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The influence of the electrolyte on the electron diffusion in mesoporous nanocrystalline TiO₂

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Abstract

Experimental studies show that the rate of electron diffusion in mesoporous nanocrystalline TiO₂ may depend on the electrolyte concentration. In the available literature, this effect is attributed to ambipolar diffusion. We present arguments and a kinetic model indicating that it might instead be connected with different arrangements of cations near the traps occupied by an electron before and after tunnelling. With a reasonable choice of the ratio of the kinetic parameters, in agreement with experiment, the model predicts that the electron diffusion coefficient at high electrolyte concentrations may be about five times higher than at low concentrations.

1. Introduction

The understanding of electron transport in mesoporous nanocrystalline electrolyte-soaked TiO₂ (with a grain size in the range of 10–80 nm) is of interest for applications in photochemical solar cells [1]. At present, this process is believed to occur via electron tunnelling between traps of different depths, leading to a distribution of jump rates. Due to the small size of the TiO₂ grains, electrons seem to migrate primarily by jumping via the surface states [2] and the migration rate may therefore depend on the ion concentration in the electrolyte outside the grains [3]. For example [3], the electron diffusion coefficient may exhibit about a fivefold increase upon increasing the molarity of the electrolyte from 20 to 500 mM. The current interpretation of these and other experimental findings is based on several complementary models, focused on the energy distribution of bandgap states [4], traps at the surface of grains [5], percolative properties of the grains [6], and/or interplay of the ion and electron diffusion [7, 8]. The latter factor, introduced in order to explain the dependence of the electron migration rate on the electrolyte composition, has been treated in terms of *ambipolar diffusion* [7, 8]. In the present paper, we show that the applicability of this concept to electron transport in TiO₂ is far from

obvious and propose an alternative explanation of the electrolyte-related effects. In addition, we briefly discuss how one can experimentally distinguish between the conventional ambipolar diffusion model and our model.

2. Ambipolar diffusion

The theory of ambipolar diffusion is explicitly based on the mean-field (MF) approximation and the quasi-neutrality (QN) condition [9]. In condensed media, these approximations usually hold on the mesoscopic scale (>100 nm). This does not guarantee however that the theory of ambipolar diffusion is really applicable in the case under consideration, because the MF approximation and QN condition can be fulfilled in other versions of the theory as well. Scrutinizing the concept of ambipolar diffusion, one can find that it implies the applicability of the MF approximation not only on the mesoscopic scale but on shorter distances as well, because the ambipolar diffusion coefficient, corresponding to collective diffusion of electrons and ions, is expressed via the phenomenological coefficients of independent diffusion of electrons and ions. In the system under consideration, the concentration of diffusing electrons is low (typically lower than or about $2 \times 10^{18} \text{ cm}^{-3}$ [7]). This means that interaction between electrons is weak and the screening of an electron trapped to the surface state takes place primarily due to its interaction with a single nearest-neighbour cation. In addition, electron tunnelling jumps occur in fact instantaneously. Such events are accompanied by local relaxation of the medium but the ions are not able to jump together with an electron. Physically, it is clear that this situation is far from the MF case and accordingly one should describe the electron–ion interaction in more detail in order to understand the electron diffusion specifics.

3. Model including local electron–ion interaction

To treat the problem, one can use the master equations taking into account electron jumps and medium reconfiguration. This approach is usually cumbersome and often contains many parameters which can hardly be quantified for the present case. To make the presentation more transparent, we employ a generic model containing a minimal number of parameters. In particular, the tunnelling electron transport is assumed to occur primarily via traps located at the solid–electrolyte interface. The traps are described by using a four-state approximation. Specifically, each trap can (i) be unoccupied (no electron in the trap) and with no cation nearby, (ii) be unoccupied but with a cation nearby, (iii) be occupied (an electron is in the trap) and with no cation nearby, and (iv) be occupied with a cation nearby. Focusing on the simplest situation when the electron concentration is low, we neglect electron–electron interaction and analyse diffusion of single electrons (the interference of electrons can be incorporated into the model in line with earlier work [4], but this is beyond our present scope). In this case, the jumps of an electron, located in trap i , to adjacent vacant traps, are described by

$$dP_0/dt = - \sum_{j \neq i} (k_{00}^j p_0^j + k_{01}^j p_1^j) P_0 + v_{10} P_1 - v_{01} c P_0, \quad (1)$$

