalization into the excited triplet state, which is called intersystem crossing.

The rapid thermalization indicates a high exchange rate between the excited singlet and the excited triplet state, which leads to the establishment of thermal and electrochemical equilibrium between the two sets of states and which causes the emission of luminescence to arise mainly from the longlived excited triplet state. Due to the long lifetime of the excited triplet state the establishment of the above-mentioned equilibria before the emission of luminescence occurs is even more probable. This qualitative argument for the establishment of an equilibrium between all excited states which participate in the emission of luminescence is sufficient for the applicability of the GPE. The individual influences of all the different kinetic processes in a DSC on this equilibrium need not be known in

Experimental evidence for the establishment of a thermal distribution within the excited states is obtained in our work from the observation that the relative distribution of the emitted photons over energy is independent of the applied voltage within the investigated voltage range. This observation is expected, if the emission arises from thermalized states and if the excitation is sufficiently small (below the laser condition).

Contrarily, if the emission arises from a non thermal distribution, a dependence of the spectrum on the applied voltage is probable.

3. Experiments

EL of the DSC was obtained by application of a forward bias to the cell. The emitted radiation was passed through a 1/4m Yobin-Yvon-monochromator with a grating blazed at 600 nm. A calibrated, liquid-N2-cooled Ge diode was used as a detector. The detector signal was observed by a current-voltage converter and a lock-in amplifier.

The integral luminescence intensity $j_{\gamma, \text{int}}$ has been measured by placing the cell at a defined distance from the detector with no other optical elements in between. In calculating the integral photon current density emitted into the solid angle 2π from the measured lock-in voltage, the following factors have been taken into account: the area of the detector and of the cell, the distance between the cell and the detector, the quantum efficiency of the Ge diode, the transimpedance of the current-voltage converter, the fact that the lock-in amplifier only measures the first Fourier-component of the signal, and Lamberts law for the angular dependence.¹¹

The measured integral luminescence intensity $j_{\gamma,int}$ is plotted as a function of the applied forward bias in Figure 1 in arbitrary units and on a logarithmic scale. It can be seen that the values

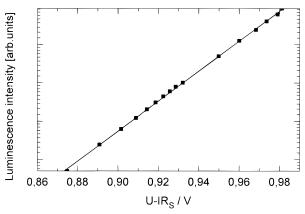


Figure 2. Luminescence intensity on a logarithmic scale as a function of the internal voltage $U_{\text{int}} = U - IR_{\text{S}}$.

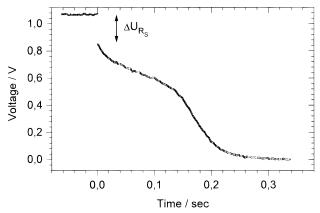


Figure 3. Voltage of the DSC after disconnection of the cell from an external source as a function of time. The very rapid voltage-drop ΔU_{R_s} immediately after the disconnection is identified as a voltage drop over a series resistance.

substantially deviate from the straight line, which would be expected from eq 10. Similar deviations from an expected exponential law are observed for the current-voltage characteristic I(U). In both cases these deviations can clearly be assigned to a voltage drop over a series resistance R_S , which might be identified with the resistance of the TCO contacts of the cell. If either $j_{\gamma,\text{int}}$ or I is plotted as a function of $U_{\text{int}} = U - IR_S$ with the proper value for R_S (14.1 Ω for this cell), which is done for $j_{\gamma,\text{int}}$ in Figure 2, the exponential dependence is confirmed.

A further confirmation for this procedure is obtained from time-resolved measurements of the voltage between the contacts of the cell. A forward bias is applied to the cell from an external source, and the voltage is measured with an oscilloscope. The time dependence of the voltage after the cell is disconnected from the source and left under open circuit conditions is shown in Figure 3. A very rapid drop of the voltage is observed immediately after the disconnection at t=0. This rapid decay of the voltage is the voltage drop over the series resistance caused by the current through the external circuit $I_{\rm ext}$, which disappears when the cell is disconnected from the source.

The rapid voltage drop ΔU_{R_s} and $I_{\rm ext}$ have been measured for different applied voltages. ΔU_{R_s} as a function of $I_{\rm ext}$ is plotted in Figure 4. The slope of this curve gives $R_{\rm S}$, and the value which is obtained matches very well the values which are obtained from the I(U) and from the $j_{\gamma, \rm int}$ (U) curves (3.5 Ω for this cell). For both cells which have been investigated in the present work, the three procedures give the same values with an accuracy of 2%.

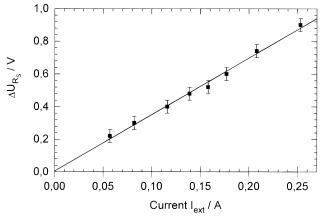


Figure 4. The voltage drop ΔU_{R_s} from Figure 3 as a function of the electric current $I_{\rm ext}$ which is flowing through the external circuit before the cell is disconnected from the external source. From the slope the value of the series resistance is 3.5 Ω .

