

Numerical Simulation of Charge Diffusion on the Surface of a Dendrimer Molecule

Artyom V. Andreyev, Oleksiy V. Klymenko

Abstract — This work presents the results of numerical simulation of charge transfer within the spherical outer shell of a dendrimer macromolecule induced by electrode polarisation on which the molecule is adsorbed. It is shown that under linear variation of the electrode potential the electric current peak contains information about the regimes of charge diffusion in the molecular shell. Thus the obtained results can be used for the determination of kinetic parameters from experimental data.

Index Terms — numerical simulation, surface diffusion, dendrimer, electrochemistry

I. INTRODUCTION

THE study of intramolecular processes is of extremely high interest both from the fundamental and practical points of view bearing in mind potential future applications in microelectronics and data storage devices. This area of research has been developing for several decades and yielded important experimental and theoretical results [1-3]. However, experimental investigation of such processes is exceptionally complicated and expensive owing to very high rates of such processes that require application of equipment with sufficiently high time resolution (of the order of nanoseconds and below). As was recently shown [4-7], intramolecular electron transfer within adsorbed large molecules can be successfully investigated by electrochemical methods. The latter works report experimental and theoretical studies of the process of electron transfer between active groups containing ruthenium atoms and located within the outer shell of a spherical dendrimer molecule adsorbed on the surface of a platinum working electrode. The application of negative voltage to the platinum working electrode with adsorbed dendrimers leads to the reduction of ruthenium atoms within active centres in the immediate vicinity of the platinum surface. It has been proposed that, following this initial reaction, the active centres within the dendrimer

outer shell begin to exchange charge between Ru(II) and Ru(III) atoms via electron tunnelling ('hopping'). The overall charge transfer in this case is reminiscent of diffusion of electrons within the outer dendrimer shell.

In order to understand the kinetics of this process we perform here the numerical simulation of electric current responses under the conditions of linear sweep voltammetry for different values of kinetic parameters which facilitates the analysis of experimental data.

II. MODEL

An adsorbed on the electrode surface dendrimer molecule is schematically shown in Fig. 1, where θ_0 is the characteristic angle reflecting the degree of dendrimer molecule deformation upon its adsorption and r_0 is the apparent radius of the adsorbed molecule. Electrode polarization enforces electron transfer (ET) between the electrode and active centres groups of the dendrimer shell located in the immediate vicinity of the electrode surface. Following the reduction of these sites the electron transfer occurs between neighbouring sites within the surface layer of the dendrimer molecule. i.e. via "hopping" diffusion of electrons. On average, due to the random character of electron transfer reactions between neighbouring sites (and, in general, a significant number of adsorbed molecules performing this in parallel), this process may be described as continuous diffusion of electrons with a diffusion coefficient D within the thin molecular shell.

The diffusion flux of electrons is then given by the first Fick's law:

$$\vec{j} = -D \text{grad } c, \quad (1)$$

where c is the surface concentration of transferred electrons in the dendrimer outer shell (in mol cm^{-2}) or, equivalently, surface concentration of reduced active sites. For the sake of simplicity we neglect here the thickness of the dendrimer shell containing active centres.

Due to the axial symmetry of the system the diffusion laws may be formulated in one of the axial cross-sections of the molecule using the spherical coordinate system centred at the dendrimer centre. Thus the flux along the meridian of the dendrimer is represented as:

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$$j = -D \frac{\partial c}{\partial l} = -\frac{D}{r_0} \frac{\partial c}{\partial \theta}. \quad (2)$$

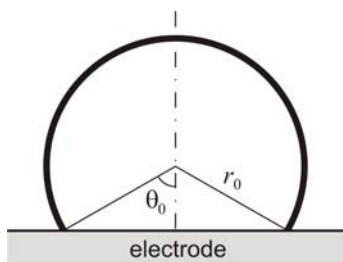


Fig.1. Scheme of a dendrimer molecule adsorbed on electrode surface

On the other hand, the charge conservation law must be obeyed, which in this case is given by the continuity relation leading to the second Fick's law:

$$\frac{\partial c}{\partial t} = -\text{div} \vec{j} = \frac{D}{r_0^2} \left(\text{ctg} \theta \frac{\partial c}{\partial \theta} + \frac{\partial^2 c}{\partial \theta^2} \right). \quad (3)$$

