

Chemical Diffusion Coefficient of Electrons in Nanostructured Semiconductor Electrodes and Dye-Sensitized Solar Cells

Juan Bisquert*

Departament de Ciències Experimentals, Universitat Jaume I, 12080 Castelló, Spain

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The properties and physical interpretation of the electron diffusion coefficient, D_n , observed in nanostructured semiconductors and dye-sensitized solar cells by small perturbation electrical and electrooptical techniques are investigated. The chemical diffusion coefficient is defined as the product of a thermodynamic factor (that accounts for the effect of nonideal statistics in a gradient of chemical potential) and a jump diffusion coefficient (that depends on average hopping distances and rates). The thermodynamic and kinetic similarities, as well as the differences, between interacting ions in the lattice and electrons in nanostructured semiconductors are discussed. From these considerations, the chemical diffusion coefficient of electrons for multiple trapping transport in nanoporous dye solar cells can be calculated indirectly, and the results are in agreement with the reduction of the kinetic-transport equations in the quasistatic approximation. The chemical diffusion coefficient in several models for electrons is discussed: for a wide but stationary distribution of sites energies, giving the Fermi-level dependent D_n [Fisher et al. *J. Phys. Chem. B* 2000, 104, 949] and for the enhancement of the diffusivity by effect of electrostatic shift of energy levels [Vanmaekelbergh et al. *J. Phys. Chem. B* 1999, 103, 747]. This last model is shown to correspond to the mean-field approximation to interaction in a lattice gas. A general expression containing all of these cases is provided, and several important consequences of the distinction between macroscopic diffusion and single particle random walk are pointed out.

1. Introduction

Nanostructured electrodes consisting on a sintered film of wide band gap semiconductor nanoparticles, deposited over a conducting substrate, have raised considerable attention in relation to several applications in photovoltaics and energy storage. The nanoporous electrodes are permeated by an electrolyte of high ionic conductivity that shields large scale electrical fields in the bulk film and maintains electroneutrality while the electron density increases in the nanoparticles. Consequently, the main contribution to the variation of the substrate potential is the change of the chemical potential of electrons in the nanoporous network,¹ and the dominant mechanism for transport of electrons in the semiconductor phase is the diffusion of electrons.

In this report, a theoretical study of the electron diffusion coefficient in nanoparticulate semiconductors permeated with a conducting medium is presented, in the framework of linear-response theory.^{2,3} The diffusion coefficient related to recovery from a small perturbation of some equilibrium condition is considered. This requirement of a small perturbation justifies a linear regime where the flux is proportional to the thermodynamic force.

The simplest version of diffusion starts from a microscopic picture of random displacement by hopping between neighbor sites in the lattice, without exclusion or disorder effects. The phenomenological flux–force linear equation (Fick's first law) is obtained by statistical calculation of the flux with respect to gradients of particle density.⁴ The macroscopic (chemical) diffusion coefficient is a constant, $D_0 = \Gamma_0 a^2/6$, where Γ_0 is the jump frequency and a is the intersite distance.

When the medium involves some kind of disorder or homogeneity, there occurs a distribution of sites occupancies and transition rates. Provided that linearity of flux and force is maintained, under small perturbation conditions, a generalized version of Fick's law can be formulated whereby the diffusion coefficient is defined as the prefactor of the gradient of concentration. However, this diffusion coefficient, D_n , may not be a constant but depends on the equilibrium state over which diffusion is measured. Indeed, measurements of TiO_2 and ZnO nanoparticulate networks by small perturbation techniques (both time transient and frequency methods) show clearly the dependence of the electron diffusion coefficient on the steady-state conditions.^{5–15} We remark that the diffusion coefficient is a magnitude of central importance in nanostructured semiconductors and dye-sensitized solar cell because it is measured directly.

One way to interpret the experimental results on the diffusion coefficient is to formulate a kinetic-transport model that includes D_n as a parameter. One can use either Fick's law or a more general model comprising average distributions of carriers in different kinds of sites that reduces to the diffusion law in some suitable condition. In fact, to explain the observations on D_n , a multiple trapping (MT) mechanism, involving distinct classes of localized and extended states, is often assumed.^{5,10,13,16,17} MT adopts the restriction that only free electrons are able to displace, whereas a distribution of localized sites traps the electrons and releases them thermally to the transport states.¹⁸

In another paper, we have discussed this approach.¹ We define a quasistatic measurement as that in which a common equilibrium of free and localized electrons persists even as the Fermi level, $\bar{\mu}_n$, varies with time, and we show quite generally¹ that the quasistatic condition allows the reduction of MT framework to the conventional diffusion equations, with the “effective” diffusion coefficient, D_n , given by

* To whom correspondence should be addressed. E-mail: bisquert@uji.es.

$$D_n = \frac{1}{1 + \frac{\partial n_L}{\partial n_c}} D_0 \quad (1)$$

where n_c is the concentration of free (conduction band) electrons, D_0 is the diffusion coefficient in the trap-free system, and n_L is the total density of localized electrons in traps.

The previous analysis¹ shows that D_n is a characteristic of a certain equilibrium state of the system. It should be therefore possible to infer the properties of D_n from the properties of the particular equilibrium state, circumventing the transport equations or at least the information in them that is removed by the quasi-equilibrium condition, such as the explicit values of trapping and detrapping rate constants. Note that this is of considerable interest, as one may be able to predict and analyze D_n equally well starting from less detailed information. This is also a powerful tool for determining D_n by an indirect method in numerical simulations, as discussed below.

To address this problem, in this paper, we follow a general description of the chemical diffusion coefficient¹⁹ in lattice gas models elaborated by Reed, Ehrlich, Gomer, Uebing, and others^{20–23} in relation to diffusion of adsorbates on surfaces, recently applied to the diffusion of Li^+ in metal–oxide intercalation materials.^{24,25} There is no restriction of dimensionality to these methods.²⁶ However, the application of these concepts of ionic diffusion, either in surface^{20–22} or bulk materials,^{24,25} has not been developed, to the best of my knowledge, to electron diffusion in nanostructured materials. Although the concept of the chemical diffusion coefficient is quite general, ion diffusion in solids is quite convenient as a reference point for electron diffusion. The reason is that ions in solids occupy localized sites at the bottom of potential wells in the structure. Double occupancy is usually forbidden by strong repulsion. So ions hopping in solids behave statistically as fermions, in the same way as the electrons in semiconductors.

The thermodynamic-kinetic structure of an array of models for electron diffusion and trapping in nanostructured semiconductors will be discussed. Schemes of the models considered are shown in Figure 1. The chemical diffusion coefficient of electrons will be found combining its thermodynamic and kinetic components. All of the results derived below will be obtained with the statistical assumption of random distributions (neglecting short-range correlations) and can be given analytically. The next two sections provide background material and definitions. Section 2 defines the chemical diffusion coefficient and associated quantities. Section 3 revises the basic features of thermodynamic aspects of diffusion of electrons through extended states and considers also a model for hopping between localized states. The rest of the paper focuses on the multiple trapping models that are frequently adopted in the literature.^{5,10,13,16} The static energy disorder will be considered in detail in section 4, and the results of mean-field theory for ionic diffusion will be shown in section 5 to correspond to the well-known effect of band unpinning in semiconductor electrochemistry.

