Effect of Energy Disorder in Interfacial Kinetics of Dye-Sensitized Solar Cells with Organic Hole Transport Material

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We describe the kinetic rates for dye regeneration in dye-sensitized solar cells with organic solid hole conductors, taking as a reference the experimental results of Haque et al. (ChemPhysChem 2003, 4, 89). Our model is based on Marcus rates for electron and hole transfer, emphasizing the Gaussian spread of energy levels in the molecular materials involved. We show that the energy disorder implies a broadening of the efficiency of hole transfer with respect to the thermodynamic driving force, as observed experimentally. The model also shows that tuning of the kinetic processes for high efficiency of energy conversion of the solar cell depends critically on the interplay between the reorganization energy and the broadening parameters of the energy distributions.

1. Introduction

The understanding and control of interfacial charge-transfer processes is a challenge for the optimization of molecular photovoltaic devices. It is broadly accepted that the efficiency of dye-sensitized solar cells (DSC) is mainly governed by the kinetics of charge transfer at the interface between the electron transport material (ETM, usually nanocrystalline mesoporous TiO_2), the dye, and the hole transport material (HTM). The initial steps of charge separation in a DSC are the injection of an electron from a photoexcited dye to the conduction band of the TiO_2 and subsequently the transfer of an electron from the HTM molecule to the dye (Figure 1). The former process is usually completed within 200 ps, and the latter, the regeneration of the oxidized dye, is completed within the nanosecond time scale for liquid electrolyte DSCs containing an iodine/iodide redox couple. Moreover, recent experimental results on solid-state DSC using organic HTM such as spiro-OMeTAD (chemical name 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9′-spiro-bifluorene) showed that the kinetics of hole injection from the dye to organic HTM occurs at least 1 order of magnitude faster. In principle, electron transfer from the semiconductor material either to the oxidized dye or to the oxidized organic HTM occurs in a longer time scale on the millisecond—microsecond range. However, under operating conditions, the solid-state DSC presents high electron recombination yields when compared with the liquid-based device.

To date, most studies on solid-state DSC photovoltaic devices have been focused on the recombination reaction between the electrons at the semiconductor and the oxidized dye or the oxidized organic HTM and how to improve the low penetration of the HTM into the pores of the semiconductor. Only a few papers have paid attention to the regeneration reaction between the oxidized dye and the HTM. However, both electron injection and electron regeneration depend on the energy level distribution at the interface between the dye and the HTM. For further improvements on solid-state DSC, it is important to understand how regeneration dynamics in solid-state DSC is affected by small changes such as the modification of the dipole moment of the HTM in the presence of supermolecular dyes with hole screening moieties. Pioneering work by Haque et al. reports the relation between the yield of hole transfer from the dye cation to the organic HTM and the thermodynamic driving force of the reaction, the free energy difference ΔG^0(HTM). The paper shows, for a wide range of organic HTM molecules based on N,N′-diphenyl-N,N′-(m-toly)-benzidine (TPD) and dyes, that the efficiency of hole transfer versus the thermodynamic driving force displays an anomalous broadening with respect to simple
charge-transfer kinetics, a broadening that was attributed to local variations in the electrostatics of the interface.

Electron and hole transfer processes at the metal–oxide (ETM)/dye layer/hole transport material in a DSC are shown schematically in Figure 1. The primary aim of this paper is to analyze in detail the conditions governing hole transfer from the photooxidized molecular layer to the HTM, which seems to be a key factor for the optimization of device performance. The HTM forms a continuous medium where injected holes can be transported and evacuated toward the collecting contact. Basic assumptions in the literature for modeling charge-transfer process at the organic/organic (O/O) interface and subsequent carrier transport in organic conductor are discussed in the following paragraphs.

