An Approach Based on Random Walks to Simulate Concentration Profiles and Current Transients in Electrochemical Processes Controlled by Mixed Diffusion-Migration

Uma Abordagem Baseada em Caminhos Randômicos para Simular Perfis de Concentração e Transientes de Corrente em Processos Eletroquímicos Controlados por Migração-Difusão Mistas

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Abstract: In this paper, the dynamics of electrode reactions under diffusion-migration control is analyzed with an approach based on random walks. The main advantage of this approach is the simplicity of the concepts involved which lead to very simple computational algorithms, avoiding the resolution of differential equations. The model was employed to obtain the profile concentrations of reversible electrode reactions, as well as current transients, for the case where diffusion and migration have comparable effects.

Key words: current transients; diffusion-migration control; random walks.

Resumo: Neste artigo, a dinâmica de reação em eletrodo sob controle de difusão-migração é analisada com uma abordagem baseada em caminhos randômicos. A principal vantagem desta abordagem é a simplicidade dos conceitos envolvidos que levam a algoritmos computacionais muito simples, evitando a resolução de equações diferenciais. O modelo foi empregado para obter os perfis de concentração de reações em eletrodo reversíveis, bem como transientes de corrente, para o caso onde difusão e migração têm efeitos comparáveis.

Palavras-chave: caminhos randômicos; controle de difusão-reação; transiente de corrente.

1 Introduction

Migration-diffusion controlled processes are important in several electrochemical issues. For instance, migration may greatly influence the electron and ions transport in films (e.g. coated electrodes). Besides, even in the absence of films, migration can also significantly speed up or slow down the transport of charged species in diluted solutions, where an exponential electric field is present in the region close to the electrode.

Some years ago, an article [1] was published in this journal in which digital simulations were employed to solve the equations associated to migration-diffusion problems in electrochemistry. There, finite difference methods were used to solve a parabolic-hyperbolic mixed differential equation.

In this article, a simple algorithm based on random walks is presented as an alternative way to simulate the current response of electrochemical systems for mixed migration-diffusion controlled processes.

It is well known that diffusion processes are related to random trajectories [2]. A typical way of modeling random trajectories in one dimension is to consider the random walk of a particle which moves to the left or to the right, with equal chances, at a constant pace. The random walk approach is still useful nowadays to simulate the time evolution of diffusion-controlled current of some systems of particular interest and, in this regard, it is worth mentioning a recent work by Feldberg [3] based on random walks in which he discusses a paradox presented by Aoki [4].

In the present work, we show that the random walk approach is not only attractive in its simplicity to study diffusion but can also be extended, within certain limits, to include migration as well –i.e. the movement of charged species induced by an electric field. Therefore, the combined effects of diffusion and migration can be analyzed and visualized with the aid of simple algorithms. The followed approach is applied to calculate concentration profiles and current transients of electrode reactions under diffusion-migration control in one dimension.

2 Model

We will consider the problem of a particle moving at random in a one-dimensional space. Let us begin considering that the particle, initially at $x = 0$, is allowed to move one step at a time at a constant pace of λ/τ seconds, where λ is the step length and τ^{-1} is the step frequency. The particle has a probability p of moving to the left ($x = - \lambda$) and 1-p of moving to the right ($x = \lambda$). The probability $P(x,t+\tau)$ of finding the particle at a distance x from the origin after an elapsed time of $t+\tau$ is

$$P(x, t+\tau) = p \cdot P(x-\lambda, t) + (1-p) \cdot P(x+\lambda, t) \tag{1}$$

If first and second order approximations, for time and displacement respectively, of a Taylor series are employed for $P(x,t)$, the following expression is obtained:

$$\frac{\partial P(x,t)}{\partial t} = (2p-1)\frac{\lambda}{\tau}\frac{\partial P(x,t)}{\partial x} + \frac{\lambda^2}{2\tau}\frac{\partial^2 P(x,t)}{\partial x^2} \tag{2}$$

