Analysis of the Mechanisms of Electron Recombination in Nanoporous TiO₂ Dye-Sensitized Solar Cells. Nonequilibrium Steady-State Statistics and Interfacial Electron Transfer via Surface States

Juan Bisquert,*,† Arie Zaban,‡ and P. Salvador§

Departament de Ciències Experimentals, Universitat Jaume I, 12080 Castelló, Spain, Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel, and Departament de Matemàtiques i Informàtica, Universitat de les Illes Balears, 07071 Palma de Mallorca, Spain

Macroscopic assemblies of semiconductor particles, with dimensions in the nanometer range, permeated with a transparent conducting phase (nanoporous electrodes) show a useful behavior in applications such as photocatalysis and dye-sensitized solar cells. A fundamental event in dye-sensitized solar cells is the recombination of photoinjected electrons with acceptor species (ionic holes) in the electrolyte phase surrounding the nanoparticles. Intrinsic semiconductor surface states play an important role in this process, not only as electron traps but also as intermediate states for electron transfer to the electrolyte (interfacial recombination centers). To describe the electron lifetime of electron trapped at band gap surface states, the concepts developed in the early analysis of recombination processes in photoconductors, such as the demarcation level, are quite useful. However, in photoelectrochemical systems (dye-sensitized solar cell), holes can be identified with oxidized, electrolyte dissolved species so that a new statistical analysis of the interfacial recombination process, considering the distribution of fluctuating, electrolyte energy levels, is required. Moreover, since in dye-sensitized solar cells the quasi-Fermi level for electrons, E_{Fn}^*, controls both the photovoltage and the rate of electron transport through the porous network, it is of great significance to find a correlation between the traps occupancy and E_{Fn}^*. We develop a consistent formulation that, fulfilling these requirements, allows to deal with an arbitrary distribution of band gap surface states. Our analysis, which is based on those physical parameters describing the probability of electron transfer among band gap surface states, the conduction band, and electrolyte levels, allows macroscopic recombination time constants to be defined. The model considers different mechanisms for the transfer of photogenerated electrons from the semiconductor to empty electrolyte levels: direct electron transfer from conduction band states, indirect transfer of electrons trapped at monoenergetic, deep surface states, and indirect transfer of electrons trapped at an exponential distribution of band gap surface states near the conduction band. The analysis shows the great influence of the distribution of electrolyte levels and band gap surface states on the electron recombination kinetics under open circuit conditions.

1. Introduction

The photoelectrochemical properties of macroscopic assemblies of semiconductor nanoparticles (nanoporous electrodes) continue to raise increasing attention.[1−17] It has been shown that a photoelectrochemical system (dye-sensitized solar cell) consisting in a framework of dye-sensitized semiconductor nanoparticles (photoelectrode) permeated with a redox electrolyte can be used for converting visible light into electricity efficiently. Electron photogeneration is achieved by photoexcitation with sub-band-gap light of dye molecules attached to the semiconductor nanoparticles surface and further electron injection from the photoexcited dye molecules into the semiconductor conduction band (cb). The reduced electrolyte species (electron donors) are able to regenerate the oxidized dye molecules. Photoinjected electrons in transit toward the current collector have a chance of reacting with "ionic holes" (elec-

trolyte oxidized species), giving rise to a recombination process which constitutes a major loss factor of the dye-sensitized solar cell.

Intrinsic semiconductor surface states (ss) play an important role in this recombination process, both as electron traps and intermediate states for electron transfer to oxidized electrolyte species. The significance of ss in the photophysical properties of nanoporous TiO₂ has been widely recognized. This issue has normally been treated under the assumption that the electrons in traps are in thermal equilibrium with the cb.[3,12,13] This implies that the quasi-Fermi level for electrons, E_{Fn}^*, not only determines the degree of occupation of cb states, but also that of surface band gap traps. However, this assumption is not realistic in a general sense, as the exchange of trapped electrons is not only restricted to the cb but involves also electrolyte species via interfacial electron transfer. Therefore, a more general approach to nonequilibrium statistics is needed.

This paper examines recombination mechanisms involving band gap ss at semiconductor nanoparticles. A physical parameter of central interest is the density of cb free electrons under nonequilibrium illumination conditions, insofar as they are the

* Corresponding author. E-mail: bisquert@uji.es.
† Universitat Jaume I.
‡ Bar-Ilan University.
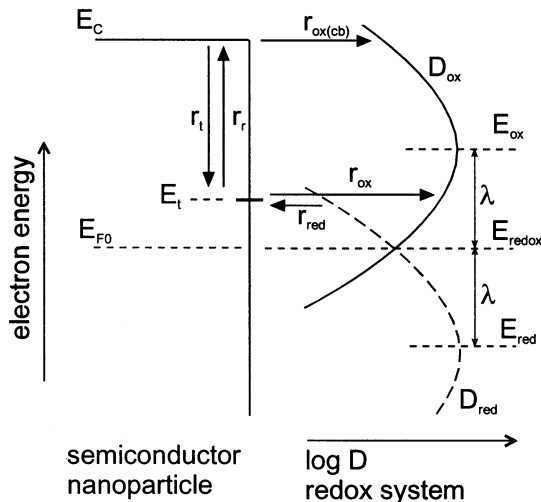§ Universitat de les Illes Balears.

Figure 1. Scheme of the processes of electron exchange among band gap ss, the conduction band, and fluctuating energy levels of the electrolyte permeating semiconductor nanoparticles in a dye-sensitized solar cell.

energy carriers of the system. Assuming that ss constitute a major pathway of electron transfer to the electrolyte, one fundamental question arising is how the lifetime of photoinjected electrons depends on their average occupancy, f. Hence, a model taking into account the occupancy of ss under steady-state illumination conditions is of prime importance. Moreover, since $E_{\mathrm{F}n}^*$ controls both the photovoltage and the rate of electron transport through the nanoporous network in a dye-sensitized solar cell,[16] it is of great significance to find a correlation between f and $E_{\mathrm{F}n}^*$.

Together with the nonequilibrium, steady-state statistics of electrons in traps, a study of the kinetics of trapping at ss and interfacial recombination of photoinjected cb electrons is presented.

2. Kinetic Model and Steady State Expressions

2.1. Photogeneration and Recombination Kinetics. Our first objective is to outline a kinetic model for photogeneration and recombination processes in a dye-sensitized solar cell. The continuity equations are defined on the basis of the rates of electron transfer among extended states of the cb, band gap ss (traps), and electronic levels of redox species in the electrolyte, according to the scheme of Figure 1. Electrons photoinjected into cb states may either diffuse away through the nanoporous network, toward the back contact, or be trapped at band gap ss. Trapped electrons can either release to the cb or be transferred to acceptor states in the solution. This framework describes the recombination via ss. Direct electron transfer from cb states to electrolyte acceptor states is ignored initially, although this type of recombination mechanism will be discussed later on.