The physics of charge transfer and transport in molecular and organic materials is dominated by charge localization resulting from polarization of the medium and relaxation of molecular ions.9 As a result of weak intermolecular interactions, the carriers in these materials are strongly localized on a molecule, and transport occurs via a sequence of charge-transfer steps from one molecule to another, similar to the hopping between defect states in inorganic semiconductors or band gap states in these materials are strongly localized on a molecule, and from polarization of the medium and relaxation of molecular organic materials is dominated by charge localization resulting following paragraphs.

In the remainder of this paper, we present a detailed theoretical investigation, which addresses the existent energy disorder in the kinetics of DSC with organic HTM. We analyze the charge-transfer rate between oxidized dye and HTM, which

\[ \rho(E,E_0,\sigma) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left[ -\frac{(E_0 - E)^2}{2\sigma^2} \right] \] (1)

where \( E_0 \) is the center of the distribution and \( \sigma \) is the width. Another important component of the transport model12 is a strongly asymmetric hopping rate of the Miller–Abrahams type, given by

\[ R(E) = A_0 \exp(-E/k_B T) \text{ if } E \geq 0 \] (2)

and

\[ = A_0 \text{ if } E \leq 0 \]

where \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( E \) is the energy separation between sites, and \( A_0 \) is the maximum hopping rate determined by the intermolecular electronic orbital overlap. Models for the injection of carriers at the metal/organic (M/O) interface, developed for organic light-emitting diodes (OLEDs), also use the Gaussian distribution.15,16 These models emphasize the combination of Gaussian energy disorder and the image force potential at the interface and also the probability for an electron injected to the acceptor layer to move away from the interface in the low mobility medium.15–18

In comparison, the charge transfer at the O/O interface has been less studied. Models developed by Arkhipov et al.19 and later applied by Blom et al.20 indicate the absence of an image force as the main factor of difference with respect to the M/O interface and also calculate the probability of an escape of injected carriers. It can be presumed that the energy levels for the charge-transfer step 4 in a DSC (Figure 1) will be arranged by reasonable selection of the materials to be energetically facilitated. Here, we will restrict our attention to the first carrier hop at the O/O interface. Therefore, the main elements of our model are the density of states in the molecular media, their extent of occupation, and the rate of charge transfer from one molecular site to another at this interface. We should mention another type of model of heterogeneous kinetics that uses a Gaussian distribution of the logarithm of the rate constant.21

For the rate of charge transfer, it is important to recognize the effect of local distortion of the organic lattice associated with the carrier transference. The electron hop occurs when the thermal fluctuation causes the starting and final site to have the same energy.22 In organic conductors, the electron and its associated distortion are referred to as a localized polaron. The high-temperature expression for polaron hopping has the same form as the expression derived by Marcus for electron transfer from a reduced to an oxidized form of a redox ion; see eq 4.23 The activation energy at high temperatures (the polaron binding energy, \( E_b \)) relates to the reorganization energy, \( \lambda \), in the Marcus formalism as \( E_b = \lambda/2 \). It is well-established that the Marcus model applies for charge transfer between redox species and organic conductors.22,24 Recently, this model has been employed for describing the field-dependent mobility in amorphous organic conductors25 and the carrier transport in molecular photovoltaic devices.26

A model of Baldo and Forrest for injection-limited OLEDs27 describes the hopping out of a Gaussian distribution of intermediate states within the organic material near the metal injection interface, toward the Gaussian distribution in the transport layer. Also, Marcus rates are adopted in ref 27 for the organic interfacial injection model. It is also mentioned in this reference that the Marcus rate reduces to the Miller–Abrahams hopping rate of eq 2 when the energy separation of the sites is much less than the polaron binding energy. This approximation is probably well-suited to the analysis of charge transport in most organic devices, as mentioned previously,12 but it misses the Marcus inversion region, which is known to be an important element for devices that produce chemical or electrical energy from sunlight. For example, in photosynthetic electron transfer, the \( \lambda \) value is optimized for each electron transfer process, so that the forward electron transfer processes proceed under optimal conditions, that is, near the top region of the Marcus parabola, whereas the energy-wasting back electron transfer process is shifted deeply into the inverted region.28 In addition, the Marcus inverted region is suggested to play an important role in the back electron transfer of electrons in DSC with a liquid electrolyte.29,30