2. Chemical and Jump Diffusion Coefficients

2.1. General Definitions. We introduce first the chemical diffusion coefficient using a phenomenological approach.¹⁹ When an electronic or ionic species diffuses in the material, the true driving force for diffusion is the gradient of its chemical potential. A linear relationship is assumed¹⁹ between the diffusive flux and the gradient of the thermodynamic chemical potential, $J = -L_0 \partial \mu / \partial x$. The coefficient of the concentration gradient in Fick's law, $J = -D_{\text{ch}} \partial n / \partial x$, is called the *chemical diffusion coefficient*.^{3,23} D_{ch} contains two components: the term

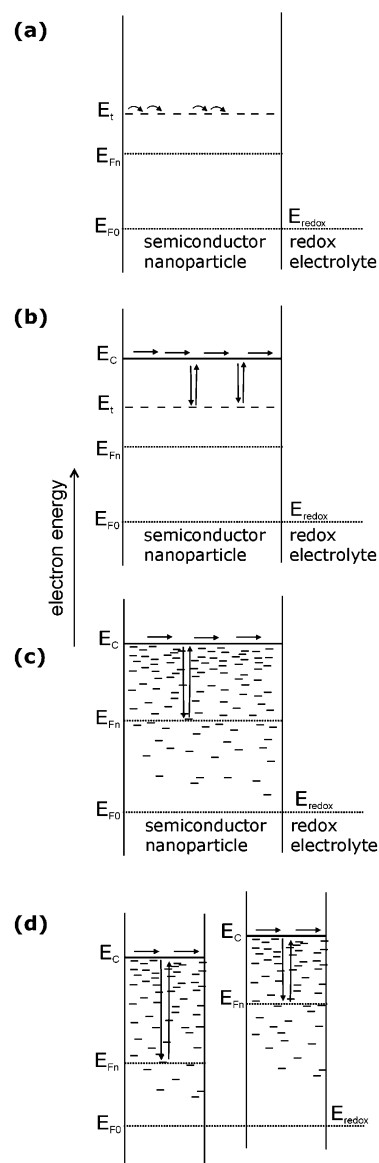


Figure 1. Schematic representation of transport processes in a nanostructured semiconductor (Fermi level E_{Fn}) permeated with a redox electrolyte (redox energy E_{redox}). (a) Hopping through a localized state at energy E_t in the band gap. (b) Transport through extended states (energy of conduction band lower edge E_c) influenced by trapping and detrapping at a monoenergetic trap (E_t). (c) Multiple trapping transport through extended states influenced by trapping and detrapping at an exponential distribution of band gap states. (d) Multiple trapping transport through extended states and an exponential distribution of localized states, in the presence of electrostatic shift of the energy levels.

$\partial \mu / \partial n$, which accounts for the difference between a gradient in concentration and a gradient in chemical potential, and a phenomenological coefficient L_0 .

More generally, the chemical diffusion coefficient D_{ch} can be derived from a microscopic approach using Green-Kubo theory.²² The definition of D_{ch} involves a statistical average (denoted by $\langle \rangle$) over the diffusion currents defined from single particle velocities, $J = \sum_{i=1}^n v_i(t)$, where n is the total number of particles per unit volume. The result can be written as^{3,22}

$$D_{\text{ch}} = \chi_T D_J \quad (2)$$

The first term in eq 2 is the thermodynamic factor, defined as

$$\chi_T = \frac{n}{k_B T} \frac{\partial \mu}{\partial n} \quad (3)$$

where k_B is Boltzmann's constant and T is the absolute temperature. The thermodynamic factor can be expressed also as

$$\chi_T = \frac{e^2 n}{k_B T C_{\text{ch}}} \quad (4)$$

where e is the absolute elementary charge, and the chemical capacitance^{1,27} (per unit volume) is given by

$$C_{\text{ch}} = e^2 \frac{\partial n}{\partial \mu} \quad (5)$$

We note that the chemical capacitance is related to the mean-square fluctuation of the particle number N in a volume V by the statistical formula²⁸

$$\langle (\delta N)^2 \rangle = \frac{k_B T V}{e^2} C_{\text{ch}} \quad (6)$$

therefore, the thermodynamic factor can be represented as

$$\chi_T = \frac{\langle N \rangle}{\langle (\delta N)^2 \rangle} \quad (7)$$

The second term in eq 2 is

$$D_J = \frac{1}{6t} \left\langle \left(- \sum_{i=1}^N \Delta r_i \right)^2 \right\rangle \quad (8)$$

where Δr_i is the displacement of the i th particle at time t . D_J , which depends on average hopping distances and hopping rates, can be thought of as a "jump" diffusion coefficient

$$D_J = \frac{1}{6} \Gamma(n) a^2 \quad (9)$$

in terms of a mean effective jump frequency $\Gamma(n)$, that varies with the occupancy of the lattice.^{21,23}

In the case of a dilute species for which the chemical potential is $\mu = \mu^0 + k_B T \ln(n/n^0)$, the chemical capacitance takes the form $C_{\text{ch}} = e^2 n / k_B T$, and consequently $\chi_T = 1$. It is thus clear that the factor χ_T measures the departure of the thermodynamic function from the ideal statistics of a dilute species. Alternatively, the departure from ideality can be given in terms of activity coefficient, γ_n , expressing the chemical potential as $\mu = k_B T \ln(\gamma_n n)$. The chemical diffusion coefficient takes the form

$$D_{\text{ch}} = \left(1 + \frac{\partial \ln \gamma_n}{\partial \ln n} \right) D_J \quad (10)$$

and the term in parentheses is the thermodynamic factor.¹⁹ Equation 10 is similar to the Darken formula for interdiffusion in solid alloys.²⁹

The chemical diffusion coefficient is measured experimentally from the response to a small step change in a parameter, such as the applied current. Classical electrochemistry techniques for this purpose include the galvanostatic and potentiostatic intermittent titration techniques.³⁰ In nanostructured semiconductors and dye-sensitized solar cells, the chemical diffusion coefficient is usually measured by either frequency or time-resolved methods involving a small perturbation of a steady state that is fixed by bias illumination or potential: electrochemical imped-

ance spectroscopy (EIS),³¹ intensity-modulated photocurrent spectroscopy (IMPS),^{5,10} and time-transient methods.^{14,32}

Incidentally, we remark that in other experimental methods based on large amplitude perturbation, such as transient photocurrents and decays of photoinjected charge, the carrier distribution departs markedly from linear response conditions, so these methods are outside the scope of this work. When the free and trapped electrons deviate from their common equilibrium, the respective chemical potentials of the species are very different, so the macroscopic diffusion equation cannot be defined. A similar problem is found when some of the localized states are surface states that enable electron transfer to the solution, because the concentration of the surface state is always below the equilibrium value.³³ Recently, we showed that the Fermi level of free electrons and surface states differs by a constant value,³⁴ and in this case, it would probably still be possible to use a common driving force $\partial \mu_n / \partial x$ for diffusion considering both kinds of states. An investigation of this problem by numerical simulation of the transport equations has been reported.¹³ In the present paper we consider diffusion effects only, when charge-transfer can be neglected.