Let us assume that free (cb) electrons, with a density $n(x)$ are trapped by a ss with a rate r_{t}; simultaneously, trapped electrons are released to the cb at a rate r_{r}. We denote as $0 \leq f \leq 1$ the filling factor of the ss, the density of trapped electrons being $n_{\mathrm{t}} = N_{\mathrm{t}}f$, where N_{t} is the density of ss per unit volume. Therefore, the net rate of trapping of free electrons will be

$$U = r_{\mathrm{t}} - r_{\mathrm{r}} \tag{1}$$

Let J be the electron flux through the nanoporous network and G the rate of photoinjection from dye molecules to the cb. In the specific case of homogeneous photoinjection, it is $G =$

$\eta\alpha_{\mathrm{abs}}I_0$, where α_{abs} is the absorption coefficient of dye molecules and η is a constant taking into account photoinjection efficiency. The continuity equation for the free electron density takes the form

$$\frac{\partial n}{\partial t} = G - \frac{\partial J}{\partial x} - U \tag{2}$$

Electrons immobilized in ss can also be transferred to the fluctuating electronic levels of the electrolyte. This electron exchange is assumed to occur without energy loss (isoenergetic electron transfer). Let r_{ox} be the rate for electron hopping from a ss to empty electrolyte levels and r_{red} the rate of electron transfer from filled electrolyte levels to ss. The balance equation for the occupancy of ss will be

$$N_{\mathrm{t}}\frac{\partial f}{\partial t} = r_{\mathrm{t}} + r_{\mathrm{red}} - r_{\mathrm{r}} - r_{\mathrm{ox}} \tag{3}$$

2.2. Steady-State Expressions. The set of eqs 1−3, supplemented with suitable boundary conditions and ion transport equations, constitutes a general model for describing the evolution of free and trapped electrons in the nanoporous semiconductor network under a specific external perturbation, provided that the rates, r_{t}, r_{r}, r_{ox}, and r_{red}, are known. These rates will be derived in the next section on the following assumptions: under thermodynamic equilibrium conditions, (a) the detailed balance principle holds, and (b) the population of an electronic state at the energy level E is described by the Fermi function

$$F(E,E_{\mathrm{F}}) = \frac{1}{1 + \exp[(E - E_{\mathrm{F}})/k_{\mathrm{B}}T]} \tag{4}$$

To simplify, we will restrict our attention to the case where n is uniform through the nanoporous film. Then eq 2 reduces to

$$\frac{\partial n}{\partial t} = G - U \tag{5}$$

which is a valid approximation under open circuit conditions. Otherwise, eq 2 must be used.[16]

Under steady-state conditions eqs 1, 3, and 5 reduce to the following system of equations:

$$G = U = r_{\mathrm{t}} - r_{\mathrm{r}} \tag{6}$$

$$r_{\mathrm{t}} + r_{\mathrm{red}} - r_{\mathrm{r}} - r_{\mathrm{ox}} = 0 \tag{7}$$

with $U = r_{\mathrm{ox}} - r_{\mathrm{red}}$, which means that at the steady state U can be identified with the recombination rate. The expression

$$G = r_{\mathrm{ox}} - r_{\mathrm{red}} \tag{8}$$

states that under open circuit conditions the net flow of electrons in and out of the semiconductor is zero.

In the presence of a distribution of band gap ss, the net trapping rate takes the form

$$U = \sum_i (r_{\mathrm{t}}^{(i)} - r_{\mathrm{r}}^{(i)}) \tag{9}$$

where the sum spans over the distribution of band gap energy levels. The occupancy of ss is then described by equations of the type

$$N_t^{(i)} \frac{\partial f^{(i)}}{\partial t} = r_t^{(i)} + r_{red}^{(i)} - r_r^{(i)} - r_{ox}^{(i)} \tag{10}$$

At the steady state

$$G = U = \sum_i (r_t^{(i)} - r_r^{(i)}) \tag{11}$$

and

$$r_t^{(i)} + r_{red}^{(i)} - r_r^{(i)} - r_{ox}^{(i)} = 0 \tag{12}$$

From eqs 11 and 12, a relationship similar to eq 8 is obtained for the balance of electrons flowing in and out of the semiconductor:

$$G = \sum_i (r_{ox}^{(i)} - r_{red}^{(i)}) \tag{13}$$

2.3. Steady-State Occupancy of cb States. Let the extended states of the cb have an energy E_c and a density N_c. At thermal equilibrium (denoted by the subscript 0), the density of electrons in cb states is $n_0 = N_c F(E_c, E_{F0})$, where E_{F0} is the Fermi level at equilibrium in the dark. In the case that $E_c - E_{F0} \gg k_B T$, eq 4 is well described by Boltzmann statistics

$$n_0 = N_c \exp[(E_{F0} - E_c)/k_B T] \tag{14}$$

Under illumination, thermodynamic equilibrium is broken, and the free electron concentration, n, increases with respect to its equilibrium value, n_0. The occupancy of cb states is then determined by the quasi-Fermi level, E_{Fn}^* ($n = N_c F(E_c, E_{Fn}^*)$). Assuming that E_c remains stationary (band edges pinning), the steady-state concentration of cb photoinjected electrons will be

$$n = n_0 \exp[(E_{Fn}^* - E_{F0})/k_B T] \tag{15}$$

Since the open circuit voltage of the solar cell is

$$V_{oc} = (E_{Fn}^* - E_{F0})/e \tag{16}$$

where e is the elementary charge, the following relationship will exist between n and V_{oc}:

$$n = n_0 \exp(eV_{oc}/k_B T) \tag{17}$$

3. Rates of Electron Exchange

3.1. Equilibrium Constraint on The Rates of Electron Exchange. Under thermal equilibrium conditions, the principle of detailed balance imposes a constraint on the rates of electron exchange between a band gap ss of energy E_t, and an electron reservoir which can be identified with either the cb or empty electrolyte levels, as explained in section 2. Then, the probability of occupation, f, of the ss increases at a rate $A(1 - f)$ and decreases at rate Bf, where A and B are constants depending on the rapidity of the exchange processes and on the availability of electronic levels in the reservoir. Under thermal equilibrium, both rates become identical, so that

$$f_0 = \frac{1}{1 + B/A} \tag{18}$$

Since the probability of occupancy of the ss under equilibrium responds to Fermi statistics (eq 4), it holds that $f_0 = F(E_t, E_{F0})$, which means that

$$B/A = \exp[(E_t - E_{F0})/k_B T] \tag{19}$$

3.2. Rate of Electron Exchange between the Conduction Band and Band Gap Surface States under Equilibrium Conditions in the Dark. The rates for electron exchange between a ss and the cb can be written as

$$r_{t0} = N_t e_{t0}(1 - f_0) \tag{20}$$

$$r_r = N_t e_r f_0 \tag{21}$$

where e_{t0} and e_r are the transition probabilities. The probability of trapping is

$$e_{t0} = v\sigma_n n_0 \tag{22}$$

where v is the thermal velocity of free electrons and σ_n the electron capture cross section of the trap (ss). From eqs 20 and 21, we have that $B/A = e_r/e_{t0}$, and from eq 19 we get that

$$e_r/e_{t0} = \exp[(E_t - E_{F0})/k_B T] \tag{23}$$

The probability of electron release from the trap (detrapping) is[18]

$$e_r = N_c \sigma_n v \exp[(E_t - E_c)/k_B T] \tag{24}$$

If we define $\bar{e}_{tr}$ as a reference probability for electron trapping when $E_t = E_{F0}$

$$\bar{e}_{tr} = v\sigma_n n_0 \tag{25}$$

We can write

$$e_{t0} = \bar{e}_{tr} \tag{26}$$

$$e_r = \bar{e}_{tr} \exp[(E_t - E_{F0})/k_B T] \tag{27}$$

so that $\bar{e}_{tr}$ corresponds to equal probabilities of electron trapping and detrapping ($e_{t0} = e_r = \bar{e}_{tr}$) for $E_t = E_{F0}$.