$$dP_1/dt = - \sum_{j \neq i} (k_{10}^j p_0^j + k_{11}^j p_1^j) P_1 - v_{10} P_1 + v_{01} c P_0, \quad (2)$$

where P_0 and P_1 are the probabilities that trap i is in states (iii) and (iv), p_0^j and p_1^j are the probabilities that vacant trap j is in states (i) and (ii), k_{00}^j , k_{01}^j , k_{10}^j , and k_{11}^j are the tunnelling rate constants (the rate-constant subscripts are interconnected with those of the trap-state probabilities and accordingly indicate the trap states before and after electron tunnelling),

v_{01} and v_{10} are the cation attachment and detachment rate constants, and c is the cation concentration.

In general, equations (1) and (2) should be complemented by terms taking into account the electron jumps back from traps j to trap i and then solved together with similar equations for other traps. Skipping a full-scale analysis of this problem, we analyse a special case which can be treated analytically. Specifically, we assume that the cation attachment and detachment are relatively rapid and accordingly close to a steady state, i.e.,

$$v_{10}P_1 \simeq v_{01}cP_0. \quad (3)$$

By definition, the total probability that trap i has an electron is $P = P_0 + P_1$. Using this relationship in combination with equation (3) yields

$$P_0 = Pv_{10}/(v_{10} + v_{01}c), \quad (4)$$

$$P_1 = Pv_{01}c/(v_{10} + v_{01}c). \quad (5)$$

For p_0^j and p_1^j , we have $p_0^j + p_1^j = 1$, and accordingly these probabilities can be represented in analogy with equations (4) and (5) as

$$p_0 = w_{10}/(w_{10} + w_{01}c), \quad (6)$$

$$p_1 = w_{01}c/(w_{10} + w_{01}c), \quad (7)$$

where w_{01} and w_{10} are the corresponding rate constants of cation attachment and detachment.

Substituting expressions (4)–(7) into equations (1) and (2) and then combining the left- and right-hand parts of the latter equations results in

$$dP/dt = - \sum_{j \neq i} r_j P, \quad (8)$$

where r_j is the effective rate constant of electron jumps from trap i to trap j , defined by

$$r_j = r_{00}^j + r_{01}^j + r_{10}^j + r_{11}^j, \quad (9)$$

with

$$r_{00}^j = \frac{k_{00}^j v_{10} w_{10}}{(v_{10} + v_{01}c)(w_{10} + w_{01}c)}, \quad (10)$$

$$r_{01}^j = \frac{k_{01}^j v_{10} w_{01}c}{(v_{10} + v_{01}c)(w_{10} + w_{01}c)}, \quad (11)$$

$$r_{10}^j = \frac{k_{10}^j v_{01} w_{10}c}{(v_{10} + v_{01}c)(w_{10} + w_{01}c)}, \quad (12)$$

$$r_{11}^j = \frac{k_{11}^j v_{01} w_{01}c^2}{(v_{10} + v_{01}c)(w_{10} + w_{01}c)}. \quad (13)$$

The electron diffusion coefficient depends on the distribution of traps and also on the distribution of the effective jump rate constants. For a given distribution of traps, one can find rate-determining jumps such that the diffusion coefficient will be proportional to the rate constants of these jumps. Thus, the dependence of the effective jump rate constants on the cation concentration (equations (9)–(13)) characterizes the dependence of the diffusion coefficient on this concentration.

4. Model predictions

Our model presented above is conceptually and mathematically simple. It contains the minimal number of kinetic parameters needed in order to describe the physics introduced. The number