One special but greatly important case of Eq. 2 is that of $p = ½$, where the particle has equal chances of moving to the right and to the left. In that case, the first term of the second member is null, and Eq. 2 turns into:

$$\frac{\partial P(x,t)}{\partial t} = \frac{\lambda^2}{2\tau}\frac{\partial^2 P(x,t)}{\partial x^2} \tag{3}$$

It is worth noting that considering $p = ½$ is an equivalent problem to that of a particle moving totally at random – in other words, the case of diffusion in one dimension. If we compare Eq. 3 with Fick's Law:

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2} \tag{4}$$

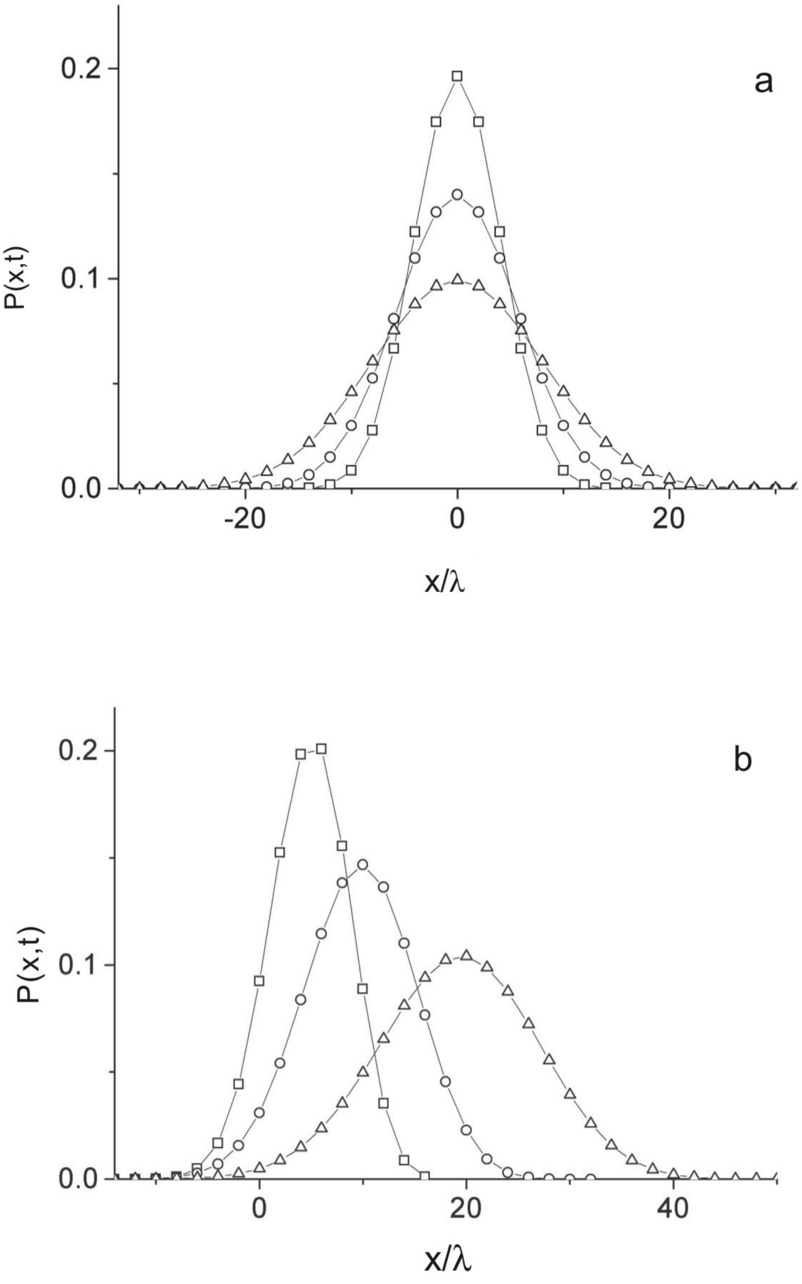
it can be readily noted that $D = \lambda^2/2\tau$.