The probability of detrapping can also be written as

$$e_r = \sigma_n v n_1 \tag{28}$$

where

$$n_1 = N_c \exp[(E_t - E_c)/kT] \tag{29}$$

3.3. Equilibrium Rates of Electron Exchange between the Semiconductor and the Electrolyte. According to Gerischer,[19] the rates of isoenergetic electron transfer between ss and fluctuating energy levels in the electrolyte depend on the densities of unoccupied, D_{ox}, and occupied electronic states, D_{red}, of electrolyte species at the energy level of the ss

$$D_{ox} = W_{ox}(E_t)c_{ox} = \frac{c_{ox}}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(E_t - E_{ox})^2}{4\lambda k_B T}\right] \tag{30}$$

$$D_{red} = W_{red}(E_t)c_{red} = \frac{c_{red}}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(E_t - E_{red})^2}{4\lambda k_B T}\right] \tag{31}$$

where c_{red} and c_{ox} are the concentrations of electrolyte reduced and oxidized species, W_{ox} and W_{red} are the probability densities of the fluctuating energy levels, E_{ox} and E_{red} are the most probable energy levels for the oxidized and reduced electrolyte species, and λ is the reorganization energy. The electrolyte redox

level is defined as

$$E_{\text{redox}} = \frac{1}{2}(E_{\text{ox}} + E_{\text{red}}) = E_{\text{redox}}^{(0)} + k_B T \ln \frac{c_{\text{red}}}{c_{\text{ox}}} \quad (32)$$

where $E_{\text{redox}}^{(0)}$ is the standard redox level for $c_{\text{red}} = c_{\text{ox}}$.

The electron-transfer rate from the ss to the empty (ox) electrolyte levels is

$$r_{\text{ox}} = N_t e_{\text{ox}} f_0 \quad (33)$$

while the rate of electron capture from ss to occupied (red) electrolyte levels is

$$r_{\text{red}} = N_t e_{\text{red}} (1 - f_0) \quad (34)$$

where the corresponding transition probabilities are defined as

$$e_{\text{ox}} = 2k_B T k_t D_{\text{ox}} \quad (35)$$

$$e_{\text{red}} = 2k_B T k_t D_{\text{red}} \quad (36)$$

k_t being the rate constant for isoenergetic electron transfer. The principle of detailed balance establishes a unique k_t in the forward and backward direction under equilibrium conditions.

From eqs 30−32, it can be written

$$e_{\text{ox}} = \bar{e}_{\text{rx}} \exp\left[\frac{1}{2k_B T}(E_t - E_{\text{redox}})\left(1 - \frac{1}{2\lambda}(E_t - E_{\text{redox}}) - \frac{k_B T}{\lambda} \ln \frac{c_{\text{red}}}{c_{\text{ox}}}\right)\right] \quad (37)$$

$$e_{\text{red}} = \bar{e}_{\text{rx}} \exp\left[-\frac{1}{2k_B T}(E_t - E_{\text{redox}})\left(1 + \frac{1}{2\lambda}(E_t - E_{\text{redox}}) + \frac{k_B T}{\lambda} \ln \frac{c_{\text{red}}}{c_{\text{ox}}}\right)\right] \quad (38)$$

where $\bar{e}_{\text{rx}}$ is an exchange probability, that corresponds to equal probabilities of trapping and detrapping ($e_{\text{ox}} = e_{\text{red}} = \bar{e}_{\text{rx}}$) for $E_t = E_{\text{redox}}$ and can be expressed as

$$\bar{e}_{\text{rx}} = k_t \sqrt{\frac{k_B T c_{\text{ox}} c_{\text{red}}}{\pi \lambda}} \exp\left[-\frac{\lambda}{4kT} - \frac{k_B T}{4\lambda}\left(\ln \frac{c_{\text{red}}}{c_{\text{ox}}}\right)^2\right] \quad (39)$$

For ss energy levels situated in the vicinity of the redox level (i.e., for $E_t - E_{\text{redox}} \ll 2\lambda$) and assuming that $k_B T \ln c_{\text{red}}/c_{\text{ox}} \ll \lambda$, eqs 37 and 38 become

$$e_{\text{ox}} = \bar{e}_{\text{rx}} \exp\left[\frac{1}{2k_B T}(E_t - E_{\text{redox}})\right] \quad (40)$$

$$e_{\text{red}} = \bar{e}_{\text{rx}} \exp\left[-\frac{1}{2k_B T}(E_t - E_{\text{redox}})\right] \quad (41)$$

If the ss is in thermal equilibrium with the electrolyte redox couple, the condition $r_{\text{ox}} = r_{\text{red}}$ determines the equilibrium occupancy of the ss, f_0. In fact, according to eq 19, $r_{\text{ox}} = r_{\text{red}}$ implies that $B/A = e_{\text{red}}/e_{\text{ox}}$, so that from eqs 40 and 41 we find that $B/A = \exp[(E_{\text{redox}} - E_t)/k_B T.]$. Therefore, $f_0 = F(E_t, E_{\text{redox}})$, which means that the occupancy of the ss is determined by the Fermi function around the redox energy of the electrolyte, E_{redox}. It should be pointed out that this is a consequence of the fact that the distribution of the fluctuating energy levels in the electrolyte has the form of the Fermi function.[19]

3.4. Thermodynamic Equilibrium Conditions in the Dark ($E_{F0} = E_{\text{redox}}$).

It is a basic thermodynamic requirement that under thermal equilibrium the free energy of electrons is the same in the different phases of the system. Therefore, in a dye-sensitized solar cell the Fermi energy, E_{F0}, must equal the average energy of electrons in the electrolyte, E_{redox}. Let us verify that the kinetic model formulated above satisfies this requirement. As stated earlier, both the density of occupation of cb states in the semiconductor particles, $n_0 = N_c F(E_c, E_{F0})$, and the probability of occupation of ss, $f_0 = F(E_t, E_{F0})$, are determined by the Fermi function around E_{F0}. On the other hand, we have shown that the occupation of the ss in equilibrium with fluctuating electronic levels in the electrolyte is defined by the Fermi function, $f_0 = F(E_t, E_{\text{redox}})$, around the redox energy, E_{redox}. Therefore, if the electron exchange from ss to both the cb and electrolyte levels occurs simultaneously, we get that $f_0 = F(E_t, E_{F0}) = F(E_t, E_{\text{redox}})$, which implies that $E_{F0} = E_{\text{redox}}$, as required.