In accord with the previous discussion, our model for hole transfer in DSC with HTM takes the Gaussian energy disorder and Marcus (polaronic) transfer rate as the main elements. This model is therefore quite similar to the Baldo and Forrest model for interfacial injection in OLEDs;27 however, as mentioned previously here, we are interested in the reverse operation mode with respect to OLEDs (i.e., not charge injection but charge extraction in a set of energetically favored processes). Particularly for the hole transfer process 4 of Figure 1, the downward energetic hop of the hole from a dye molecule to HTM may intersect the Marcus inverted region if the energy gap at this step is large.
Figure 2. Scheme of the energetics governing hole and electron transfer to HTM (center of the DOS $E_H = 0$ eV, Fermi level at $E_F = 0.3$ eV) in a dye-sensitized solar cell. (a) Hole transfer from photooxidized dye molecules (redox potential $E_{0D} = 0$ eV, illumination quasi-Fermi level $E_{0D} = -0.1$ eV, and dispersion $\sigma_D = 0.1$ eV) to HTM. (b) Electron transfer from ETM levels (Gaussian distribution centered at conduction band $E_C$ with dispersion $\sigma_S = 0.2$ eV) to HTM.

is directly related to the yield measured by Haque et al.\textsuperscript{3} We pay special attention to the consequences of energy disorder in the organic materials involved, and we finally discuss the implications for the rate of recombination of electrons photo-injected in the nanostructured semiconductor material. These issues have strong implications for the efficiency of dye solar cells using organic hole conductors.

2. Model

According to the preceding discussion, we adopt the following assumptions, which are represented schematically in Figure 2.

2.1. Density of States in the Hole Transport Layer. With respect to the Gaussian dispersion of the hole acceptor HOMO (highest occupied molecular orbital) energy levels that are characteristic of organic conductors, the probability density of a molecule in the HTM being in the energy-state $E_p$ will be described by the expression $\rho_D(E_p,E_{0D},\sigma_D)$, which defines a normalized density of states (NDOS) centered at $E_{0D}$ with dispersion $\sigma_D$. The distribution of vacant hole (electron occupied) states is given by the product of the NDOS and Fermi distribution

$$F(E - E_F) = \frac{1}{1 + e^{(E - E_F)/k_BT}}$$

2.2. Density of States in the Dye Molecules. Since the dye molecules in the DSC are located at the interface between ETM and HTM, it is reasonable to assume that the ground-state hole levels in the oxidized dye are also affected by a strong energy disorder, which we take also with the Gaussian form in an expression $\rho_D(E_p,E_{0D},\sigma_D)$. $E_{0D}$ is the equilibrium redox potential of the dye as measured at a metal electrode in solution phase;

Figure 3. Rate of hole transfer from completely photooxidized dye molecules to HTM in a dye-sensitized solar cell as a function of the Fermi level position in the HTM, normalized to maximum value. Values of the dispersion in the dye Gaussian DOS ($\sigma_D$) and HTM Gaussian DOS ($\sigma_F$) are indicated, and the HTM Gaussian DOS centered at $E_{0F} = 0.3$ eV is shown. Also shown (thin lines) are the occupied hole states when the Fermi level is $E_{0F} = 0.6, 0.7$ eV.

Therefore, $-\Delta G_{D\rightarrow HTM} = E_{0F} - E_{0D}$. In thermal equilibrium, the probability of a hole state at the energy $E_p$ being occupied is $\{1 - F(E_p - E_{0F})\}$ with respect to the dye Fermi level $E_{0F}$.

2.3. Rate of Charge Transfer. For the probability of hole transfer from an occupied dye energy level to a vacant HTM level, we take the expression of the Marcus model

$$R(E_p - E_F) = A \exp \left[ \frac{(\lambda + E_p - E_D)^2}{4k_BT} \right]$$  

(4)

where $A$ is a prefactor containing the transfer frequency and $\lambda$ is the reorganization energy.