One way to obtain the probability density distribution $P(x,t)$ in the absence of migration effects (i.e. modification of concentration are due exclusively to diffusion effects) is to solve Eq. 4 under certain boundary conditions. We will adopt a different approach here, consisting in employing Eq. 1 to generate a computer simulation to describe the displacement of a particle (in this context, the "particle" can also be an ion or a molecule). If we consider that the space in which the particle moves is infinite in both directions and the particle is moving totally at random, with equal chances to the left and to the right, then $p = ½$. We introduce the initial condition $P(0,0) = 1$ to ascertain that the particle is initially at $x = 0$, and then a computational loop can be implemented to increase the number of steps and follow the evolution of $P(x,t)$ for a number of steps $n = t/\tau$. A rather simple algorithm (see Appendix) used to carry out such calculations yields graphs such as those shown in figure 1a, which exhibit the well known shape of a bell, centered at the origin.

It is interesting to consider the physical meaning of p. If $p = ½$, as discussed above, the particle moves totally at random, which leads to diffusion equations. On the other hand, $p \neq ½$ means that the particle has a preferential direction to which it moves with higher chances. A value of $p \neq ½$ means that the particle has a tendency to go to one of the sides, but is also affected by some randomness. Clearly, $p \neq ½$ is related to the presence of forces acting on the particle that induce movements in a preferential direction. If we consider a charged particle, the interaction with an electric field may give rise to such forces, inducing a preferential direction for the particle to move, which depends on the strength of the interaction between the charged particle and the electric field. The higher the field intensity, the more p deviates from ½.

Some simulated probability profiles are shown in Figure 1b for different values of p, ranging between 0.5 and 0.65, for the case of infinite diffusion in one dimension. It can be seen that a value of p different than ½ provokes a net displacement of the mean value of x.

Figure 1. Probability of finding the particle at a distance x from his original position after n steps: n = 16 (□), 32 (○), and 64 (Δ) for p = 0.5 (a) and p = 0.65 (b)



Actually, it can be shown from a basic combinatory analysis that the mean value of x is $n\lambda(2p-1)$, where $n = t/\tau$ is the number of iterated steps. Thus, if we consider that the particle is under the effect of an electric field, the field imposes a net mean velocity of $(2p-1)\lambda/\tau$. Following a similar reasoning as to the one employed to obtain the Stokes-Einstein relation, we can realize that this constant mean velocity is the consequence of the compensation of the electric force $F_e = ze\varphi$ and friction forces $F_v = 6\pi r\eta(2p-1)\lambda/\tau$, where ze is the electric charge of the particle, φ is the electric field, r the particle's radium, and η the medium viscosity. After introducing the Stokes-Einstein relation $D = kT/6\pi r\eta$ (where k is the Boltzmann constant and T the temperature), and rearranging, we finally arrive to:

$$p = \frac{1}{2} - \frac{ze\varphi\lambda}{4kT} \tag{5}$$

Moreover, reintroducing p in Eq. 3, it is possible to figure out a familiar expression for diffusion-migration in one dimension in a constant electric field, which can be obtained after taking the divergence of the Nernst-Planck equation [5]:

$$\frac{\partial P(x,t)}{\partial t} = \frac{ze\varphi D}{kT}\frac{\partial P(x,t)}{\partial x} + D\frac{\partial^2 P(x,t)}{\partial x^2} \tag{6}$$

It is worth noting that, in this context, the probability density function and the concentration are directly proportional.

3 Simulations of current transients of electrode reactions under one-dimension semi-infinite conditions

Let us consider a redox species Ox that suffers an electron transfer reaction at a planar electrode of the type: $Ox + n_e e \rightarrow Red$. We will assume that this is a fast reaction, carried out in such conditions that its rate is determined by the transport of Ox. The aim is to find the current evolution after a potential step applied to the electrode. The electrode potential, initially at equilibrium conditions (i.e. null current), is changed to a constant value in which limit cathodic current conditions apply. Once the reaction is started, diffusion and migration act on Ox particles; while diffusion always promotes the arrival of fresh Ox species, the electric field action depends on the charge of the species and field gradient.