3.5. Semiconductor−Electrolyte Electron Exchange Rates under Equilibrium.

Under illumination (photoinjection of electrons from the dye to the cb states), the quasi-Fermi level moves upward, $E_{Fn}^* > E_{F0}$, as indicated by eq 5. The trapping probability of cb electrons by ss is then

$$e_t = v\sigma_n n \quad (42)$$

which can be referred to the trapping probability under equilibrium in the dark

$$e_t = e_{t0}\frac{n}{n_0} = \bar{e}_{\text{tr}}\frac{n}{n_0} \quad (43)$$

Therefore, it can be written that

$$e_r/e_t = \exp[(E_t - E_{Fn}^*)/k_B T] \quad (44)$$

The filling factor of the ss, f, also increases with respect to f_0, the trapping rate becoming

$$r_t = N_t e_t (1 - f) \quad (45)$$

The corresponding nonequilibrium values of r_r, r_{ox}, and r_{red} are those in eqs 21, 33, and 34, respectively, with f substituting to f_0. The probabilities e_r, e_{ox}, and e_{red} are those given by eqs 27, 35, and 36.

Additional effects of the photoinjection of excess electrons into the cb, are, on one hand, the downward shift of E_{redox} as c_{red} decreases and c_{ox} increases and, on the other hand, the upward shift of the semiconductor energy levels (bandedges unpinning), which affects n_0, insofar as the additional negative charge accumulated at the ss becomes compensated by a potential drop at the Helmholtz layer. For simplicity, unless otherwise stated, these effects will be omitted.

3.6. Direct Electron Transfer from cb States to the Electrolyte.

As noted before, the occupancy function of cb states is $f^{(\text{cb})} = F(E_c, E_{Fn}^*)$. On the other hand, the rates of electron exchange between cb states and electrolyte levels are

$$r_{\text{ox}}^{(\text{cb})} = N_c f^{(\text{cb})} e_{\text{ox}}^{(\text{cb})} \quad (46)$$

$$r_{\text{red}}^{(\text{cb})} = N_c (1 - f^{(\text{cb})}) e_{\text{red}}^{(\text{cb})} \quad (47)$$

Under thermodynamic equilibrium in the dark it must be $r_{\text{ox}}^{(\text{cb})} = r_{\text{red}}^{(\text{cb})}$, which implies that

8778 *J. Phys. Chem. B, Vol. 106, No. 34, 2002*

Bisquert et al.

$$f_0^{(cb)}(E_c) = \frac{e_{red}^{(cb)}}{e_{red}^{(cb)} + e_{ox}^{(cb)}} \qquad (48)$$

Since $f_0^{(cb)} = F(E_c, E_{F0})$, it results that $E_{F0} = E_{redox}$.

Moreover, the rate of recombination of free electrons is $U = r_{ox}^{(cb)} - r_{red}^{(cb)}$. However, far from equilibrium, and under the assumption that $r_{red}^{(cb)} \ll r_{ox}^{(cb)}$, the net rate of electron transfer to the electrolyte becomes

$$U = e_{ox}^{(cb)} n \qquad (49)$$

4. Nonequilibrium Steady-State Statistics of Electrons in Surface States: The Demarcation Level

By combining eq 7 with 20, 21, 33, and 34 after substituting f_0 by f, we obtain the following expression for the occupation factor of ss under open-circuit, nonequilibrium steady-state illumination conditions:

$$f(E_t) = \frac{e_t + e_{red}}{e_t + e_{red} + e_r + e_{ox}} \qquad (50)$$

Eq 50 allows to establish a relationship between f and E_{Fn}^*. The filling of electron traps produces different effects. A shallow trap in thermal equilibrium with the cb slows down electron transport, without contributing significantly to the recombination process. By contrast, electrons trapped in deep band gap ss have a large chance of recombining with electrolyte electron acceptors (oxidized species). Moreover, a fully occupied deep trap gives rise to a saturation recombination current, while the recombination current through a partially occupied ss increases with the photon irradiation intensity. These features were clarified in the early analysis of photoconductivity in semiconductors,[20] where the concepts of demarcation level and the nonequilibrium statistics for electrons and holes in traps were developed.[21,22] In the following we conduct a similar analysis for the case of a dye-sensitized solar cell. This analysis introduces new aspects in the description of the recombination process, due to the existence of a statistical distributions of electrolyte acceptor levels (ionic holes) not present in the case of a photoconductor, where photogenerated holes are exclusively associated to the valence band.

Let us first consider the case of a band gap shallow trap (ss) which does not behave as a recombination center (i.e., $e_r \gg e_{ox}$). In this case we have

$$N_t \frac{\partial f}{\partial t} = r_t - r_r \qquad (51)$$

and according to eq 44 the nonequilibrium steady-state occupancy, f, is exclusively determined by the quasi-Fermi level ($f = F(E_t, E_{Fn}^*)$). This means that if E_{Fn}^* lies above E_t, the trap is fully occupied ($f \approx 1$), while $f = 1/2$ for $E_t = E_{Fn}^*$. Moreover, for E_{Fn}^* lying below E_t, the trap is in thermal equilibrium with the cb ($n/n_t = (N_c/N_t) \exp[-(E_c - E_t)/k_B T]$).

The situation is completely different in the general case of a ss that exchanges electrons efficiently with electrolyte species (i.e., for $e_{ox} \gtrsim e_r$). For the sake of simplicity, the rate of electron capture from electrolyte reduced species, r_{red}, can be neglected in eq 3, so that

$$N_t \frac{\partial f}{\partial t} = r_t - r_r - r_{ox} \qquad (52)$$
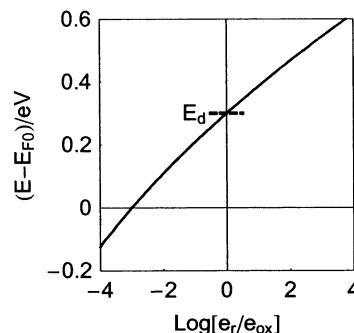

Figure 2. Representation of the ratio of the probability of emission to the cb, e_r, with respect to the probability of hopping to acceptor electrolyte levels, e_{ox}, as a function of the energy level of the band gap ss. The equilibrium Fermi level, $E_{F0} = E_{redox}$, is taken as reference energy. Values of $\bar{e}_{tr}/\bar{e}_{rx} = 10^{-3}$ ($E_d = 0.30$ eV), $\lambda = 1$ eV, and $c_{ox} = c_{red}$ are assumed.

By comparison with eq 51 (i.e., for $e_r \gg e_{ox}$), an additional term, r_{ox}, appears in eq 52, and f decreases. This means that in a dye-sensitized solar cell, the position of E_{Fn}^* with respect to E_t does not in general provide a direct measure of the ss occupancy; or in other words, f does not only depend on the difference $E_{Fn}^* - E_t$, but on the ratio e_r/e_{ox}. This result is in contradiction with the widespread idea that, in general, $E_{Fn}^* - E_t$ detemines the occupation of band gap energy levels. In a general way, the only possible statement is that E_{Fn}^* exclusively determines the concentration of free electrons at the cb.