The initial condition ($t = 0$) to the diffusion equation (3) is given by

$$c(0, \theta) = 0. \quad (4)$$

The boundary conditions reflect the symmetry of the system, i.e. when $\theta = \pi$

$$\left. \frac{\partial c}{\partial \theta} \right|_{\theta=\pi} = 0, \quad (5)$$

and kinetics of electron transfer from the electrode into the dendrimer molecule:

$$-D \left. \frac{\partial c}{\partial l} \right|_{\theta=\theta_0} = -k_b c + k_f (c^0 - c), \quad (6)$$

where k_b and k_f are the rates of forward and reverse reactions (viz. reduction of active centres in the immediate vicinity of the electrode surface and their oxidation, respectively), and c^0 is the surface concentration of active sites within the dendrimer outer shell. ET rates are given by the Butler-Volmer theory as [8]:

$$k_f = k_0 \exp \left(-\frac{\alpha F}{RT} (E - E_0) \right); \quad (7a)$$

$$k_b = k_0 \exp \left(\frac{(1-\alpha)F}{RT} (E - E_0) \right), \quad (7b)$$

where k_0 is the standard rate constant; E is the electrode potential; E_0 is the formal redox potential; α is the transfer coefficient; F is the Faraday constant; R is the gas constant; T is the absolute temperature. The physical meaning of k_0 in this case is somewhat different from the classical heterogeneous rate constant in electrochemistry (see a thorough discussion of this point in [5]) but this is not important for the model considered here.

The electric current flowing in the system is given by:

$$i = \frac{dN}{dt} F, \quad (8)$$

where N is the number of electrons (in moles) transferred onto the dendrimer molecule(s). In the case of a single molecule one has:

$$\frac{dN}{dt} = j 2\pi r_0 \sin \theta_0. \quad (9)$$

Substitution of (2) and (9) into (8) yields the following expression for the electric current:

$$i = F j 2\pi r_0 \sin \theta_0 = -2\pi D F \sin \theta_0 \left. \frac{\partial c}{\partial \theta} \right|_{\theta=\theta_0} = -2\pi D F c^0 \sin \theta_0 \frac{\partial u}{\partial \theta} \quad (10)$$

A. Dimensionless model

The introduction of dimensionless time and concentration as

$$\tau = \frac{Dt}{r_0^2}; \quad u = \frac{c}{c^0}, \quad (11)$$

allows obtaining the following dimensionless diffusion equation

$$\frac{\partial u}{\partial \tau} = \text{ctg} \theta \frac{\partial u}{\partial \theta} + \frac{\partial^2 u}{\partial \theta^2}. \quad (12)$$

The initial condition (4) becomes:

$$u(0, \theta) = 0. \quad (13)$$

The boundary conditions (5) and (6) take the following forms, respectively:

$$\left. \frac{\partial u}{\partial \theta} \right|_{\theta=\pi} = 0; \quad (14)$$

$$\left. \frac{\partial u}{\partial \theta} \right|_{\theta=\theta_0} = (K_f + K_b) u - K_f, \quad (15)$$

where

$$K_f = K_0 \exp(-\alpha \varepsilon); \quad (16a)$$

$$K_b = K_0 \exp((1-\alpha)\varepsilon), \quad (16b)$$

are the dimensionless forward and reverse rate constants

with $K_0 = \frac{r_0 k_0}{D}$ being the normalized standard rate

constant and $\varepsilon = \frac{F}{RT} (E - E^0)$ the dimensionless electric potential.

In the case of linear sweep (or cyclic) voltammetry the electrode potential varies according to the equation:

$$E = E_{st} + vt, \quad (17)$$

where E_{st} is the initial potential and v is the voltage scan rate. Introducing the corresponding dimensionless parameters as

$$\varepsilon_{st} = \frac{F}{RT} (E_{st} - E_0); \quad \sigma = \frac{F}{RT} \frac{r_0^2}{D} v \quad (18)$$

results in the following dimensionless expression for the

potential variation:

$$\varepsilon = \varepsilon_{st} + \sigma\tau. \quad (19)$$

Finally, the dimensionless current for a single adsorbed dendrimer molecule is defined as

$$f = \frac{i}{2\pi D F c^0} = -\sin\theta_0 \left. \frac{\partial u}{\partial \theta} \right|_{\theta=\theta_0}. \quad (20)$$