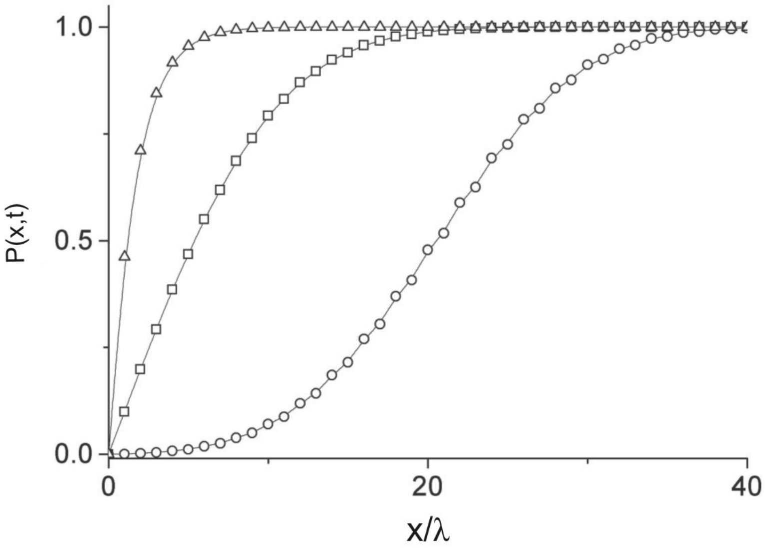
Under limit current conditions, as soon as Ox species reach the electrode, they are immediately converted into Red, and therefore the condition $P(0,t) = 0$ must apply. We will consider also that the solution has a volume large enough so that the bulk concentration remains constant, which can be expressed in terms of a time independent probability of finding Ox species at very remote distances from the electrode, and therefore the condition $P(+\infty,t)$ also applies.

It is interesting to visualize the combined effects of migration and diffusion on the concentration profiles, shown in Figure 2 for different values of p and an elapsed time of 64 τ. It is worth noting that these curves are very similar to those presented in [1], which were obtained using finite difference methods to solve the differential equation associated to the migration-diffusion problem.

If $p = ½$, the concentration profile exhibit the well known shape expected under the condition of semi-infinite diffusion, which could be expressed in terms of the error function. However, for $p = 0.65$, the profile is displaced to lower values of x, towards the electrode. This is a consequence of the attractive action of the electric field. On the other hand, for $p = 0.35$, the action of the electric field is to repel the ions, and the profile is clearly displaced away from the electrode –indeed, the area closest to the electrode is quickly depleted from ions, due to the combined action of the reaction at the electrode and the electric field pushing the ions away from the electrode.

We will look now for a convenient expression for the current. One way is to find an expression for the flux from the integration of Eq. 6. However, we will consider a shortcut provided by the context of the present model. It can be noted that only molecules at a distance λ from the electrode might reach its surface in a lapse of time of τ; moreover, a fraction p of those molecules will actually move to the left, towards the electrode and consequently react.

Figure 2. Concentration profiles for a redox species reacting at the electrode ($x = 0$*) under diffusion control (*$p = ½$*, □) and diffusion-migration control with *$p = 0.65$* (△) and *$p = 0.35$* (○) at *$t = 64\ \tau$



Therefore, the number of reacting species during the lapse between t and t + τ is related to the current by:

$$i(t) = n_e FAC\lambda p \frac{P(\lambda,t)}{\tau} \tag{7}$$

where F is the Faraday constant, A the electrode area, and C the bulk concentration of Ox species.