At this point, the introduction of the demarcation level concept[20] is useful. As before, let us assume two types of electron transitions from ss, either to the cb or to empty electrolyte levels, which are described by the probabilities e_r and e_{ox}, respectively. It must be realized that according to eqs 27 and 37 $e_r/e_{ox} = \bar{e}_{tr}/\bar{e}_{rx}$ for $E_t = E_{F0}$. For $E_t > E_{F0}$ is $e_r/e_{ox} > \bar{e}_{tr}/\bar{e}_{rx}$, since the probability of emission from ss to the cb increases more rapidly than that of hopping to empty electrolyte levels. In fact, using the simplified form of e_{ox} (eq 40), we get

$$\frac{e_r}{e_{ox}} = \frac{\bar{e}_{tr}}{\bar{e}_{rx}} \exp\left[\frac{1}{2k_B T}(E_t - E_{F0})\right] \qquad (53)$$

The level at which $e_r/e_{ox} = 1$ is called the demarcation level, E_d.[20] At room temperature, a simple estimation of E_d using eq 40 leads to

$$E_d = E_{F0} - (0.115 \text{ eV}) \log\left(\frac{\bar{e}_{tr}}{\bar{e}_{rx}}\right) \qquad (54)$$

For an accurate determination of E_d, such as that shown in Figure 2, the more general formulation for e_{ox} (eq 37) must be used.

It is important to constate that for $E_t \gg E_d$, it is $e_r \gg e_{ox}$, f being described by the Fermi−Dirac statistics around E_{Fn}^*. Moreover, in the nanoporous system E_d does not depend on the illumination intensity (E_{Fn}^*). This contrasts with the case of a solid-state photoconductor where E_d is very sensitive to the density of photogenerated holes in the valence band (illumination intensity).[20]

According to eq 54 the ratio $\bar{e}_{tr}/\bar{e}_{rx}$, settles the demarcation level (Figure 2). Values of the steady-state occupancy, f, as a function of E_{Fn}^*, under different illumination intensities are illustrated in Figure 3. Under thermodynamic equilibrium ($E_{Fn}^* = E_{F0}$), f is deffined by the Fermi function (diagram a). Out of equilibrium (illumination conditions), f (dashed curve) departs
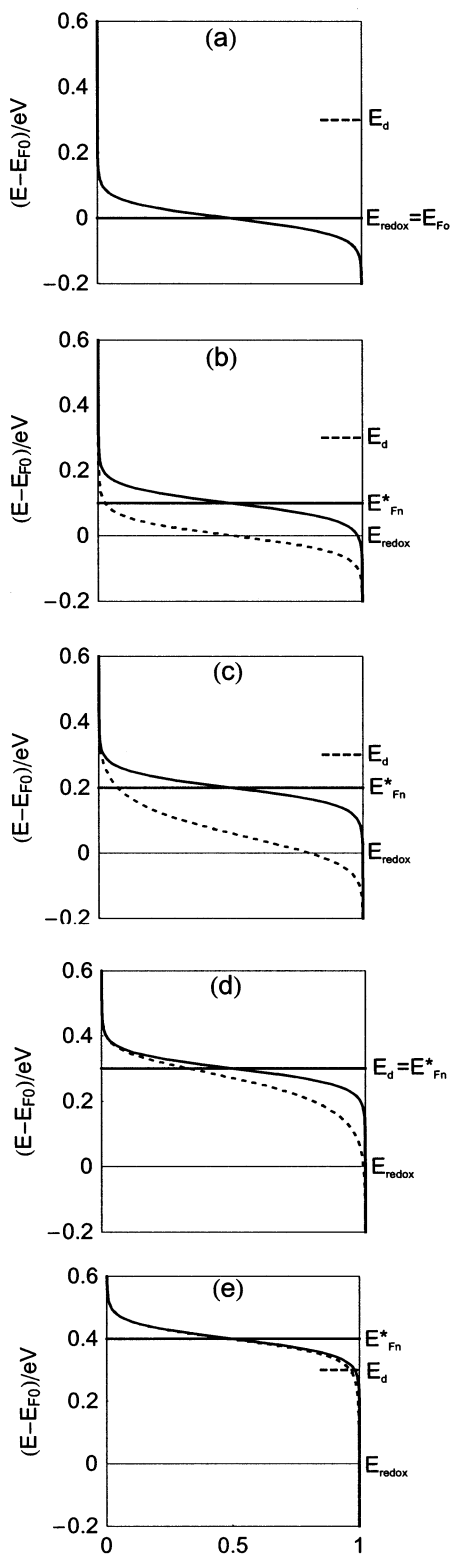
Figure 3. Snapshots of the probability of occupation (f) of a band gap ss under nonequilibrium, steady-state conditions at different photoinjection rates (values of ($(E_{Fn}^* - E_{F0})/e = 0$, 0.1, 0.2, 0.3, and 0.4 V, from top to bottom). The thick horizontal line represents E_{Fn}^*, the short dashed line the demarcation level, E_d, the continuous curve the probability of occupancy, f, when the rate of electron exchange with the electrolyte is neglected (i.e., for $e_{ox} = e_{red} = 0$), and the dashed curve f for simultaneous electron exchange from ss to both cb states and fluctuating electronic states in the electrolyte.

heavily from the Fermi function (continuous curve). For instance, for $E_{Fn}^* - E_{F0} = 0.1$ V and $E_t = E_{F0}$ (diagram b), $f \approx$

0.5, in spite of the fact that E_{Fn}^* is 0.1 V above E_t, and $f \approx 1$ would be expected. This is due to the small value of the ratio of exchange probabilities ($\bar{e}_{tr}/\bar{e}_{rx} = 10^{-3}$) so that the rate at which electrons are transferred to the electrolyte from the ss is much larger than that required for full occupancy (i.e., most of electrons trapped at the ss are efficiently transferred to the electrolyte, the ss behaving like active recombination centers). At a higher illumination level ($E_{Fn}^* - E_{F0} = 0.2$ V), both f and n and also r_{ox} increase (diagram c). When E_{Fn}^* meets the demarcation level (diagram d), the ss is almost totally occupied ($f \approx 1$), and the recombination rate saturates. For $E_{Fn}^* > E_d$ (diagram e) f is again described by the Fermi function, as in case a.

5. Recombination Rate Dependence on the Illumination Intensity in TiO₂ Dye- Sensitized Solar Cells

A point of considerable practical interest in dye-sensitized solar cells is that concerning the recombination rate dependence on the illumination flux, I_0, in the presence of band gap ss. The kinetic model outlined in the previous section can be applied to this case, provided that the distribution of band gap ss and the fundamental kinetic constants are specified. The actual distribution of band gap ss in nanoporous TiO₂ and their participation in recombination in dye-sensitized solar cells is still an open question. Recombination mechanisms (electron transfer from the solid to empty electrolyte levels) can involve (i) direct electron transfer from cb states, (ii) indirect transfer of electrons trapped at monoenergetic, deep ss, or (iii) indirect transfer of electrons trapped at an exponential distribution of band gap ss near the cb. Let us consider the three cases separately.