2.2. Diffusion of a Lattice Gas. The elementary step of ion transport in solids or surfaces is the hopping of ions between stationary positions formed by neighbor potential wells in the structure. The most extended methods for dealing with ionic diffusion are the lattice gas models^{22,24–26,35} that assume a regular arrangement of sites for thermally activated hopping over energy barriers. The effects of interactions and energy disorder on ionic diffusion in solids can be treated at different levels of complexity. We provide a brief comment on these methods, as some of the results for ions in the lattice gas are quite useful for diffusion of electrons, our topic of interest.

For noninteracting ions, in the case in which all site energies are considered uniform, the structure of the chemical diffusion coefficient is very simple and is reviewed in section 3.1. However, for charged ions, it is necessary to consider the Coulombic interaction between particles, both between moving species among themselves and between these and the lattice atoms. These effects introduce a considerable difficulty, even for uniform distribution of energies. The rates of ion jumps between neighbor sites depend on the heights of the energy barriers, and these in turn depend on the distribution of other moving ions around the site. Furthermore, the interactions create aggregation or phase separation, so that the equilibrium arrangement of ions in the lattice is far from the random distribution implicit in the statistics of uncorrelated particles.

In a rigorous description of interactions in the lattice gas model, it is therefore required to consider the details of the local environment of the diffusing species. Statistically, interactions in the lattice are described by potential energy terms that depend on the occupancies of neighbor sites, next-neighbors, etc. It is rather complicated to obtain analytical expressions for thermodynamic factors and chemical diffusion coefficients in these interacting many-body systems, though methods have been given.³⁵

Numerical simulations allow the properties of these systems to be investigated. It is possible to obtain D_{ch} directly by maintaining the required densities at each end of the diffusion region and calculating the associated flux. However, more commonly, the quantities χ_T and D_J related to linear response are evaluated separately and then combined to form D_{ch} by the so-called indirect method,³⁶ see refs 24–26 and 35. The term χ_T can be determined in grand canonical Monte Carlo simulations by use of the fluctuation formula in eq 7. The kinetic factor is obtained by monitoring the random walk in the lattice

$$D^* = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle \sum_{i=1}^N (\Delta r_i)^2 \rangle \quad (11)$$

More precisely, eq 11 defines the tracer diffusion coefficient, D^* , that reflects random walks of a particle, whereas the jump (or kinetic) diffusion coefficient defined by eq 8 reflects diffusion of the center of mass of N particles. The squared sum in eq 8 results in $N(N-1)$ terms, whereas the tracer diffusion coefficient includes only N diagonal terms. The difference between these two coefficients (the Haven ratio) is small (usually less than a factor of 2).

The experience of simulation on ion diffusion in the lattice gas model with equivalent sites shows that there is no simple dependence of D_{ch} on χ_T , i.e., that changes on the two terms of eq 2 seem to cancel each other to some extent. We remark also that, in models with strong structural or dynamic disorder, eq 11 does not generally lead to a constant, because the mean displacement follows an anomalous diffusion law, $\langle \Delta r^2 \rangle \propto t^a$, ($0 < a \leq 1$).³⁷

One way to approach the question of energy distribution in more simple terms is to assume a *static* distribution of energy sites. The sites have different binding energies for ions, but these energies are independent of occupation of neighbor sites. Because particles do not interact with each other, the random distribution is valid, and the probability of occupancy of each level is determined by Fermi-statistics with a common chemical potential (Fermi level) for the different levels. However, in this approach, the carriers interact in a certain sense, because a carrier in a localized site exerts an infinite repulsion over others attempting to hope to that site. Consequently, the statistics departs strongly from dilution when the Fermi level is near or above site energy, and thermodynamic factors become quite large. The two-state system, composed of a fast (shallow) transport state and a deep (trapping) state, has been analyzed to a considerable extent of detail both for ions diffusing in the bulk³⁸ and in a surface³⁹ and is discussed in section 4.1. This approach is extended readily to a continuous distribution of sites energies and finds immediate application in nanostructured semiconductors with both extended transport states and localized states in the band gap; it corresponds to the multiple trapping model for electron transport, section 4.2.

Another relatively simple way to treat the interactions in the lattice gas model, further discussed below, is obtained by replacing the local interactions by an averaged field (molecular field) which is determined by the distribution of charged particles and which in turn governs the distribution itself.⁴⁰ This is a *mean field approximation* that gives readily analytical expressions, as reminded in section 5.1. Again, the independent particle occupation function (Fermi–Dirac for each energy level) is valid in this approach, because the Bragg–Williams approximation makes the assumption of random distribution of particles.⁴⁰ In the presence of intense interactions, i.e., when the distribution departs strongly from random arrangements, the results of this method are crude as compared with the exact ones. However, it must be remarked that the mean-field approximation is really useful for studying nontrivial interacting system.⁴¹

3. Diffusion of Electrons through Extended States

3.1. Diffusion of Noninteracting Ions. As a simple illustration of the derivation of the chemical diffusion coefficient, we consider the Langmuir isotherm for a regular lattice of ion sites²¹ (which is equivalent to Fermi–Dirac statistics, eq 17 below)

$$\mu = \mu^0 + k_B T \ln[\theta/(1-\theta)] \quad (12)$$

where $\theta = n/N$ is the fraction of the total number of sites, N per unit volume, that is occupied by particles. The concentration term in eq 12 arises from the entropy of ions distributed randomly over the lattice, while μ^0 indicates site energy on a suitable reference scale. In the lattice gas the mean effective jump frequency is $\Gamma(\theta) = \Gamma(0)(1-\theta)$, which gives the number of jumps into empty sites per unit time. The chemical capacitance per lattice site^{1,42} takes the form

$$e^2 \frac{\partial \theta}{\partial \mu} = \frac{e^2}{k_B T} \theta(1-\theta) \quad (13)$$

hence the thermodynamic factor is

$$\chi_T = \frac{1}{1-\theta} \quad (14)$$

Consequently, the chemical diffusion coefficient is independent of the concentration, $D_{\text{ch}} = \Gamma(0)a^2/6$.

As a special case of eq 12, we obtain for $\theta \ll 1$ (i.e., $\mu \ll \mu^0$) the diluted limit corresponding to Boltzmann statistics, in which case $\chi_T = 1$, as commented above. In the low concentration limit, there is no restriction for hopping to neighbor sites. The jump diffusion coefficient takes the constant value of ordinary random walk $D_J = D_0 \equiv \Gamma(0)a^2/6$, and therefore, $D_{\text{ch}} = D_0$.

Returning to arbitrary concentration, the jump diffusion coefficient can be written $D_J = (1-\theta)D_0$ in terms of the diluted value. So we note that the chemical diffusion coefficient equals the dilution limit, $D_{\text{ch}} = D_0$, at all θ values, because the dependence of χ_T on concentration compensates that of D_J exactly.⁴³ This feature is observed also in some interacting lattice gases, as mentioned in the Introduction.