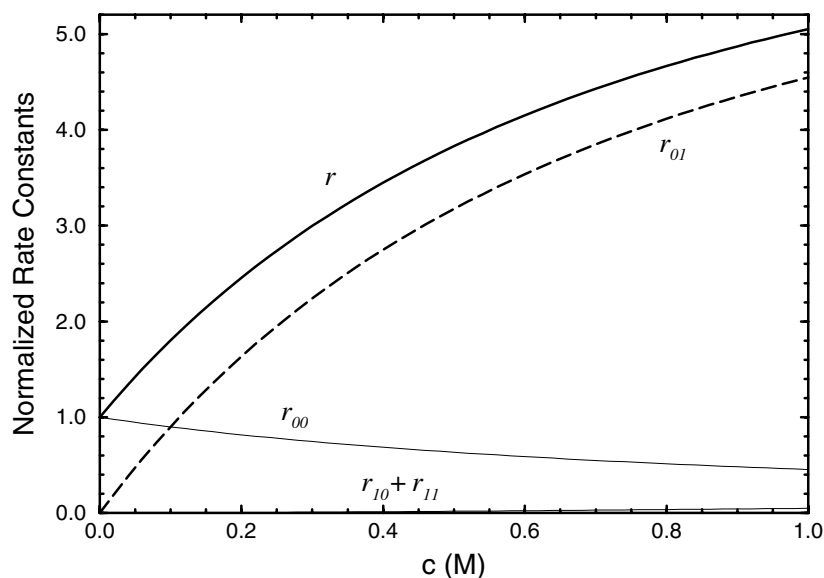


Figure 1. Effective jump rate constant, r_j , and its components, r_{00}^j , r_{01}^j , and $r_{10}^j + r_{11}^j$, as a function of the electrolyte concentration. All the values are normalized to k_{00}^j . (Note that the value of $r_{10}^j + r_{11}^j$ is small and the corresponding curve is nearly invisible.)

of the parameters is however apparently rather large and at present they can hardly be obtained from experiment. Nevertheless, the final results (equations (9)–(13)) depend only on ratios of the parameters, and accordingly the situation with validation of the parameters is really not so severe as it might seem at first sight. To illustrate the model predictions, it is instructive to show the dependence of r_j (equation (9)) on c for presumably reasonable ratios of various rate constants in expressions (10)–(13).

To validate the choice of the model parameters, it is appropriate to recall that the ratio of the tunnelling rate constants is expected to depend first of all on the energetics of jumps. In particular, the famous Marcus theory [10] predicts that the jump rate is proportional to $\exp[-(E_r - J)^2/(4E_r k_B T)]$, where E_r is the reorganization energy of the medium, and J the reaction exothermicity. Typically, the reorganization energy is appreciable, $E_r \simeq 1$ eV $> |J|$. In this so-called ‘normal’ region, the jump rate increases with increasing J .

The situations when an electron has or has no cation nearby both in the initial and final states are more or less equivalent, and accordingly we use $k_{11}^j/k_{00}^j = 1$. The jumps in the cases when an electron has a cation nearby in the initial state and does not contact a cation in the final state are energetically less favourable (i.e., $J < 0$), and we employ $k_{10}^j/k_{00}^j = 0.01$. The situation when an electron has no cation nearby before a jump and contacts a cation after a jump is energetically more favourable ($J > 0$), and we put $k_{01}^j/k_{00}^j = 100$. The presence of an electron on a trap makes the location of a cation nearby more probable. Thus, we should have $v_{01}/v_{10} > w_{01}/w_{10}$. To be specific, we use $v_{01}/v_{10} = 1$ M $^{-1}$ and $w_{01}/w_{10} = 0.1$ M $^{-1}$.

With the parameters above, the effective jump rate constant (figure 1) exhibits a five times increase with increasing ion concentration, c , from zero to 1 M. Quantitatively, this effect is similar to that observed experimentally [3]. Physically, the increase of the effective jump rate is related to more favourable conditions for electron tunnelling in the situations when an electron has no cation nearby before the jump and contacts a cation after the jump. With

increasing c , the corresponding contribution, r_{01}^j , to the effective jump rate constant rapidly becomes dominating. The important point is that this term has little in common with ambipolar diffusion, because it cannot be expressed via the phenomenological coefficients of independent diffusion of electrons and ions.

5. Conclusion

In summary, we have illustrated that the dependence of the rate of electron diffusion in mesoporous nanocrystalline TiO₂ on electrolyte concentration is probably related to different arrangements of cations near the traps occupied by an electron before and after tunnelling.

Finally, we may briefly comment on how one can experimentally distinguish between the conventional ambipolar diffusion model and our model. Physically, it is clear that in the limit when the electrolyte concentration is high and the electron diffusion is controlled by electron jumps the two models can hardly be discriminated. If however the electrolyte influences the electron diffusion, the temperature dependences of the apparent electron diffusion coefficients predicted by the two models are different. Specifically, the ambipolar diffusion model indicates that the temperature dependence of the electron diffusion coefficient should coincide with that of the electrolyte diffusion [7]. In contrast, our model does not directly relate these two temperature dependences. This difference can be used as the simplest indicator of what is going on.

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