5.1. Direct Electron Transfer from Conduction Band States. This the only possible recombination mechanism in the absence of band gap ss-mediated electron transfer. Under open circuit, illumination conditions, $G = U = r_{ox}^{(cb)}$ and eq 49 determine the free electron concentration, n

$$n = \frac{G}{e_{ox}^{(cb)}} \tag{55}$$

so that

$$\frac{d \log n}{d \log G} = 1 \tag{56}$$

and from eqs 15 and 16

$$\frac{dV_{oc}}{d \log I_0} = 2.30 \frac{k_B T}{e} \tag{57}$$

i.e., a 59 mV/decade variation is expected in the representation of V_{oc} versus log I_0.

5.2. Recombination through Monoenergetic Surface States. Experimental evidence exists for a deep ss in nanoporous TiO₂, some 0.6 eV below the cb edge.[6,7,14,23] Electron transfer through a monoenergetic ss is well documented in electrochemical studies on single-crystal semiconductor electrodes.[24,25] In particular, it was shown that the steady-state cathodic dark current involved in the electroreduction of electrolyte species via ss increases with the electrode potential, up to a point where the ss occupation saturates. In the case of SrTiO₃ and TiO₂ electrodes, the saturation current regime for a deep ss was identified by varying the concentration of acceptor ions in the electrolyte.[25,26] In the area of dye-sensitized nanoporous solar cells, Peter and co-workers have pointed out the kinetic

limitations imposed by recombination via deep traps, as well as the role of the demarcation level.[9] Usami and Ozaki have studied recombination mechanisms according to a transport model taking into account the recombination rate predicted by Schockley−Read statistics.[15]

Let us consider the probability of electron exchange between ss and electrolyte levels as a determinant factor of the time constants involved in the recombination process.

The rate of recombination of cb free electrons is given by eq 1. Under nonequilibrium steady-state illumination conditions, the recombination rate can be defined from eqs 21 (written as $r_r = N_t e_t f$), 45, and 50, as

$$U = N_t \frac{e_t e_{ox} - e_r e_{red}}{e_t + e_{red} + e_r + e_{ox}} \tag{58}$$

This expression can be simplified if we neglect the probability of electron transfer to ss from reduced electrolyte species ($e_{red} \approx 0$). Then, the rate of recombination of free electrons can be expressed according to the standard Schockley−Read model formalism[15,27]

$$U = N_t \frac{e_t e_{ox}}{e_t + e_r + e_{ox}} = \frac{n c_{ox}}{\tau_{ox0}(n + n_1) + \tau_{t0} c_{ox}} \tag{59}$$

where n_1 was defined in eq 29 and the time constants for electron transfer from ss to the electrolyte and from the cb to the ss are defined respectively as

$$\tau_{t0} = [N_t v \sigma_n]^{-1} \tag{60}$$

$$\tau_{ox0} = [N_t 2 k_B T k_t W_{ox}(E_t)]^{-1} \tag{61}$$

Two limit cases can be considered:
(a) The limiting step is electron trapping by ss ($\tau_{t0} \gg \tau_{ox0}$) so that

$$U = N_t e_t = \frac{n}{\tau_{t0}} \tag{62}$$

(b) The limiting step is the transfer of electrons trapped at ss to the electrolyte ($\tau_{ox0} \gg \tau_{t0}$); hence

$$U = N_t e_{ox} = \frac{c_{ox}}{\tau_{ox0}} \tag{63}$$

which implies a saturation current independent of n and I_0.

More generally, a certain degree of band unpinning (E_t shifts with respect to the electrolyte energy levels so that W_{ox} depends on the light intensity) may be considered. In this case

$$\tau_{ox0}^{-1} = N_t k_t \sqrt{\frac{k_B T}{\pi \lambda}}$$
$$\exp\left\{-\frac{[E_t^* - E_{redox} - \lambda + k_B T \ln(c_{red}/c_{ox})]^2}{4 \lambda k_B T}\right\} \tag{64}$$

where $E_t^* = E_c^* - E_c + E_t$, with $(E_t^* - E) = (E_c^* - E_c)$ representing the energy shift.

In the following we analyze the dependence of n and f on the photoinjection rate, G.

It must be remarked that a realistic picture of the recombination process must consider simultaneously both indirect electron transfer from ss and direct electron transfer from cb states (eq 55) to the electrolyte so that, in general, a term $n e_{ox}^{(cb)}$, taking
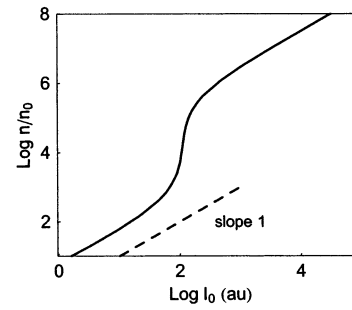

Figure 4. Dependence of the free electron density, n, on the illumination intensity at the steady state for combined indirect electron transfer (recombination) from monoenergetic ss ($E_t = E_{F0} = 0$ eV, $N_t = 10^{16}$ cm^{-3}) and direct electron transfer from the conduction band to electrolyte levels. Values of $E_c = 0.8$ eV, $\lambda = 0.5$ eV and $\bar{e}_{tr}/\bar{e}_{rx} = 10^{-2}$ ($E_d = 0.20$ eV), are assumed, $\bar{e}_{rx}$ being the same for ss than for conduction band states. The dashed straight line is a reference slope related to eqs 56 and 70.

into account this last contribution, must be added to eqs 6 and 8, which become

$$G = N_t \left[\frac{n}{n_0} \bar{e}_{tr}(1 - f) - e_r f\right] + n e_{ox}^{(cb)} \tag{65}$$

$$G = N_t [e_{ox} f - e_{red}(1 - f)] + n e_{ox}^{(cb)} \tag{66}$$

For small enough G values, corresponding to low illumination intensity, such that n is small and $n e_{ox}^{(cb)} \ll G$, the following relationship between the free electron density and the trap occupancy is obtained for the case that $e_{red} \ll e_{ox}$

$$n = n_0 \frac{(e_{ox} + e_r) f}{\bar{e}_{tr}(1 - f)} \tag{67}$$

Moreover, eq 66 becomes

$$f = \frac{G}{N_t e_{ox}} \tag{68}$$

so that combining eqs 67 and 68, we get

$$n = n_0 \frac{(1 + e_r/e_{ox})G}{N_t \bar{e}_{tr}(1 - f)} \tag{69}$$

If we assume that e_{ox} does not depend on I_0 (i.e., there is no shift of the energy levels of the semiconductor with respect to electrolyte energy levels as f increases), eq 67 allows dn/df to be calculated; then from eq 68, df/dG can be found. For the case of a deep trap ($E_{F0} < E_t < E_d$), where $e_{ox} \gg e_r$, e_{red}, eq 69 leads to

$$\frac{d \log n}{d \log G} = \frac{1}{1 - f} \tag{70}$$

As can be seen in Figure 4, a slope unity is obtained for $f \ll 1$ (small enough illumination intensity). As far as G increases and the trap becomes occupied, n grows up and the second term in eqs 65 and 66 cannot be neglected (i.e., recombination via direct electron transfer from cb states and via indirect electron transfer from ss become comparable). For high values of G the term $n e_{ox}^{(cb)}$ becomes predominant, and eq 55 is again valid (it substitutes to eq 66) so that once more (d log n)/(d log G) = 1.