III. NUMERICAL SIMULATIONS

The diffusion problem (14)-(17) was solved using the fully implicit finite difference scheme [9] with second order approximation of first and second derivatives in θ and first order approximation in time. The resulting linear tridiagonal systems were solved by the Thomas algorithm [10]. It should be noted that the cotangent function being a factor at the first derivative in θ tends to $-\infty$ as $\theta \rightarrow \pi$. However, this fact does not spoil the convergence of the linear solver due to off-diagonal dominance. Indeed, consider the employed finite difference scheme:

$$\begin{aligned} -\frac{\Delta\theta^2}{\Delta\tau} u_j^n &= \left(1 - \frac{\Delta\theta}{2} \cot\theta_j\right) u_{j-1}^{n+1} + \left(2 + \frac{\Delta\theta^2}{\Delta\tau}\right) u_j^{n+1} + \\ &+ \left(1 + \frac{\Delta\theta}{2} \cot\theta_j\right) u_{j+1}^{n+1}, \end{aligned} \quad (21)$$

where u_i^k is the value of the dimensionless concentration at grid node with the coordinates $\theta_i = \theta_0 + i\Delta\theta$ and $\tau_k = k\Delta\tau$ where $\Delta\theta$ and $\Delta\tau$ are the grid step sizes in angle and time. Note that in the limit $\theta \rightarrow \pi$ the cotangent function asymptotically tends to $-1/(\pi - \theta)$, so that in this limit (to be more precise, when the finite difference scheme corresponds to the penultimate grid point at $\theta = \pi - \Delta\theta$) the latter equation reduces to

$$-\frac{\Delta\theta^2}{\Delta\tau} u_j^n = 1.5 u_{j-1}^{n+1} + \left(2 + \frac{\Delta\theta^2}{\Delta\tau}\right) u_j^{n+1} + 0.5 u_{j+1}^{n+1}, \quad (22)$$

and that diagonal dominance is strictly preserved since $2 + \frac{\Delta\theta^2}{\Delta\tau} > 1.5 + 0.5$ despite apparently infinite coefficient in the original differential equation.

Numerical convergence tests have shown that the relative error in the numerically computed electric current (20) remains under 0.1% for the considered ranges of parameter values for the grid size $N_\theta \times N_\tau = 1000 \times 4000$. The program for the numerical simulation was written in Borland C++ Builder 6 and executed on a PC based on Intel Pentium 4 processor at 3GHz with 512MB of RAM.

IV. RESULTS

The analysis of the dimensionless model reveals that the current response f of the dendrimer to electrode polarisation depends on three parameters being the

characteristic adsorptive deformation angle θ_0 , the dimensionless heterogeneous rate constant K_0 and the dimensionless voltage scan rate σ . It is clear that the above parameters determine the diffusion regime in the dendrimer shell. Most notably, the finite number of active centres borne by one dendrimer macromolecule implies that it also has finite capacity of electron uptake. This is reflected, under sufficiently slow voltage scan rates, in a bell-shaped current response with the current decaying to zero after all the active centres of the dendrimer have been reduced (see Fig. 2a). Such a voltammetric shape is typical for adsorbed species or thin layer cells [8] where the time constant of reaction or mass transport is negligible versus the time constant of the excitation potential variation. On the other hand, when the latter time constant is small compared to the characteristic diffusion time (i.e. the voltage scan rate is high) the charge transfer occurs as though in an infinite space (i.e. the diffusion layer thickness is significantly smaller than the length of the dendrimer meridian $l = r_0(\pi - \theta_0)$) with the typical voltammetric waveshape shown in Fig. 2b. Accordingly, there are two main limiting regimes which are clearly observed in the dependence of the dimensionless peak current on the scan rate σ and the heterogeneous rate constant K_0 presented in Fig. 3 for a fixed value of the angle $\theta_0 = 0.1$.