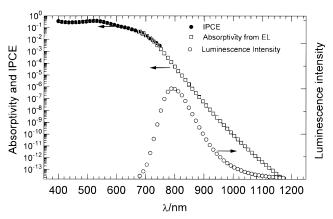


Figure 5. Electroluminescence spectrum of the DSC (open circles) and the absorptivity which has been calculated from it by division by $(\hbar\omega)^2 \exp(-\hbar\omega/kT)$ (squares). The obtained relative values for the absorptivity have been fitted to the measured IPCE (full circles).

The slope of the $j_{\gamma,\text{int}}$ ($U-IR_S$) curve (Figure 2), which should be equal to e/kT according to eq 10, corresponds to a temperature of 298 K, which is in good agreement with the measured room temperature of 300 K.

The proportionality between $j_{\gamma, \text{int}}$ and $\exp(eU_{\text{int}}/kT)$ shows that $\Delta\mu_{\rm D}$ and U_{int} are related by

$$eU_{\rm int} = \Delta\mu_{\rm D} + {\rm const.}$$
 (11)

Now we will show, that measurements of absolute luminescence intensities can be used to determine the constant which appears in eq 11.

Absolute values for the spectral energy current density are difficult to obtain experimentally. The emitted photon current spectrum for an applied voltage of 1.4 V is shown in Figure 5 in arbitrary units. The spectrum resembles the spectrum of the dye in solution.³ It is not surprising that the position of the luminescence maximum at 793 nm is red-shifted with respect to the luminescence maximum of the dye in solution, which is at 755 nm.³ This is due to the fact that the dye is adsorbed on a TiO₂ surface. Such a red-shift accompanying dye adsorption on a TiO₂ surface has been reported for similar ruthenium complexes^{18–20} and also for rhodamine B on ZnO electrodes.²¹ It is a further confirmation that the emission of photons does not arise from desorbed dye molecules.

According to eq 10, division of $dj_{\gamma}(\hbar\omega)$ by $(\hbar\omega)^2 \exp(-\hbar\omega/kT)$ yields $A(\hbar\omega)$ in relative units. As mentioned above, these

TABLE 1

ι_{D}
35
38
90
93
95
3:

relative values have to be fitted to a measured value of the absorptivity. Transmission measurements are not a practical method to obtain the very small values of the absorptivity of the dye in the spectral range where the emission of EL occurs because in such an experiment the absorption of light by other components of the cell (e.g., the electrolyte or desorbed dye molecules) or scattering of light cannot be distinguished from the absorption of the adsorbed dye.

An alternative method, which is applicable to solar cells, is the measurement of the incident photon to current conversion efficiency (IPCE), which is defined as the number of electrons flowing through the external circuit per incident photon under monochromatic illumination. As the electrons from the excited state of the dye are quickly injected into the TiO₂ conduction band and then transported to the contact of the cell with a very high efficiency, the IPCE is in good approximation equal to the absorptivity of the adsorbed dye. The values of the IPCE, which have been measured with monochromatic light of low intensity, which was modulated at frequencies as low as 1 Hz, while the cell was simultaneously illuminated with intense white bias light, can thus be used to transfer the calculated relative values obtained from the luminescence spectrum into absolute values, which is done in Figure 5.

The absorptivity, which now is known in absolute units, is used to integrate eq 10 over the whole spectrum, yielding a relation between $j_{\gamma,\rm int}$ and $\Delta\mu_{\rm D}$. This relation is used to calculate $\Delta\mu_{\rm D}$ from the measured integral luminescence intensity $j_{\gamma,\rm int}$. As the values for the absorptivity are experimental data, the integration of the emitted spectral photon current must be carried out numerically.

The values of $\Delta\mu_{\rm D}$ extracted from the experiment are compared with $e(U-IR_{\rm S})$ in Table 1.

The deviations of $eU_{\rm int} = e(U - IR_{\rm S})$ from $\Delta\mu_{\rm D}$ are on the order of kT which corresponds to a deviation of the luminescence intensity by approximately a factor of 3. This is within the uncertainty of the calculated integral luminescence-intensity. The main error originates from fitting the relative values of the absorptivity to the measured IPCE.

4. Conclusion

It has been shown that EL of DSCs can be measured and that the emission of light arises from the adsorbed dye molecules.

The generalized Planck equation (GPE) has been used to obtain $\Delta\mu_D$, the difference between the chemical potentials of dye molecules in the ground state and in an excited state, from experimental values for the integral luminescence intensity. Thermal and chemical equilibria between the excited singlet and the excited triplet state must be assumed for the applicability of the GPE.

We observe that the values of $\Delta\mu_D$, which are obtained from the EL, agree with the internal voltage $U_{\rm int}$, which is the applied voltage corrected for a voltage drop over a series resistance $R_{\rm S}$.