3.2. Diffusion of Free Electrons. The thermodynamic chemical potential of free electrons in the nanoporous semiconductor is the electrochemical potential or Fermi level, which can be expressed as

$$\bar{\mu}_n \equiv E_{Fn} = E_c + \mu_n = E_c + k_B T \ln(n_c/N_c) \quad (15)$$

The term E_c (conduction band energy) is $E_c = -e\varphi$, where φ is the Galvani potential in the semiconductor phase with respect to the electron at rest in a vacuum. The term μ_n is the chemical potential of electrons. N_c is the effective density of conduction band states. The energy scales for the electrochemical potential of electrons are discussed in ref 44. The third equality in eq 15 assumes classical statistics in the nondegenerate case ($E_c - E_{Fn} \gg k_B T$). In the simulations presented below the Fermi level is limited to increase up to 0.25 eV below the conduction band, to avoid the free electrons entering degenerate statistics. In degeneration the activity coefficient of electrons departs markedly from $\gamma_n = 1$,^{45–47} so the thermodynamic factor should become large. This effect may be eventually significant for measurements of the diffusion coefficient in highly doped nanostructured semiconductors.

Here, however, we are concerned with low-doped nanoparticles, which enable a substantial variation of the electron chemical potential (Fermi level position along the band gap), and we assume $E_c - E_{Fn} \gg k_B T$. This is generally satisfied due to band unpinning when $E_{Fn} \rightarrow E_c$, as discussed in section 5. In these conditions, the statistics of conduction band electrons is identical to a lattice gas, eq 12, with $\theta = n_c/N_c$ and $\theta \ll 1$. Therefore, $\chi_T = 1$ and $D_{\text{ch}} = D_J$. For conduction band electrons in the nondegenerate case, the jump diffusion coefficient is a constant, D_0 , and hence, $D_{\text{ch}} = D_0$. Of course this is well-known: The normal diffusion equation for electrons indicates

that D_0 is the chemical diffusion coefficient. In crystalline, trap-free semiconductors, linear-response conditions are valid even for large variations of the Fermi level in the band gap, provided that transport of hot carriers in higher conduction band levels can be neglected.

In contrast to ions hopping in the lattice, for transport of conduction band electrons D_0 is governed by a relaxation time τ between successive collisions with various obstacles in the crystal or between electron–phonon transitions. However, we consider in the following a model of electrons *hopping* between localized sites, and we obtain also $D_{\text{ch}} = D_0$, i.e., the normal Fick's law for conduction band electrons.

3.3. Diffusion by Hopping at a Localized State. Let us consider the transport of electrons by hopping between localized sites, all at the same energy level E_t , and with concentration N_t , as illustrated in Figure 1a. This model is just a reformulation of that presented in section 3.1, but it has physical interest in relation to the conduction in an impurity band that has been amply studied.⁴⁸ However, we give a rather simple version of this last problem neglecting the effects of interactions and percolation. Our model may not be of direct interest to conduction in nanostructured TiO_2 , but it is illustrative of the features of the chemical diffusion coefficient of electrons.

The occupancy of the trap level is given by

$$f_t(E_t - \bar{\mu}_n) = F(E_t - \bar{\mu}_n) \quad (16)$$

where

$$F(E_A - \bar{\mu}_n) = \frac{1}{1 + e^{(E_A - \bar{\mu}_n)/k_B T}} \quad (17)$$

is the Fermi–Dirac distribution function. The density of carriers is $n_t = N_t f_t$, and the chemical capacitance and thermodynamic factor have the same expressions as in eqs 13 and 14 (with $\theta = f_t$). The mean effective jump frequency is $\Gamma(\theta) = \nu(1 - \theta)$, where the hopping rate constant ν for electron hopping from an occupied site to an empty site at the distance $R = (N_t)^{-1/3}$ has the form $\nu = \nu_0 \exp(-2R/a)$, in terms of the decay length a of the wave function in the localized state and the attempt-to-hop frequency ν_0 .⁴⁹ If we define the diffusion coefficient in the dilute limit ($E_{Fn} \ll E_t$) as $D_0 = R^2 \nu / 6$, we obtain the jump diffusion coefficient $D_J = (1 - f_t) D_0$.

Figure 2 shows the features of this model. The trap is filled when the Fermi level crosses the site energy, as seen in panel a, with the corresponding peak of the chemical capacitance, panel b. When $E_{Fn} > E_t$, the thermodynamic factor increases by orders of magnitude because of the departure from ideality by the exclusion “interaction”, panel c. At the same time, the jump diffusion coefficient decreases considerably due to scarcity of vacant neighbors to accept hopping electrons, panel d. These effects in the occupancy dependencies of χ_T and D_J compensate exactly and the chemical diffusion coefficient is a constant, $D_n = D_0$. We remark that these results should not be taken too literally, because percolation effects become essential when the concentration of vacant sites is low.⁴⁸ However, the model illustrates well the considerable difference between the chemical and jump diffusion coefficient when the statistics departs from dilution.

This simple model also shows that macroscopic diffusion through a localized level has similar features, for $E_{Fn} \ll E_t$, as diffusion through conduction band states in a crystalline material. When the material contains a wide distribution of energies of localized sites, the hopping transport becomes much more complicated, because it is necessary to consider the combination of hopping at different distances and hopping at

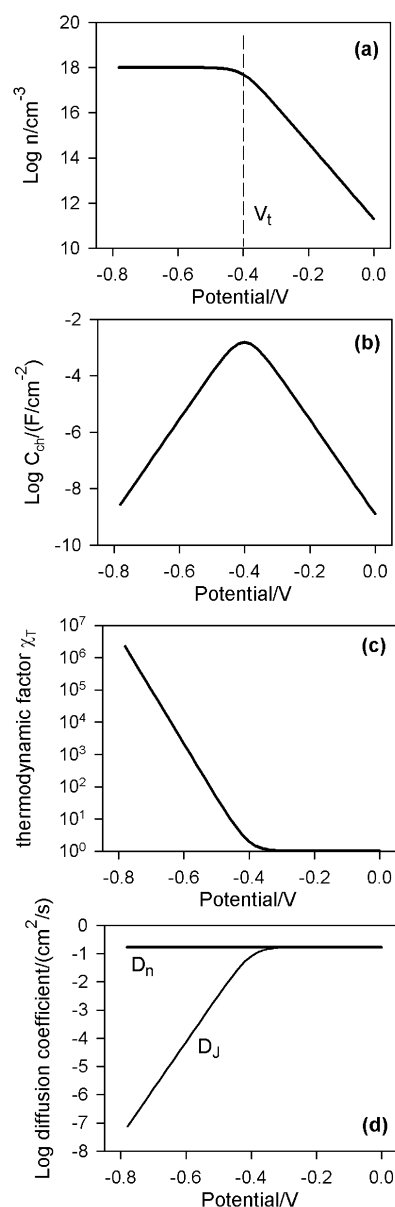


Figure 2. Representation of several quantities for charge accumulation and diffusion by hopping between localized states in a nanostructured semiconductor electrode of thickness $L = 10 \mu\text{m}$ with a single band gap state (conduction band is not shown). $V = -E_{Fn}/e$ is the Fermi level potential and $V_t = -E_t/e = -0.4 \text{ V}$ is the trap potential with respect to a reference in solution. (a) Isotherm (total charge vs potential). (b) Chemical capacitance. (c) Thermodynamic factor. (d) Jump (D_J) and chemical (D_n) diffusion coefficients. Parameters: $N_t = 1.0 \times 10^{18} \text{ cm}^{-3}$, $T = 300 \text{ K}$, $\nu_0 = 10^{12} \text{ s}^{-1}$, $a = 10^{-7} \text{ cm}$.

different levels.^{48,50} However, in some cases, especially for an exponential distribution of traps, it is shown that the most probable hops end at a given energy level, the transport energy level, regardless of the starting point, see ref 51 and references therein. In this case, the hopping mechanism becomes similar to the MT mechanism. We are currently investigating this hopping model.