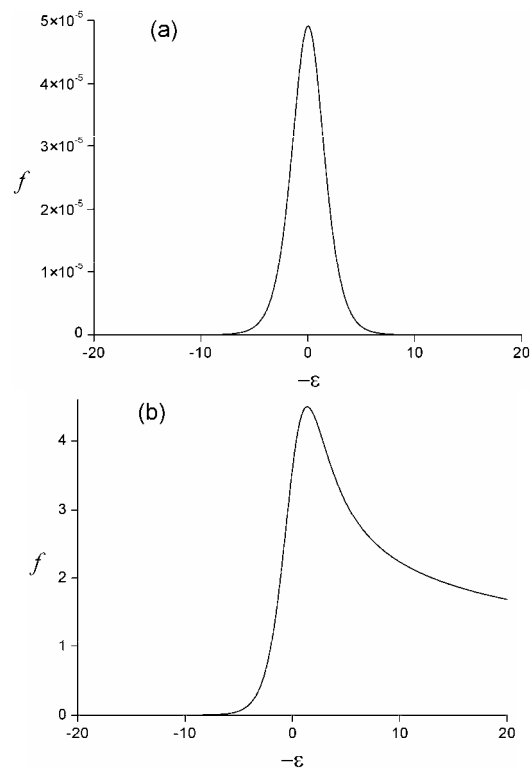


Fig. 2. Simulated linear sweep voltammograms for $K_0 = 10^6$, $\theta_0 = 0.1$ and scan rates (a) $\sigma = 10^{-4}$ and (b) $\sigma = 10^4$

The first regime, characteristic of adsorbed species or thin layer cells, corresponds to low values of σ when the peak current is proportional to the dimensionless scan rate [8]. The peak current under the second regime of unconstrained diffusion encountered under high scan rates is proportional to the square root of the scan rate [8]. This is exemplified in Fig. 4a which shows the cross-section of the surface in Fig. 3 along the $\log \sigma$ axis. Thus the slope of this curve in the range $\log \sigma < -2.5$ is equal to unity and it is $1/2$ for $\log \sigma > 2$ with a smooth transition from one limiting regime to the other.

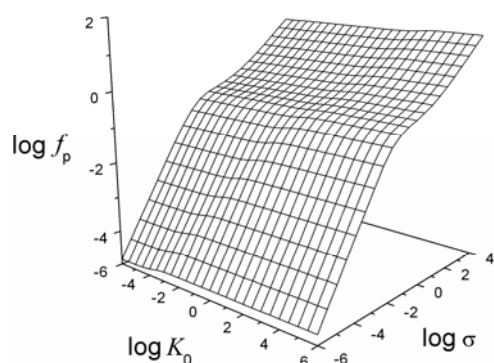
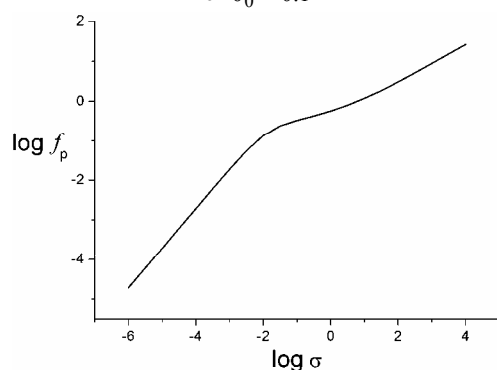
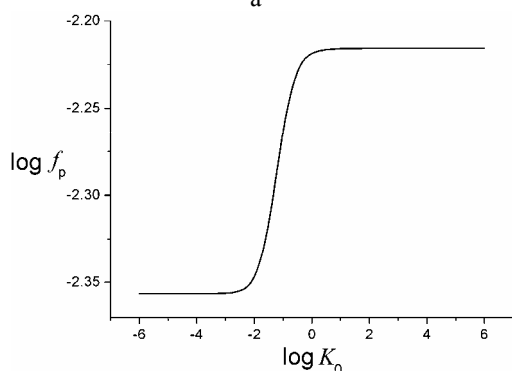


Fig. 3. Dependence of peak current on heterogeneous kinetics and scan rate for $\theta_0 = 0.1$



a



b

Fig. 4. Cross-section of surface in Fig. 3 along the line $\log K_0 = 6$ showing two different limiting regimes: "thin layer" regime for low values of σ (slope=1) and unconstrained diffusion for high values of σ (slope = $1/2$) – (a); cross-section of surface in (a) along the line $\log \sigma = -3.5$ showing variation between reversible and irreversible behaviour – (b)

The variation of the peak current f_p with the normalised heterogeneous rate constant is less pronounced on the scale of Fig. 3, but nevertheless it reveals the reversible ($K_0 \rightarrow \infty$) and irreversible ($K_0 \rightarrow 0$) kinetic limits for high and low values of K_0 , respectively. This is illustrated in Fig. 4b which depicts the cross-section of the $\log f_p$ surface from Fig. 3 along the line $\log \sigma = -3.5$ revealing the sigmoidal transition between the two limiting regimes. It may be observed in Fig. 3 that the transition between the irreversible and reversible limits shifts towards higher values of K_0 with increasing scan rate. This is again conditioned by the relative magnitudes of the kinetic time constant determined by K_0 and the time allocated to mass transport through the dimensionless voltage scan rate σ .