Finally, the rate of hole transfer from dye molecule to HTM molecule is given by

$$r_{D\rightarrow HTM}[-\Delta G_{D\rightarrow HTM}] = \int \rho_D(E_p,E_{0D})[1 - F(E_p - E_{0D})]\rho_D(E_p,E_{0D})F(E_p - E_{0F})R(E_p - E_F)dE_p$$  

(5)

where $E_{0F}$ is the Fermi level in the HTM.

3. Results and Discussion

3.1. Occupancy of the Transport Manifold in the Hole Transport Material. Application of OMeTAD as HTM in a DSC usually implies the use of electronic dopants, such as antimony salts, to achieve oxidation of the HTM and therefore increase the number of hole acceptor states.\textsuperscript{31} However, a large extent of oxidation of the HTM to increase the $p$-type character is not generally necessary to achieve good device performance. For example, Lenzmann et al.\textsuperscript{32} have reported solid-state DSC, where the hole conducting material is a metal deposited on top of the dye, and efficient charge separation can also be achieved in the absence of $p$-type functionality. OMeTAD in DSC is usually kept below 1% doping to ensure transparency of the material for light penetration over several micrometers.

In our case where the $p$-type character of the HTM is assumed, it is well-known\textsuperscript{31,34} that if the density of holes in the HOMO transport states is very low, the distribution of holes is given to a good approximation by a Gaussian centered at $\sigma_D^2/k_BT$ above the mean of the DOS, independently of the position of the Fermi level. However, this Boltzmann regime is obtained only when the Fermi level is higher than $\sigma_D^2/k_BT$ above the mean of the DOS. In the examples shown in Figure 3, this regime of occupancy in the upper tail of the DOS is not yet obtained, and the effective center of the hole distribution changes with increasing Fermi level. Nonetheless, in Figure 3, it is observed...
that when the Fermi level is above the mean of the DOS (and a sufficient step of the free energy is available), the rate of transfer takes the maximum value with respect to hole occupancy since there are plenty of vacant sites for accepting hole transfer from dye molecules.

In highly doped HTM, with $E_{FP}$ situated below the mean of the Gaussian DOS, the situation is different. Obviously, when the DOS becomes progressively filled with holes, the rate of transfer from the dye increases swiftly, see Figure 3. This effect may become a limiting factor for dye regeneration if the holes transferred in the HTM are not rapidly evacuated from the interface toward bulk states. This could be expected due to the low mobility that is characteristic of organic conductors, for example, hole mobility in spiro-OMeTAD is in the range of $10^{-4} \text{cm}^2/\text{V s}$.\(^{35}\)

In inorganic semiconductor crystals such as silicon with valence and conduction bands, extrinsic doping increases the conductivity without major modification of the density of extended states. But, doping an organic HTM has strong effects due to carrier localization effects.\(^{36}\) Holes in doped sites are extended states. But, doping an organic HTM has strong effects without major modification of the density of valence and conduction bands, extrinsic doping increases the transfer from dye molecules.

To a sufficient step of the free energy is available, the rate of transfer increases from 20 to 80% in a transition interval of about 0.3 eV. Therefore, these experimental results (indicated in Figure 4b) are in good agreement with the model simulation for $\sigma_D = 0.2$ eV and $\sigma_P = 0.1$ eV and also for $\sigma_D = 0.1$ eV and $\sigma_P = 0.2$ eV. But, our recent determination of the DOS in spiro-OMeTAD\(^{38}\) shows that the energy dispersion in this hole conductor is quite low, $\sigma_P = 0.065$ eV. The conclusion is that DSC with organic HTM is strongly influenced by energy dispersion in dye energy levels.