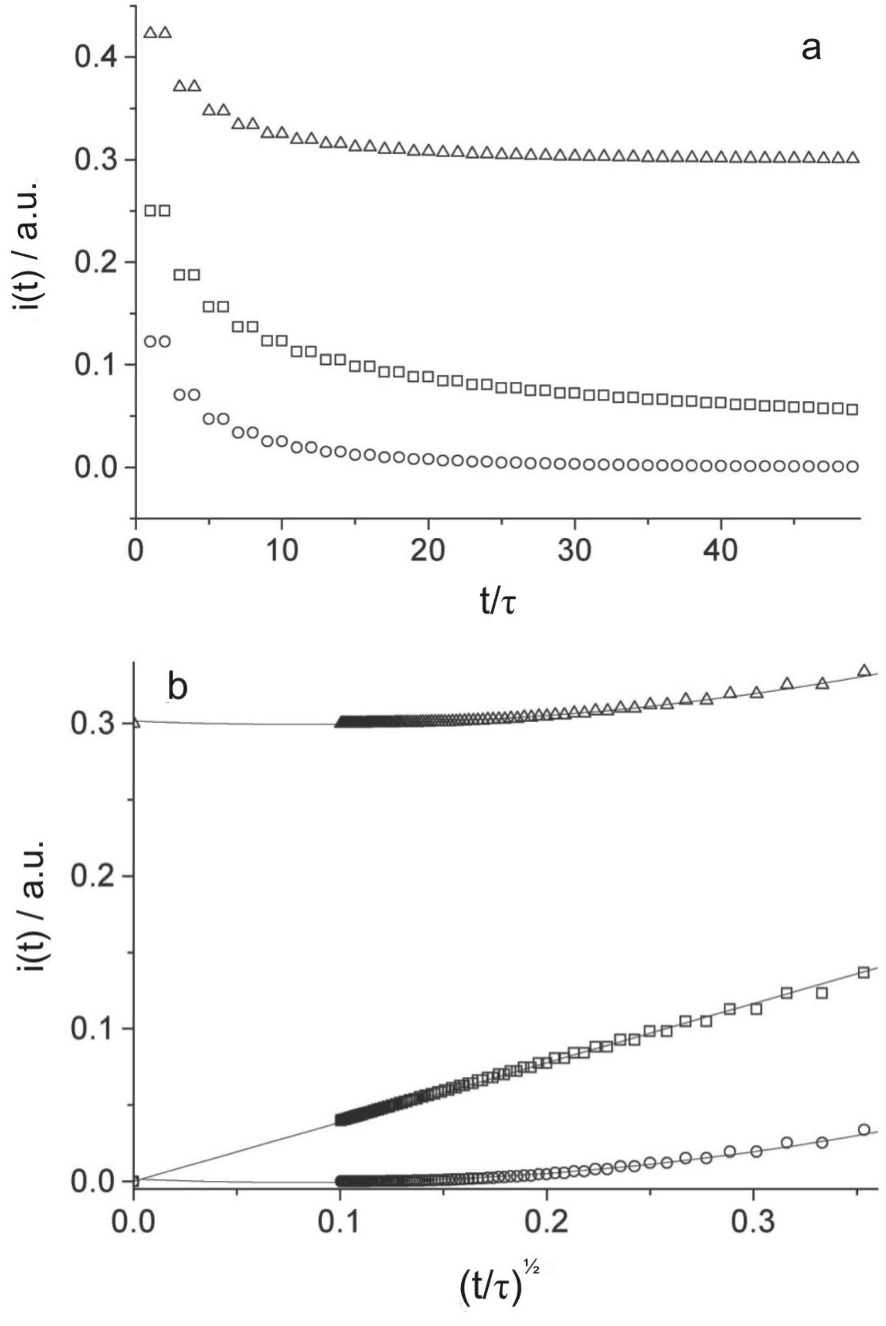
In this way, the simulation of the concentration profiles also provides an expression for the current through the value of P(λ,t).