In the remainder of this article, we consider only the MT model, in which the probability of electrons hopping between a distribution of localized states is assumed to be negligible, with respect to thermal release to an extended state.¹⁸ Here, we assume that the conduction band states of a crystalline semiconductor constitute the extended states.

4. Diffusion and Trapping

4.1. Single Trap Level (Two-State Model for Diffusion and Trapping). Figure 1b illustrates the microscopic events in diffusion of conduction band electrons, with number density n_c , in a nanoporous semiconductor with a localized level in the band gap, of energy E_L , with number density of trapped electrons n_L . We remark that the frequency features of this model (for ions diffusion) have been solved completely.³⁸ In the following paragraphs, the indirect construction of the chemical diffusion coefficient found in ref 38 in the low frequency limit (and previously reported in the literature⁵²) is made from its components, χ_T and D_J .

The total number of electrons is

$$n = n_c + n_L \quad (18)$$

and the equilibrium distributions of free and localized electrons (f_L being the fractional occupancy of localized sites, $n_L = N_L f_L$), are given by

$$n_c(E_c - \bar{\mu}_n) = N_c e^{(\bar{\mu}_n - E_c)/k_B T} \quad (19)$$

$$f_L(E_L - \bar{\mu}_n) = F(E_L - \bar{\mu}_n) \quad (20)$$

We obtain the thermodynamic factor using eq 3

$$\chi_T = \frac{n}{n_c} \left(1 + \frac{\partial n_L}{\partial n_c} \right)^{-1} \quad (21)$$

The mean effective jump frequency is obtained from the MT condition that only free electrons contribute to the diffusion process; thus, $\Gamma(\theta) = n_c \tau^{-1}/n$. The jump diffusion coefficient becomes

$$D_J = \frac{n_c}{n} D_0 \quad (22)$$

In the calculation of the chemical diffusion coefficient, D_{ch} , taking the product of χ_T in eq 21 and D_J in eq 22, the prefactors containing the steady-state densities (n_c, n) cancel out. The result is the same as eq 1. The effective diffusion coefficient of eq 1, D_n , is therefore interpreted as the chemical diffusion coefficient of electrons, so that the general identity $D_{ch} = D_n$ holds in the quasistatic conditions. To emphasize: eqs 21 and 22 constitute the separation of the chemical diffusion coefficient of eq 1 into thermodynamic factor and jump diffusion coefficient.

The effect of trapping in the chemical diffusion coefficient is dominant when $\partial n_L / \partial n_c \gg 1$. In this case, the approximation

$$D_n = \left(\frac{\partial n_c}{\partial n_L} \right) D_0 \quad (23)$$

can be used. The behavior of thermodynamic and diffusion parameters in this model is shown in Figure 3. The main feature of this model is the abrupt transition of the chemical diffusion coefficient from the trap-limited diffusion regime, at $E_{Fn} < E_L$, to the free electrons diffusion regime at $E_{Fn} > E_L$, as shown in Figure 3b. When the trap is filled, MT ceases, and D_n increases from the value of eq 23 to D_0 .

4.2. Multiple Trapping. The previous calculation for a single localized level can be extended to a distribution in energies of localized states in the band gap, as shown in Figure 1c. For the electrons, this is a noninteracting case, as mentioned in the Introduction in relation to the lattice gas. Therefore, all of the band gap states can be treated independently so that Fermi statistics applies to each. Provided that there is some small

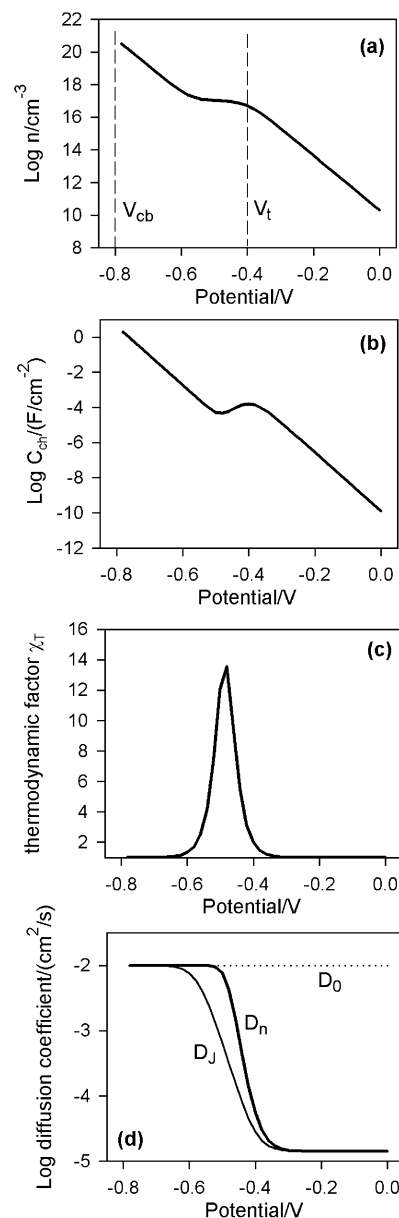


Figure 3. Representation of several quantities for charge accumulation and diffusion by multiple trapping in a nanostructured semiconductor electrode of thickness $L = 10 \mu\text{m}$ with a monoenergetic band gap state. $V = -E_{Fn}/e$ is the Fermi level potential, $V_{cb} = -E_c/e = -0.8 \text{ V}$ is the conduction band potential, and $V_L = -E_L/e = -0.4 \text{ V}$ is the trap potential with respect to a reference in solution. (a) Isotherm (total charge vs potential). (b) Chemical capacitance. (c) Thermodynamic factor. (d) Free electrons diffusion coefficient (D_0) and jump (D_J) and chemical (D_n) diffusion coefficient. Parameters: $N_c = 6.8 \times 10^{20} \text{ cm}^{-3}$, $N_L = 1.0 \times 10^{17} \text{ cm}^{-3}$, $T = 300 \text{ K}$, $D_0 = 10^{-2} \text{ cm}^2/\text{s}$.

interaction, all of the states are subjected to a common Fermi level. In the MT model, the mechanism of exchange that communicates the band gap states bringing them to a common equilibrium, is the electronic transitions between localized and extended transport states. In conclusion for any distribution of localized levels with abundance $g(E)$ (the density of states at the energy E in the band gap) occupancies are given by $f_L(E - \bar{\mu}_n) = F(E - \bar{\mu}_n)$. The total density of trapped electrons is obtained by

$$n_L = \int_{E_v}^{E_c} g(E) f_L(E - \bar{\mu}_n) dE \quad (24)$$

Taking the derivative of eq 24 with respect to $\bar{\mu}_n$ and integrating by parts, we get⁴²

$$\frac{\partial n_L}{\partial \bar{\mu}_n} = \int_{-\infty}^{+\infty} \frac{\partial g(E)}{\partial E} f_L(E - \bar{\mu}_n) dE \quad (25)$$

Using in eq 25 the zero temperature limit of the Fermi function, i.e., a step function at $E = \bar{\mu}_n$ separating occupied from unoccupied states, it follows that

$$\frac{\partial n_L}{\partial n_c} = \frac{k_B T}{n_c} g(\bar{\mu}_n) \quad (26)$$

The calculation of χ_T and D_J gives the same results as above, eqs 21 and 22. Equations 23 and 26 imply that

$$D_n = \frac{n_c}{k_B T} g(\bar{\mu}_n)^{-1} D_0 \quad (27)$$

so that in the case of a wide distribution of traps the chemical diffusion coefficient becomes strongly dependent on the Fermi level (or equivalently, on the concentration). This is indeed often observed for dye-sensitized solar cells, as commented in the Introduction. The calculation of chemical diffusion coefficient for different kinds of traps distributions is given in ref 16. In the following, we revise an important case in detail and show also the thermodynamic quantities.