3.2. Dye Regeneration under Transient Excitation Conditions. We consider the conditions of measurement of an excitation pulse as in transient absorption spectroscopy. As the lifetime of the dye cation is probably less than the inverse rate of the dye to dye cation transfer, the dye cation population is not thermalized within its DOS, and all the states in the energy distribution are equally likely occupied with holes, so that the occupation function has the same shape as the DOS. This situation can be described taking $E(D) - E(D)$ as a constant factor. Results of the calculation of $\gamma(D) - \gamma(D)$ in these conditions, for a modest amount of energy disorder $\sigma_D = \sigma_P = 0.1$ eV, are shown in Figure 4a. A maximum occurs near the point where the free energy difference equals the reorganization energy, as expected from the Marcus model. Further increasing the free energy decreases the rate of hole transfer. Although this effect is quite obvious, it should be further remarked on due to the practical implications: even in the absence of marked energy disorder, the efficiency of dye regeneration depends on the reorganization energy associated to hole injection to the HTM.

Results, adding stronger energy disorder to the picture, are shown in Figure 4b, for a characteristic value of $\lambda$ for charge transfer in organic conducting molecules.\(^{27}\) We observe that the larger energy disorder in the HTM extends the region of effective transfer while the maximum transfer point remains at $-\Delta G(D) = \lambda$. Large energy dispersion in the dye alone has exactly the same effect. This is easily understood because in these calculations, the DOS both in dye and in HTM are practically full of the corresponding electronic species. Finally, strong disorder in both dye and HTM molecules further broadens the region of effective charge transfer.

3.3. Dye Regeneration under Steady-State Excitation Conditions. Let us consider the working conditions of solar cell operation. Under steady-state illumination, the HOMO levels of the dye are subjected to several processes: excitation, deexcitation, regeneration from HTM, and electron injection from ETM, some of which are indicated in Figure 1. A steady-state distribution will be established that depends on the kinetic rates of the different transfer currents. Although the resulting occupation is not a thermal distribution, it is likely that the broadened dye HOMO will be predominantly occupied with electrons in the lower energy levels and empty in the upper
ones. In fact, for the probability of excitation and subsequent photoinjection to ETM to be high, as expected in the solar cell, a steady-state population of electrons in the HOMO of the dye is required. Therefore, in first approximation, we describe the occupancy under stationary illumination with eq 3 and an effective quasi-Fermi level $E_D$ (see Figure 2a), and we calculate the rate of hole transfer at different positions of the effective quasi-Fermi level. The results shown in Figure 5 indicate that the rate of transfer is reduced at the positive values of $\Delta G_{D-HTM}$, which is expected since a higher $E_D$ reduces the hole occupancy in the deeper states of the Gaussian DOS. As a consequence, a large driving force $-\Delta G_{D-HTM}$ is necessary for efficient dye regeneration in working conditions because the transference at $\Delta G_{D-HTM} \approx 0$ is largely suppressed.

3.4. Recombination (Back Electron Transfer) at Steady-State. We may ask also if a strong dispersion of the energy levels of the HTM has a significant influence in the process of electron injection from the ETM to the HTM (recombination). Since the LUMO (lowest unoccupied molecular orbital) of OMeTAD is far above the bottom of the conduction band of TiO$_2$, we consider direct injection of ETM electrons into the occupied hole levels of the HOMO of HTM as the dominant recombination pathway. We find the recombination rate performing a similar calculation as that detailed previously. A dispersion of electron levels in the ETM, $E_S$, is described in the form of a Gaussian $\rho_S(E_S,E_C,\sigma_S)$, for levels below the conduction band at $E_C$ (see Figure 2b). This is convenient to quantify the energy dispersion in the ETM in the same manner as in the HTM, as it is well-known that the DOS in nanostructured TiO$_2$ is an exponential distribution.\(^{39}\) For electron transfer from ETM levels to vacant electron (hole) levels in the HOMO of the HTM, we also use the Marcus model, with the same factor $A$ as in eq 5. This model has good results for describing electron transfer in DSC with liquid electrolytes.\(^{30,39,40}\) We take the situation in which the Fermi level of the ETM is close to the conduction band, and we have the rate of recombination as

$$r_{ETM-HTM}[-\Delta G_{D-HTM}] = \int \int \rho_S(E_S,E_C)\rho_P(E_p) dE_S dE_C [1 - F(E_p - E_{pp})] dE_p$$