Alternatively, these results can be expressed in terms of the time constants τ_{t0} and τ_{ox0}. In fact, eq 68 gives

Electron Recombination in Nanoporous TiO₂

J. Phys. Chem. B, Vol. 106, No. 34, 2002 **8781**

$$f = \frac{G\tau_{ox0}}{c_{ox}} \tag{71}$$

and eq 67 can be written as

$$n = \frac{\tau_{t0}c_{ox} + \tau_{ox0}n_1}{c_{ox} - G\tau_{ox0}}G \tag{72}$$

which is equivalent to eq 59.

5.3. Recombination through a Distribution of Band Gap Surface States. Let us adapt the steady-state eqs 11−13 to a continuous distribution of band gap ss so that $N_t^{(i)} \rightarrow N_t(E)$, which is the concentration of ss per unit of volume and unit of energy (cm^{-3} eV^{-1}). According to eqs 11 and 12, the rate of recombination of cb electrons can be written as

$$U = \int_{E_v}^{E_c}[r_{ox}(E) - r_{red}(E)]\,dE \tag{73}$$

or, more explicitly

$$U = \int_{E_v}^{E_c}N_t(E)\{f(E)e_{ox}(E) - [1 - f(E)]e_{red}(E)\}\,dE \tag{74}$$

In general, the nonequilibrium steady-state occupancy of each energy level, $f(E)$, varies between 0 and 1, and the electron-transfer probabilities $e_{ox}(E)$ and $e_{red}(E)$ have the Gaussian form defined by eqs 30 and 31 and schematized in Figure 1. Therefore the analytical solution of eq 74 is complicated and must be solved numerically. For instance we can solve eq 74 by fixing values E_{Fn}^* and obtaining $U(E_{Fn}^*)$; then we get $U(n)$ through eq 15. Since $G = U$ at the steady state, $n(G)$ is then known. This is the method used to plot n versus I_0 in Figure 5, which will be further discussed.

We can better understand the type of behavior involved in eq 74 by adopting simplifying assumptions. Let us first assume that the recombination kinetics from all the ss of the distribution $N_t(E)$ is slow enough ($e_r(E) \gg e_{ox}(E)$) that the ss's are in thermal equilibrium with the cb (this is equivalent to assume that all ss lie above E_d). $f(E)$ is then described by the free electron quasi-Fermi level E_{Fn}^*, as already explained in Section 4. This means that recombination takes place solely through those ss below E_{Fn}^* so that for $e_{ox} \gg e_{red}$ and $E_{Fn}^* > E_{F0}$, the recombination rate can be written

$$U = \int_{E_{F0}}^{E_{Fn}}N_t(E)e_{ox}(E)\,dE \tag{75}$$

It must be emphasized that there is no a priori justification for this assumption, which is adopted exclusively for the sake of simplicity. However, in this particular case where $f(E_t) = 1$, for $E_t < E_{Fn}^*$, the recombination rate, U, increases with G as far as E_{Fn}^* goes up, and the number of filled ss (recombination centers) increases. Furthermore, U in eq 75 is affected by the varying density of acceptors states in the electrolyte (eq 30) at $E_t = E_{Fn}^*$. This behavior is different than that outlined in Section 5 for the case of a monoenergetic ss, where the increase of U was exclusively due to the increase of f.

An exponential tail of band gap electronic states near the cb is a common property of amorphous semiconductors. An exponential distribution of bulk band gap states has also been invoked for explaining dispersive transport properties in nanoporous TiO₂[3,8,10,11] and surface recombination processes in nanostructured semiconductor electrodes.[3,10,12] Therefore, it is interesting to discuss the characteristics of this type of distribution. We will assume that $N_t(E)$ in eq 74 responds to the
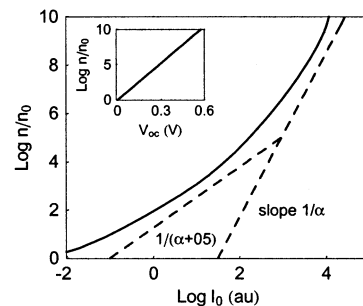

Figure 5. Dependence of the free electron density, n, on the illumination intensity at the steady state for recombination through an exponential distribution of band gap ss near the cb edge, with $\alpha = T/T_c = 0.30$.[11] Values of $\bar{e}_{tr}/\bar{e}_{rx} = 10^{-2}$ ($E_d = 0.20$ eV), $E_c = 0.6$ eV, and $\lambda = 0.5$ eV ($E_c - E_{ox} = 0.1$ eV) are assumed. The straight lines represent reference slopes, $1/(\alpha + 0.5)$ and $1/\alpha$, according to eqs 83 and 81, respectively. The inset shows the free electron density dependence on $((E_{Fn}^* - E_{F0})/e)$, assuming band edges pinning.

following exponential function:

$$N_t(E) = \frac{\Theta_t}{k_B T_c}\exp[(E - E_c)/k_B T_c] \tag{76}$$

where Θ_t represents the total volume density of ss and the parameter T_c is a characteristic temperature that defines the tail shape (broadening) of the exponential distribution. We also define a coefficient $\alpha = T/T_c$.

Let us consider two particular cases:

(a) $e_{ox}(E) \approx$ const., corresponding to a flat distribution of energy electrolyte levels, which is more or less the case where E_{Fn}^* is located around the maximum, E_{ox}, of the Gaussian distribution of electrolyte empty levels (see Figure 1). Then eq 75 becomes

$$U = e_{ox}\int_{E_{F0}}^{E_{Fn}}N_t(E)\,dE \tag{77}$$

or, in other words

$$U = e_{ox}n_t \tag{78}$$

Since the concentration of electrons trapped at ss is[28]

$$n_t = \frac{\Theta_t}{1 - \alpha}\left(\frac{n}{N_c}\right)^\alpha \tag{79}$$

eq 78 becomes

$$U = e_{ox}\frac{\Theta_t}{1 - \alpha}\left(\frac{n}{N_c}\right)^\alpha \tag{80}$$

The condition at the steady state that $G = U + ne_{ox}^{(cb)}$, for $G \gg ne_{ox}^{(cb)}$, leads to the proportionality $n \propto G^{1/\alpha}$ so that

$$\frac{d\log n}{d\log G} = \frac{1}{\alpha} \tag{81}$$

A similar result was found by Schlichthröl et al.[3] (they use the notation $m_c = k_B T_c/e$ for the tailing parameter).