In a real experimental situation the only readily measurable parameter is the apparent size of the dendrimer molecule r_0 . However, even the determination of this parameter requires the usage of sophisticated instrumentation such as scanning tunnelling microscope. On the other hand, the actual shape of the adsorbed molecule is unknown, which in terms of the assumptions made here implies that the angle θ_0 characterising the extent of dendrimer deformation is unknown. Nonetheless this information may be accessed through electrochemical measurements over a range of voltammetric scan rates followed by a theoretical analysis of the shapes and magnitudes of recorded electric currents. To this end the working surface presented in Fig. 5 provides a means to analyse the peak current data as function of θ_0 and σ . Note here that the values of θ_0 close to π are included for completeness of the results but they correspond to a physically unrealistic situation. In fact, high values of θ_0 represent a virtually flattened molecule which means a complete loss of shape and structure. Hence the current model is not applicable under such extreme conditions. However, the values of θ_0 below ca. $2\pi/3$ seem reasonable and thus the respective part of the $\log f_p$ surface in Fig. 5 may be used for the analysis of experimental data.

As in the results presented in Fig. 3 the peak current dependence on σ has two distinct limits the first of which corresponds to the reduction of all active centres within the dendrimer outer shell while the second limit represents unconstrained diffusion. In the first limit, the variation of $\log f_p$ with θ_0 for a fixed value of σ is a decaying function which is explained simply by the reduction of the exposed surface area of the dendrimer and hence the fewer active centres, whose number is proportional to $(1 + \cos \theta_0)\sigma$. In the second limiting situation (i.e. under unconstrained diffusion conditions) the variation of $\log f_p$

with θ_0 for a fixed value of σ is not monotonic. Indeed, since in this case the dimensionless diffusion layer thickness (relative to the dendrimer radius) is much smaller than $\sin \theta_0$ (see above) the overall number of active sites that have been reduced during the voltammetric scan (and the peak current f_p) for very high values of σ is proportional to $\sin \theta_0 \sigma^{-1/2}$. This is clearly observable from the computed results presented in Fig. 5.

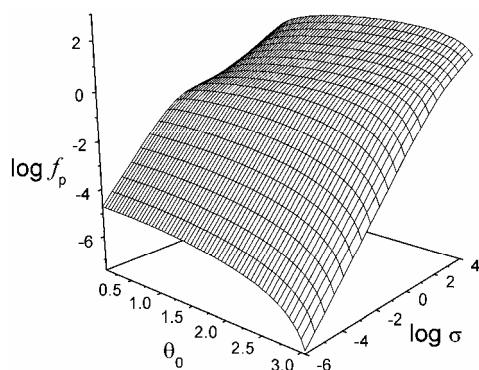


Fig. 5. Dependence of dimensionless peak current on scan rate σ and angle θ_0 characterizing dendrimer deformation upon adsorption on electrode surface in the limit $K_0 \rightarrow \infty$

V. CONCLUSION

The numerical simulation of diffusion within the thin spherical outer shell of a dendrimer molecule has yielded general results describing the behaviour of the peak current under linear sweep voltammetry. The limiting kinetic regimes identified in this work may be readily used for determining the predominant diffusional regime within the molecular shell from experimental data. Nevertheless, a more accurate determination of the values of main kinetic parameters may require a full curve fitting procedure employing the current model.

The physicochemical model considered in this work represents, in fact, a more general paradigm of two-dimensional diffusion processes occurring on curved surfaces. Subsequently this paradigm has been extended for a more complicated system involving cluster formation and growth on a spherical surface leading to moving boundary of the diffusion domain and its application to a real biological experiment [11, 12]. This confirms the importance of the present work for different areas of modern science.

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