Results for the electron transfer rate, as a function of $-\Delta G_{D-HTM}$, normalized to $r_{D-HTM}(\lambda_D)$, are presented in Figure 6. This figure illustrates the significance of electron recombination with respect to the efficiency of dye regeneration. Note that the horizontal axis in Figure 6 is, as before, $-\Delta G_{D-HTM} = E_P - E_D$. As a reference, the rate of transfer when the polymer DOS is 99% full of holes is shown. In this case, the maximum transfer occurs when the center of the HTM DOS lies at $E_P = E_C - \lambda$, as expected. Next consider the case that the Fermi level in the HTM is $E_{FP} = E_{F_P} + 2.35\sigma_P = E_{F_P} + 0.47$ eV (at 1% hole occupancy). It is observed that the charge transfer from the semiconductor is suppressed when $-\Delta G_{D-HTM} = E_P - E_D$ is large. The reason for this is the following. In contrast to Figure 4, now the role of the HTM is that of electron acceptor at hole-occupied sites. The HTM DOS is populated with holes in a small Gaussian-like distribution at the top edge of the DOS, as discussed previously (see Figure 3). The maximum of transfer yield is therefore obtained close to the point $E_P = E_C - \lambda - 2.35\sigma_P$ where the maximum of $R(E_{FP})$ occurs. When $-\Delta G_{D-HTM} = E_P - E_D$ becomes larger than this value, there are no further hole-occupied states that are separated by the energy $\lambda$ from the bottom of the conduction band, and therefore, the transference decreases, while it continues to increase in the case in which the DOS is full of holes, indicated as a reference in Figure 6.

In the low-doped case, it is observed that a strong energy dispersion in the HTM moves the hole-occupied states upward in energy with respect to the center of the DOS and produces the match of electron acceptor states in the HTM with electron donor states in the ETM. This causes a significant probability of electron transfer, about 1% of the dye regeneration probability at the value $-\Delta G_{D-HTM} = 0.3$ eV, which is the optimum situation of $E_{FP}$ for the efficient dye regeneration, as shown previously in Figure 4. It should be further remarked that electron and hole currents toward the HTM contain additional factors related to the total number of states, $N$. Clearly, the number of states in the ETM, $N_S$, is usually much larger than the density of dye molecules at the surface, $N_D$; therefore, the recombination current will be much enhanced with respect to the rate shown in Figure 6. It therefore appears to be critically important to reduce the energy disorder in the HTM in a DSC for obtaining efficient dye regeneration while avoiding a huge recombination of the electrons injected to the semiconductor.

4. Conclusion

In conclusion, we have stressed the importance of the energetic disorder on both the dye and the organic conductor. The existence of local variations induces dispersions ($\sigma$) of the
energy levels at the interface between the dye/HTM and the ETM/HTM interfaces. Such dispersion induces the system toward a large average $\Delta G_D^{\text{HTM}}$ to achieve high yields of hole transfer, as demonstrated experimentally. We have shown with our model that for a certain $\lambda$ ($\approx 0.3$ eV), the observed broadening, with a large regeneration rate even at $\Delta G = 0$, is mainly caused by disorder on the dye, while the disorder is small in the HTM (for OMETAD, we have estimated $\sigma = 65$ meV). A broadening of the DOS for a low-doped HTM material will also increase significantly the rate of direct electron transfer at the ETM/HTM interface. Thus, the optimization of the photo-voltaic device is likely to be related to the minimization of the energetic disorder at the device, and therefore, a better performance of the device is observed as expected from our theoretical model.

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References and Notes