If the electric field is constant at all distances, so is p. It can be noted that P(λ,t), and consequently the current, tend to zero for $p < ½$. On the other hand, for $p > ½$, P(λ,t) has a finite value and, as a consequence, the current reaches a steady state value. This value can be calculated noting that in steady state there is a net movement of species towards the electrode of (2p-1)Cλ every τ seconds, and arrive to the following expression for the steady state current.

$$i(+\infty) = \frac{n_e FAC\lambda}{\tau}(2p-1) \tag{8}$$

If we combine this with Eq. 7 we conclude that $P(\lambda,+\infty) = (2p-1)/ p$. The simulated current transients are shown in Figure 3, as well as i vs. $t^{-½}$ plots.

Figure 3. Current transients for different p values of 0.5 (□), 0.35 (○) and 0.65 (△) under diffusion and diffusion-migration control: (a) i vs t, and (b) i vs t-½.

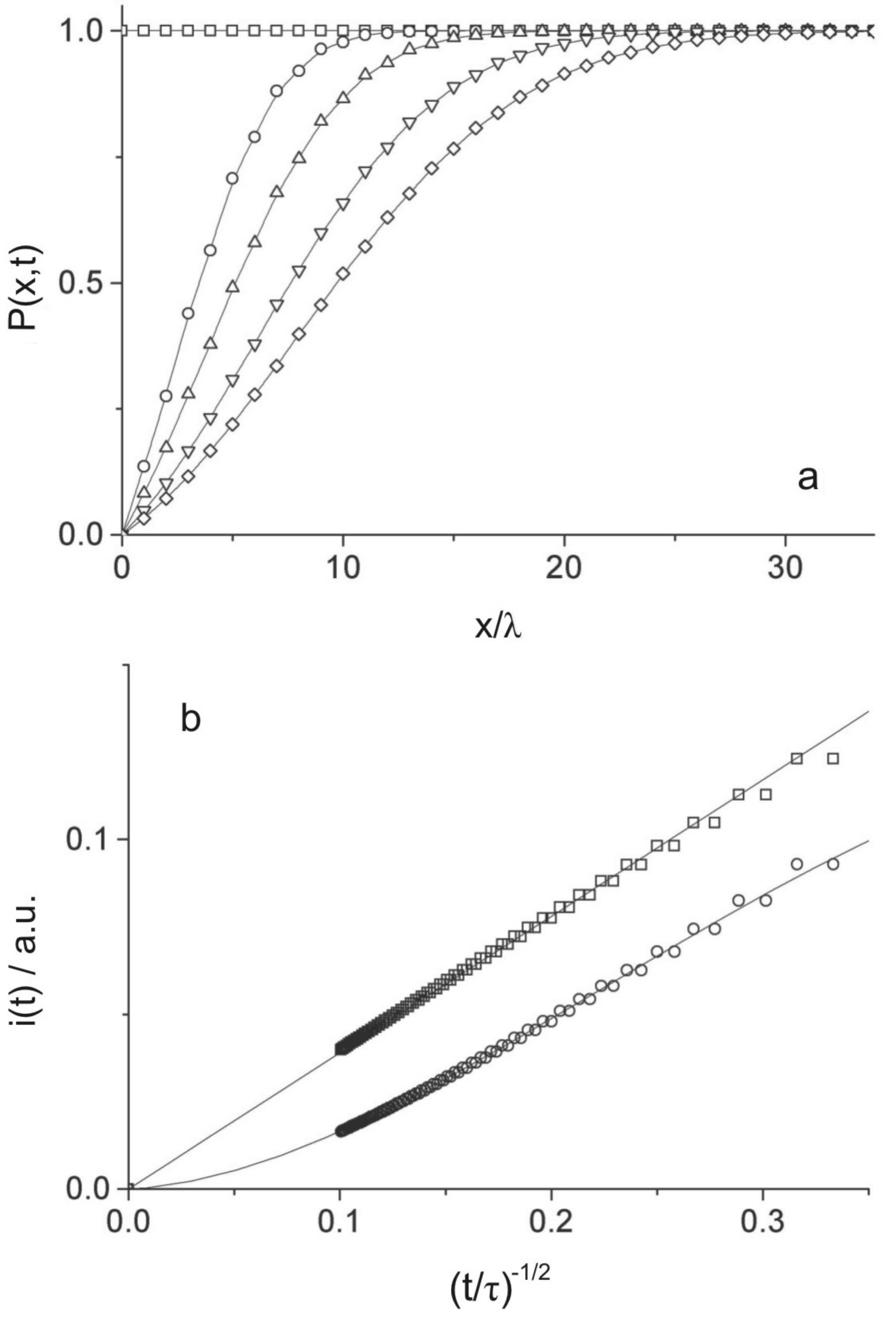


It can be noted that only if $p = ½$ there is a linear relation between i vs. $t^{-½}$, as expected according to the Cottrell equation; otherwise, the current decays faster to the final value, which is zero for $p < ½$, and proportional to 2p-1 for $p > ½$.

Although the presence of a constant electric field in the electrolyte phase might be of use in some cases, such as films in which the electric field is constant, it is not the most common scenario in electrochemistry. In electrochemical systems, there is usually an electric field (a potential drop) in the interphases, in a relatively small volume of the system as compared with the whole.

As an example of interest, we will consider the case in which an oxidized species Ox, coming from the bulk where the electric field is practically null, must travel across an exponential electric field to get close enough to the electrode to suffer an electron transfer reaction at the outer Helmholtz plane. For $V_0 < \frac{2kT}{ze}$, the electric potential can be expressed appropriately [6] with an exponential dependence on distance from the electrode: $\varphi(x) = -V_0 \kappa e^{-\kappa x}$. We will carry out a simulation of a reasonable condition of V_0 = 2kT/ze and $\lambda = 0.1\kappa^{-1}$ where the electric field has a repulsive action against the Ox ions. Figure 4 shows the simulated concentration profile at different times; it can be seen that they show combined features of those observed for the presence of constant field and the absence of field (pure diffusion). The current transient shows that the current decays more quickly in the presence of this field than under pure diffusion, and a deviation from the ½ exponent expected from Cottrell equation is observed, too.

Figure 4. (a) Concentration profiles for a redox species reacting at the electrode under diffusion-migration control with exponential electric field at different times since the beginning of the reaction: t/τ = 0 (□), 16 (○), 32 (△), 64 (▽), 99 (◇). (b) Current transients for p = ½ (□) and p with an exponential dependence of potential with the distance from the electrode (○)



4 Conclusions

An approach based on random walks has been introduced to simulate concentration profiles and current transients of electrode reactions under mixed diffusion-migration control. This approach provides a computationally simple way to simulate the time evolution of systems under the action of mild electric potential fields (in the order of kT/e) under semi-infinite conditions in one dimension. The model might be adapted to study other systems of interest, such as electroactive polymer films.

5 References

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Appendix

Algorithm in QuickBasic used to calculate the concentration profile displayed in Figure 2, and also to calculate the current transients shown in Figure 3. Concentration profiles are saved as "p-x.txt" and current transients as "i-t.txt", both as comma separated values (CSV).

```
CLS
INPUT “Value of p = ”, p
INPUT “Number of iterations = ”, n
DIM P(n+1,n+2)
OPEN “c:p-x.txt” for output as #1
OPEN “c:i-t.txt” for output as #2
FOR x = 0 TO n+1
P(0,x) = 1
NEXT x
P(0,0) = 0
FOR t = 1 TO n
FOR x = 1 TO n
P(t,x) = p * P(t-1,x-1) + (1-p) * P(t-1,x+1)
P(t,0) = 0
P(t,n+1) =1
IF t = n AND P(t,n+1) >< 0 THEN PRINT #1, x, P(t,x)
NEXT x
PRINT #2, t, P(t,1)
NEXT t
END
```