4.3. Exponential Distribution. Let us consider the exponential distribution with tailing parameter T_0 (with $\alpha = T/T_0$), the significance of which has been discussed in ref 1

$$g(E) = \frac{N_L}{k_B T_0} \exp[(E - E_c)/k_B T_0] \quad (28)$$

Assuming $n_L \gg n_c$ (i.e., MT conditions), we obtain the following results, cf. ref 1:

$$n_L = N_L e^{(\bar{\mu}_n - E_c)/k_B T_0} \quad (29)$$

$$C_{ch}^{(trap)} = e^2 \frac{N_L}{k_B T_0} e^{(\bar{\mu}_n - E_c)/k_B T_0} \quad (30)$$

$$\chi_T = \frac{T_0}{T} \quad (31)$$

$$D_J = \frac{n_c}{n_L} D_0 = \frac{N_c}{N_L} \exp\left[(\bar{\mu}_n - E_c)\left(\frac{1}{k_B T} - \frac{1}{k_B T_0}\right)\right] D_0 \quad (32)$$

$$D_n = \frac{\partial n_c}{\partial n_L} D_0 = \frac{N_c T_0}{N_L T} \exp\left[(\bar{\mu}_n - E_c)\left(\frac{1}{k_B T} - \frac{1}{k_B T_0}\right)\right] D_0 \quad (33)$$

The features of this model are shown in Figure 4 with realistic parameter values. The results of eqs 29–33 correspond to the potentials at which the Fermi level is far below the conduction band edge. For the typical values of the tailing parameter, $\chi_T \approx 5$ at room temperature, according to eq 31. The constancy of χ_T is a property of certain distribution of localized states, in which $\partial n_L / \partial n_c \propto n_L / n_c$. Because of this, in the MT model, the entire Fermi-level dependence of the chemical diffusion coefficient is due to the jump diffusion coefficient. The panel d illustrates the fact that χ_T and D_J do not compensate in the MT regime.

Figure 4 also shows the evolution of parameters when Fermi level approaches the conduction band and $n_c \approx n$ (see eqs 21

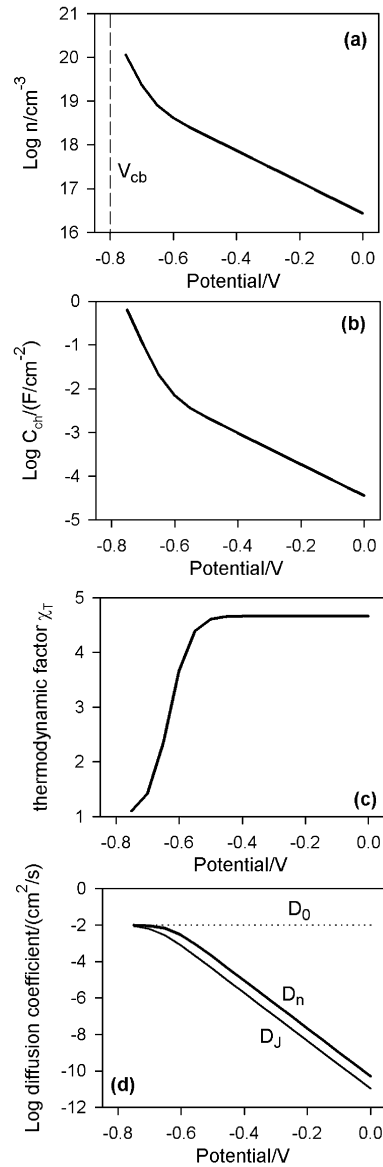


Figure 4. Representation of several quantities for charge accumulation and diffusion by multiple trapping in a nanostructured semiconductor electrode of thickness $L = 10 \mu\text{m}$ with an exponential distribution of band gap states. $V = -E_{Fn}/e$ is the Fermi level potential and $V_{cb} = -E_c/e = -0.8 \text{ V}$ is the conduction band potential with respect to a reference in solution. (a) Isotherm (total charge vs potential). (b) Chemical capacitance. (c) Thermodynamic factor. (d) Free electrons diffusion coefficient (D_0) and jump (D_J) and chemical (D_n) diffusion coefficient. Parameters: $N_c = 6.8 \times 10^{20} \text{ cm}^{-3}$, $N_L = 2.0 \times 10^{19} \text{ cm}^{-3}$, $T = 300 \text{ K}$, $T_0 = 1400 \text{ K}$, $D_0 = 10^{-2} \text{ cm}^2/\text{s}$.

and 22). Here MT trapping ceases to hold, and both D_J and D_{ch} approach D_0 , as corresponds to dilute statistics ($\chi_T = 1$). However, such direct observation of the free electrons diffusion coefficient may be difficult in practice, due to band edge shift, as discussed below.

5. Diffusion with Trapping and Electrostatic Band Shift

5.1. Diffusion of Interacting Ions in the Mean-Field Approximation. A qualitative and simple picture of ion diffusion in the lattice gas with interactions is obtained in the mean field (Bragg–Williams) approximation, whose result is the Frumkin isotherm

$$\mu = \mu^0 + k_B T \ln[\theta/(1 - \theta)] + b k_B T \theta \quad (34)$$

where b is the adimensional interaction parameter (molecular field). This model is widely used in the analysis of ion diffusion in lithium intercalation materials, where the interaction term refers to forces between intercalated ions and strain fields caused by expansion or contraction of the lattice.^{53–55} The chemical capacitance takes the form

$$e^2 \frac{\partial \theta}{\partial \mu} = \frac{e^2}{k_B T} \left[b + \frac{1}{\theta(1-\theta)} \right]^{-1} \quad (35)$$

The thermodynamic factor is

$$\chi_T = \frac{1}{1-\theta} + b\theta \quad (36)$$

If the jump diffusion coefficient is approximated by its value $D_j = D_0(1-\theta)$ for a noninteracting lattice gas, the chemical diffusion coefficient is given by^{55,56}

$$D_{ch} = D_0[1 + b\theta(1-\theta)] \quad (37)$$

D_{ch} increases (decreases) for repulsive (attractive) interactions. This is because the interactions modify the energy level of intercalated ions, as indicated in eq 34. If the interactions are of electrostatic nature, the thermodynamic chemical potential of eq 34 can be separated into a chemical potential and an electrostatic term, and it is recognized as the normal expression of the electrochemical potential in electrochemistry. Indeed, the term $b k_B T \theta$ in eq 34 could be viewed as a modification of the electrical component of the electrochemical potential (i.e., a change in internal energy per particle). This separation relies on the fact that in the Bragg–Williams approximation the molecular field affects all of the ions in the same way.