(b) $e_{ox}(E)$ is not constant. If we assume that $E_{Fn}^* - E_{redox} \ll 2\lambda$, i.e., for E_{Fn}^* far away from E_{ox}, we can express e_{ox} as in eq 40. Substituting eqs 40 and 76 in eq 75 and performing the integration, we find that

$$U = \frac{\Theta_t \bar{e}_{\text{redox}} N_c^{1/2}}{[1 + 1/(2\alpha)] n_0^{1+\alpha}} n^{(\alpha+1/2)} \tag{82}$$

which implies that $n \propto G^{1/(\alpha+1/2)}$. In eq 82 the exponent α is due to the upward increase of the density of ss, while the exponent $1/2$ is due to the density of acceptor electrolyte states which increases as E_{Fn}^* goes up (see Figure 1). Therefore

$$\frac{d \log n}{d \log G} = \frac{1}{\alpha + 1/2} \tag{83}$$

By combining cases a and b, for E_{Fn}^* changing from E_{F0} to E_{ox}, and assuming that $\alpha \approx 0.3$,[11] we can see that $(d \log n)/(d \log G)$ increases with light intensity from 1.25, for $E_{Fn}^* < E_{\text{ox}}$, to 3.3, for $E_{Fn}^* = E_{ox}$. These results, together with the exact numerical solution of eq 75, are shown in Figure 5. A monotonic increase of the slope $(d \log n)/(d \log G)$ as G increases can be seen. However, as already shown in Figure 4, as far as $ne_{\text{ox}}^{\text{(cb)}} \leq U$, this slope starts to decrease (not shown in Figure 5), becoming $(d \log n)/(d \log G) = 1$ for $ne_{\text{ox}}^{\text{(cb)}} \approx U$, at high enough illumination intensity.

6. Conclusions

A general formulation for the recombination process in nanoporous semiconductor electrodes permeated with a redox electrolyte (e.g., dye-sensitized solar cells) has been developed. The model is based on physical parameters describing probabilities of electron transfer between band gap ss, the cb, and electrolyte levels.

A point of conceptual and practical interest refers to the extent to which the concept of quasi-Fermi level (E_{Fn}^*) determines the occupancy (f) of band gap ss under nonequilibrium steady-state illumination conditions. Our analysis shows that f may depart significantly from the value expected for the case where the ss are considered to be in thermal equilibrium with the cb. It is shown that thermal equilibrium conditions only take place for those ss that lie above the demarcation level, E_d (i.e., the energy level for which the rate of electron transfer from ss to the cb and from ss to empty electrolyte levels become identical). Furthermore, it can be seen that E_d does not depend on the illumination intensity, which means that the number of band gap ss in thermal equilibrium with the cb increases with light intensity.

We have analyzed different recombination mechanisms (electron transfer from the solid to empty electrolyte levels): (i) direct electron transfer from cb states to empty electrolyte levels, (ii) indirect transfer of electrons trapped at monoenergetic, deep ss, and (iii) indirect transfer of electrons trapped at an exponential distribution of band gap ss near the cb. Under open circuit, nonequilibrium illumination conditions, in cases i and ii, the free electron density is found to depend linearly on the illumination intensity. The main difference between cases i and ii lies in the charge stored at the semiconductor surface in case ii, which may produce an upward shift (unpinning) of the semiconductor energy levels. In case iii, the recombination rate strongly depends on I_0, as the overlapping between filled ss and empty electrolyte levels is very sensitive to E_{Fn}^*.

References and Notes

(1) O'Regan, B.; Moser, J.; Anderson, M.; Grätzel, M. *J. Phys. Chem.* **1990**, *94*, 8720.

(2) Södergren, S.; Hagfeldt, A.; Olsson, J.; Lindquist, S. E. *J. Phys. Chem.* **1994**, *98*, 5552.

(3) Schlichthröl, G.; Huang, S. Y.; Sprague, J.; Frank, A. J. *J. Phys. Chem. B* **1997**, *101*, 8141.

(4) de Jongh, P. E.; Vanmaekelbergh, D. *Phys. Rev. Lett.* **1996**, *77*, 3427.

(5) de Jongh, P. E.; Vanmaekelbergh, D. *J. Phys. Chem. B* **1997**, *101*, 2716.

(6) Boschloo, G.; Goossens, A. *J. Phys. Chem.* **1996**, *100*, 19489.

(7) Boschloo, G.; Fitzmaurice, D. *J. Phys. Chem. B* **1999**, *103*, 2228.

(8) Dloczik, L.; Ileperuma, O.; Lauerman, I.; Peter, L. M.; Ponomarev, E. A.; Redmond, G.; Shaw, N. J.; Uhlendorf, I. *J. Phys. Chem. B* **1997**, *101*, 10281.

(9) Franco, G.; Gehring, J.; Peter, L. M.; Ponomarev, E. A.; Uhlendorf, I. *J. Phys. Chem. B* **1999**, *103*, 692.

(10) Nelson, J. *Phys. Rev. B* **1999**, *59*, 15374.

(11) Könenkamp, R. *Phys. Rev. B* **2000**, *61*, 11057.

(12) van de Lagemaat, J.; Frank, A. J. *J. Phys. Chem. B* **2000**, *104*, 4292.

(13) Vanmaekelbergh, D.; de Jongh, P. E. *Phys. Rev. B* **2000**, *61*, 4699.

(14) Wang, H.; He, J.; Boschloo, G.; Lindström, H.; Hagfeldt, A.; Lindquist, S. *J. Phys. Chem. B* **2001**, *105*, 2529.

(15) Usami, A.; Ozaki, H. *J. Phys. Chem. B* **2001**, *105*, 4577.

(16) Bisquert, J. *J. Phys. Chem. B* **2002**, *106*, 325.

(17) Fabregat-Santiago, F.; Garcia-Belmonte, G.; Bisquert, J.; Zaban, A.; Salvador, P. *J. Phys. Chem. B* **2002**, *106*, 334.

(18) Shockley, W.; Read, W. T. J. *Phys. Rev.* **1952**, *87*, 835.

(19) Gerischer, H. *Z. Phys. Chem. NF* **1960**, *26*, 223.

(20) Rose, A. *Concepts in Photoconductivity and Allied Problems*; Interscience: New York, 1963.

(21) Rose, A. *Phys. Rev.* **1955**, *97*, 322.

(22) Simmons, J. G.; Taylor, G. W. *Phys. Rev. B* **1971**, *4*, 502.

(23) Redmond, G.; Fitzmaurice, D.; Grätzel, M. *J. Phys. Chem.* **1993**, *97*, 6951.

(24) Vandermolen, J.; Gomes, W. P.; Cardon, F. *J. Electrochem. Soc.* **1980**, *127*, 324.

(25) Salvador, P.; Gutiérrez, C. *J. Electrochem. Soc.* **1984**, *131*, 326.

(26) Tafalla, D.; Salvador, P. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 475.

(27) Tyagi, M. S. *Introduction to Semiconductor Materials and Devizes*; John Wiley and Sons: New York, 1991.

(28) Bisquert, J.; Zaban, A. *Appl. Phys. A*, in press.