Thus the dependence of the EL intensity on the applied voltage allows us to determine the value of R_S . The same value for R_S is obtained from the current-voltage characteristic and

also from time-resolved measurements of the voltage between the contacts of the cell after the cell is disconnected from an external source and left under open circuit conditions. The agreement of these independent methods ensures the correct assignment of the value of the series resistance. The series resistance might be due to the resistance of the TCO electrodes and due to contact resistances.

In silicon solar cells the difference of the quasi-Fermi-energies (the electrochemical potentials) for conduction-band and valence-band at best equals the applied voltage multiplied by e, the elementary charge. In a DSC, the internal voltage multiplied by e is equal to the difference between the Fermi-energy of the TiO_2 -conduction-band at the front contact and of the redox-potential of the electrolyte at the back contact.

$$eU_{\rm int} = \eta_{\rm TiO_2,front} - \eta_{\rm el,back}$$
 (12)

Our investigations show that the internal voltage also coincides with the difference of chemical potentials $\Delta\mu_D$ of the adsorbed dye molecules in the ground state and in an excited state:

$$eU_{\rm int} = \Delta\mu_{\rm D} = \mu_{\rm D^*} - \mu_{\rm D} = \eta_{\rm TiO_2,front} - \eta_{\rm el,back} \quad (13)$$

In the dye studied in this work, the transition from the ground state to the lowest excited state can be described as a metal-to-ligand charge transfer (MLCT). The ligand participating in optical transitions is one of the 4,4'-dicarboxy-2,2'- ligands, which serve to attach the Ru complex to the surface of the TiO₂.⁴ Electron transfer (in both directions!) is therefore likely to occur at high rates between the TiO₂ conduction band and the excited state. Contrarily, in the metal centered (MC) ground-state, electron transfer between the molecule and the electrolyte is more probable, because the electron is located relatively far away from the TiO₂.

These considerations explain at least qualitatively that electrochemical equilibria exist at the location of the dye molecules between electrons in the TiO_2 and the molecules in the excited state and between the redox system in the electrolyte and the molecules in the ground state, which is expressed by eq 5. Eqs 5 and 13 yield

$$eU_{\rm int} = \eta_{\rm TiO_2, dye} - \eta_{\rm el, dye} = \eta_{\rm TiO_2, front} - \eta_{\rm el, back}$$
 (14)

Our experiments show that the difference of chemical potentials of the dye molecules at the location of the adsorbed dye equals within an uncertainty of kT the difference of electrochemical potentials at the contacts, i.e., the internal voltage. In other words, no significant voltage losses occur in the investigated cells due to the transport of charge carriers.

Acknowledgment. We thank J. Gehring and L. Dloczik for the cell preparation.

References and Notes

- (1) O'Regan, B.; Grätze, M. Nature 1991, 353, 737.
- (2) Fraunhofer Institut für Solare Energiesysteme, PV-Charts, http://www.ise.fhg.de/kallab/Pvcharts.html, September 1997.
- (3) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6328.
 - (4) Hagfeld, A.; Grätzel, M. Chem. Rev. **1995**, 95, 49.
- (5) Athanassov, Y.; Rotzinger, F. P.; Péchy, P.; Grätzel, M. J. Phys. Chem. B 1997, 101, 2558.
 - (6) Smestad, G. Sol. Energy Mater. Sol. Cells 1994, 32, 273.
 - (7) Lasher, G.; Stern, F. *Phys. Rev.* **1964**, *133*, 2A, *A553*.
 - (8) Würfel, P. J. Phys. C 1982, 15, 3967-3985.

- (9) Würfel, P.; Finkbeiner, S.; Daub, E. Appl. Phys. A 1995, 60, 67.
- (10) Feuerbacher, B.; Würfel, P. J. Phys. Chem. 1990, 2, 3803.
- (11) Schick, K.; Daub, E.; Finkbeiner, S.; Würfel, P. Appl. Phys. A 1992, 54, 109.
 - (12) Ross, R. T. J. Chem. Phys. 1967, 46, 4590.
 - (13) Ross, R. T.; Hsiao, T. L. J. Appl. Phys. 1977, 48, 4783.
 - (14) Bolton, J. R.; Archer, M. D. J. Phys. Chem. 1991, 95, 8453.
 - (15) Ross, R. T. Photochem. Photobiol. 1975, 21, 401.

- (16) Trupke, T.; Daub, E.; Würfel, P. Sol. Energy Mater. Sol. Cells 1998, 53, 103.
 - (17) Band, Y. B.; Heller, D. F. Phys. Rev. A 1988, 38, 1885.
- (18) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J. J. Am. Chem. Soc. 1985, 107, 2988.
- (19) Nazeeruddin, M. K.; Liska, P.; Moser, J.; Vlachopoulos, N.; Grätzel, M. Helv. Chim. Acta 1990, 73, 1788.
 - (20) Gulino, D. A.; Drickhammer, H. G. J. Phys. Chem. 1984, 88, 1173.
 - (21) Gerischer, H.; Willig, F. Topics Curr. Chem. 1976, 61, 31.