In general, for the interacting systems, the thermodynamic factor exerts a major impact on the chemical diffusion coefficient. As an extreme example, consider attractive interactions strong enough that $b < -4$ (temperature below critical). Then at certain concentrations, the chemical capacitance of eq 35 is undefined, and χ_T and D_{ch} become zero and negative. This anomaly arises because the system undergoes a phase transition; ions aggregate in some regions and leave other areas vacant, or else an order–disorder transition occurs, so that the gradient of chemical potential becomes unstable. Further discussion of these characteristics in relation to lithium insertion in metal oxides is presented in ref 55.

5.2. Diffusion of Electrons with Electrostatic Shift of Energy Levels. In the nanostructured semiconductors permeated with an ionically conducting electrolyte, we find an effect on the diffusion of electrons that is formally similar to mean field interaction between ions in the lattice. Both the molecular field in the Bragg–Williams approximation to interacting ions in the lattice, and the shift of electrostatic potential in nanostructured semiconductors share the feature that all of the particles in the system are affected in exactly the same way.

The electroneutrality requirement imposes that the total concentration of electrons in nanoparticles (eq 18) $n = q_s/e$, where q_s is the ionic charge (per unit volume) in the liquid side of the oxide/electrolyte interface at the particles surface. Assuming that the Galvani potential in the liquid phase is not affected by the redistribution of ionic charge (because of high ionic density), the result of electron charging is a change of the Galvani potential into the nanoparticles by $\Delta\varphi = -\Delta q_s/(pC_H)$. Here C_H is the specific Helmholtz capacitance per microscopic surface unit, p is the ratio of internal surface to volume, and we denote $C_H = pC_H$. For an electrode composed of particles of radius r and void fraction f_v , $p = (4\pi r^3/3)^{-1}(4\pi r^2)(1-f_v) =$

$3(1-f_v)/r$. This effect can be viewed as a change of the conduction band position with respect to vacuum level and it is usually known as band unpinning, as indicated in Figure 1d. Therefore

$$\bar{\mu}_n = E_{c0} + \frac{e^2}{C_H} n + \mu_n \quad (38)$$

Here E_{c0} is the lower edge of the conduction band at $C_H \rightarrow \infty$, and μ_n is chemical potential of the electrons. Equation 38 is seen to correspond to *repulsive* interactions in the lattice gas model in the mean field approximation, eq 34; however, no direct repulsion of electrons is considered in eq 38. The thermodynamic factor is

$$\chi_T = \frac{n}{n_c} \left(1 + \frac{\partial n_L}{\partial n_c} \right)^{-1} + \frac{e^2}{k_B T C_H} n \quad (39)$$

Using the jump diffusion coefficient of eq 22, i.e., assuming that it is not modified by the shift of the bands, we obtain for the chemical diffusion coefficient

$$D_n = \left(\frac{1}{1 + \partial n_L / \partial n_c} + \frac{e^2}{k_B T C_H} n \right) D_0 \quad (40)$$

We remark that eq 40 is the more general result for the chemical diffusion coefficient presented in this paper. It extends the result in eq 1 to the case of electrostatic band edge shift, and it is valid also for static distributions of localized levels in the band gap.

5.3. Exponential Distribution. In Figure 5, we have extended the previous calculations presented in Figure 4 for exponential distribution and conduction band electrons, including now the effect of band edge shifts, by means of eqs 38–40. Note that the band shift is caused by modification of the electrostatic potential difference at the nanoparticle/electrolyte interface, so in this case, the measured capacitance, C_{μ} , is an *electrochemical capacitance*⁵⁷ containing both electrostatic and chemical capacitor contributions (for details on this point see ref 42):

$$C_{\mu} = (C_H^{-1} + C_{ch}^{-1})^{-1} \quad (41)$$

where the chemical capacitance includes both traps and conduction band components, $C_{ch} = C_{ch}^{(trap)} + C_{ch}^{(cb)}$.¹ The band shift becomes significant when C_{ch} approaches the value of $C_H = pC_H$.

The quantities in Figure 5 are plotted twice with respect to different potential scales. The left column shows the Fermi level in the x axis, i.e., the measured electrode potential (or photovoltage in the case of photoinjection) with respect to a reference in solution. The right column, on the other hand, shows in the x axis the “real” evolution of the Fermi level toward the conduction band, as previously shown in Figure 4. The dependence of total electron concentration, n , in the right panel of Figure 5a is the same as that in Figure 4a, but the rest of quantities are influenced by the conduction band shifting away when the Fermi level rises.

The evolution of the jump diffusion coefficient is just the expected behavior for MT transport: when the Fermi level increases, deep traps are filled, so the random walk of a particle becomes faster. Figure 5d shows that D_j increases by orders of magnitude with increasing E_{Fn} until the point at which the traps are all filled, where D_j stabilizes at the value of free electrons, D_0 . In this process, the chemical diffusion coefficient first follows the exponential increase of D_j , in the range in which

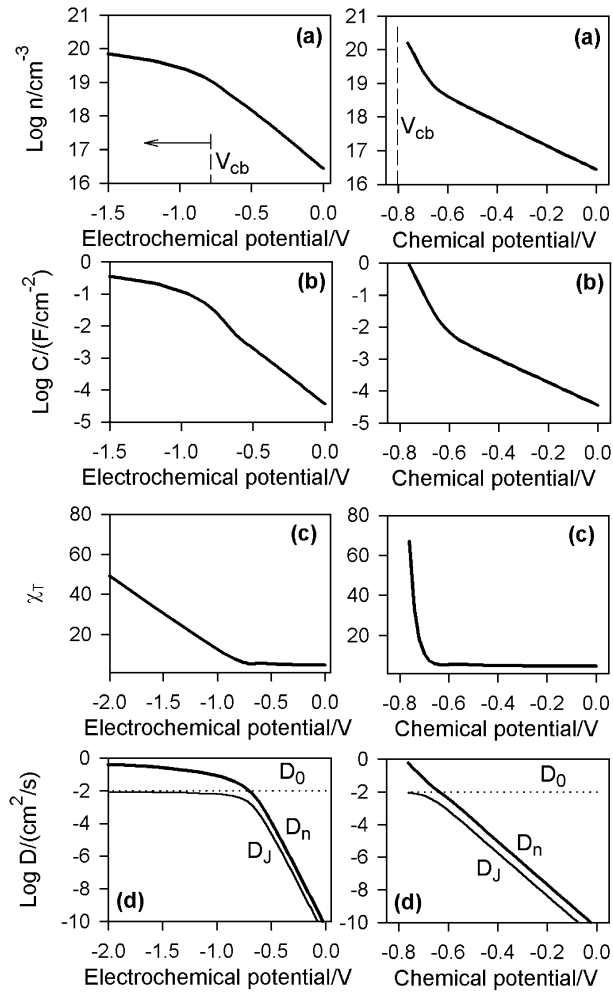


Figure 5. Representation of several quantities for charge accumulation and diffusion by multiple trapping in a nanostructured semiconductor electrode with an exponential distribution of band gap states. In the left column the potential $V = -E_{Fn}/e$ is the Fermi level potential with respect to a reference in solution. To remove the effect of bandshift in the potential scale, in the right column the potential shown is the distance of the Fermi level with respect to the lower conduction band edge, $V = -(E_{Fn} - E_c)/e$, i.e., the chemical potential of electrons, and $V_{cb} = -E_c/e = -0.8$ V is the conduction band potential. (a) Isotherm (total charge vs potential). (b) Electrochemical capacitance. (c) Thermodynamic factor. (d) Free electrons diffusion coefficient (D_0) and jump (D_J) and chemical (D_n) diffusion coefficient. Parameters: $N_c = 6.8 \times 10^{20} \text{ cm}^{-3}$, $N_L = 2.0 \times 10^{19} \text{ cm}^{-3}$, $T = 300 \text{ K}$, $T_0 = 1400 \text{ K}$, $D_0 = 10^{-2} \text{ cm}^2/\text{s}$, $c_H = 10 \mu\text{F}/\text{cm}^2$, $p = 3(1 - f_v)/r = 1.5 \times 10^6 \text{ cm}^{-1}$, $C_H = pc_H = 15 \text{ F}/\text{cm}^2$. The capacitances are given per unit substrate area for an electrode of thickness $L = 10 \mu\text{m}$ with nanoparticles of radius $r = 10 \text{ nm}$ and void factor $f_v = 0.5$.

band unpinning is negligible. Subsequently, the shift of the conduction band (analogous to a repulsive interaction in the lattice gas with mean-field forces) causes a significant value of the thermodynamic factor, as shown in Figure 5c. This effect has a major impact on the chemical diffusion coefficient, as observed in Figure 5d. At the more negative potentials D_n increases notoriously over the free electrons value, D_0 , by a factor ≈ 60 , which is due entirely to the thermodynamic factor, χ_T . The physical explanation for this effect, given first in ref 58 (see below), is that the application of a change of the electrochemical potential, ΔE_{Fn} , to measure D_{ch} , causes an additional drift force that enhances diffusion.

5.4. Box Distribution. We now derive a special case of eq 40 following the alternative procedure indicated in ref 58. Vanmaekelbergh and de Jongh use the combined expression of

drift and diffusion components for the particle flux in terms of the gradient of the electrochemical potential⁵⁹

$$J = u_0 n_c \left[-\frac{1}{e} \frac{\partial \bar{\mu}_n}{\partial x} \right] \quad (42)$$

where $u_0 = eD_0/k_B T$ is the mobility. The variation of the Galvani potential (i.e., the local conduction band level) relates to the surface charging as

$$\frac{\partial \varphi}{\partial x} = \frac{1}{C_H} \frac{\partial q_s}{\partial x} = -\frac{e}{C_H} \frac{\partial n_L}{\partial n_c} \frac{\partial n_c}{\partial x} \quad (43)$$

and eq 42 takes the form

$$J = -\left(1 + \frac{e^2}{k_B T C_H} \frac{\partial n_L}{\partial n_c}\right) D_0 \frac{\partial n_c}{\partial x} \quad (44)$$

In ref 58, the particular case of a box distribution of localized states of width ϵ_L is considered

$$g(E) = N_L/\epsilon_L \quad (45)$$

In this case

$$\frac{\partial n_L}{\partial n_c} = \frac{N_L k_B T}{n_c \epsilon_L} \quad (46)$$

and therefore, when Helmholtz layer charging becomes significant, the apparent diffusion coefficient increases by a constant factor due to the drift component, as follows:⁵⁸

$$J = -\left(1 + \frac{N_L e^2}{\epsilon_L C_H}\right) D_0 \frac{\partial n_c}{\partial x} \quad (47)$$

Notice that eq 47 corresponds to our general result in eq 40; however, eq 40 contains an additional factor $(\partial n_c/\partial n_L)$ due to the reduction of the chemical diffusion coefficient by trapping and detrapping (eq 23) not considered in eq 47. The result of eq 40 for the box distribution of traps is obtained using eq 46, and it gives

$$D_n = \left(\frac{\epsilon_L}{N_L} + \frac{e^2}{C_H}\right) \frac{n_c}{k_B T} D_0 \quad (48)$$

6. Conclusion and Outlook

Depending on the experimental or simulation technique that is used for investigating electron diffusion in nanostructured semiconductors, it becomes necessary to carefully distinguish the following diffusion coefficients:

(a) In steady state measurements, only the free electrons diffusion coefficient, D_0 , determines the photocurrent. Normally D_0 cannot be measured directly from steady-state measurements; other information is needed, concerning the free carrier density and lifetime.¹

(b) Random walk simulations near equilibrium conditions provide the jump (or tracer) diffusion coefficient, D_J , that describes the average mean square displacement of a carrier with time.

(c) The change of the system under a small perturbation of carrier density is described by the chemical diffusion coefficient. D_{ch} is composed of two factors: The thermodynamic factor, χ_T , that accounts for the difference between a gradient in concentration and a gradient in chemical potential, and the jump diffusion coefficient, D_J . Kinetic or transient electrical and

electrooptical techniques, such as EIS and IMPS, in quasistatic conditions, permit the measurement of the chemical diffusion coefficient, D_{ch} . The thermodynamic factor can be investigated independently, through the chemical capacitance.^{1,42}

We have described D_{ch} and the associated quantities in two cases that make use of independent electrons statistics and can therefore be solved completely near equilibrium: multiple trapping transport in a stationary distribution of site energies and electrostatic shift of energy levels. The comparison of these effects indicates that χ_{T} exerts a varying influence on the observed chemical diffusion coefficient and may compensate or not the steady-state dependence of the jump diffusion coefficient. We found that there is no compensation of χ_{T} and D_{J} in the multiple trapping model, so that the dependence of D_{n} on concentration, found experimentally, can be attributed to the jump diffusion coefficient.

For interacting systems, the effect of χ_{T} can be large, so D_{ch} could be affected by modifications of the environment of carriers, for instance the electrolyte conditions, that change the electrochemical potential of electrons in the semiconductor nanoparticles by interaction effects. Experimental evidence in nanostructured electrodes indicates a dependence of electron transport properties on the surrounding medium.^{9,60,61} The details of such variations have not been clarified yet, so one can only speculate that the contribution of interactions and in particular local conditions of shielding could be exert a relevant influence on D_{ch} . For example, electrons interact with the solid lattice constituting polarons, and Coulomb repulsion becomes significant when many electrons are packed into a nanoparticle. Furthermore, electrons travelling in low-conducting media form long-range polarization that modifies their mobility.^{61,62} Our results presented in this paper show the thermodynamic components of the diffusion coefficient, D_{n} , that is measured in nanostructured semiconductors by small perturbation kinetic techniques. The relevance of the expression $D_{\text{n}} = \chi_{\text{T}} D_{\text{J}}$ is demonstrated for electron diffusion, and this equation may be useful for considering the transport of electrons that, in addition to follow trapping and detrapping events, interact nontrivially with the surrounding medium. This matter is left for future investigations.

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