

Modeling of electrocatalytic processes at conducting polymer modified electrodes

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A mathematical model of electrocatalytic processes taking place at conducting polymer modified electrodes has been developed. The model takes into account the diffusion of solution species into a polymer film, diffusion of charge carriers within the film, and a chemical redox reaction within the film. The space- and time-resolved profiles for reactant and charge carrier concentration within the film, as well as dependencies of electric current on the concentration of solute species, reaction rate constant and thickness of a polymer layer have been obtained and discussed. It has been shown that, even at a relatively fast diffusion of charge carriers within the conducting polymer film, exceeding the diffusion rate of reactant by two orders of magnitude, electrocatalysis of solute species at conducting polymer modified electrodes proceeds within the polymer film rather than at the outer polymer/solution interface, i.e., electrocatalytic conversion follows a redox-mechanism rather than metal-like one. Based on the results obtained, optimization of reaction system parameters could be made for any particular case to get an optimum efficiency or reactant to product conversion.

KEY WORDS: modeling, electrocatalysis, reaction-diffusion, conducting polymer, polyaniline

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1. Introduction

Conducting polymers are novel synthetic materials, which possess unique properties, differing them from nearly all organic materials ever, synthesized [1–3]. Among many, an important and promising property of these materials is their ability to catalyze some electrochemical oxidation and/or reduction processes of solution species [4]. This phenomenon is expected to be potentially useful in important fields of applied electrochemistry like electrosynthesis and electroanalysis. Moreover, these expectations are fuelled by the low cost and ease of preparation of these materials, unlike the traditional electrocatalysts like, e.g., finely dispersed platinum group metals. Conducting polymers can be simply obtained in appropriate form like thin films covering electrodes, by using chemical or electrochemical polymerization performed in a simple aqueous solution containing appropriate monomers.

One of a few fundamental problems that should be solved for the successful application of conducting polymers in electrocatalytic systems is the question on the location of a reaction zone during electrochemical redox process. Any electrocatalytic conversion of solute species at a conducting polymer covered electrode should be considered as consisting of a few simple processes [4]. These are as follows:

1. The diffusion of solute species through the porous conducting polymer film placed at electrode surface, toward the reaction zone.
2. Chemical redox reaction between the diffusing species and catalytically active centers within the polymer film, i.e., the electron exchange process.
3. The diffusion of charge carriers, i.e., holes or electrons, from the underlying electrode surface through the polymer layer to reaction zone (or catalytically active centers).
4. The diffusion of reaction products out of a polymer layer into the bulk of solution.

Indeed, except for the diffusion of charge carriers within the polymer film, all remaining processes are characteristic for any electrocatalytic process, occurring at electrode/solution interface. For metal electrodes, the diffusion of charge carriers is out of any consideration because of indefinitely fast electron transfer within the bulk of this electrode material. In this case, electrocatalytic processes are properly described by electrochemical kinetics. However, in case of conducting polymers as electrode materials or electrode modifiers, the charge transfer proceeds at a finite rate, since the electric conductivity of these materials is lower than that of metals. Typically, the conductivity of conducting polymers resembles that of semiconductors, reaching the lower limit of metal conductivity in some cases. Thus, because of a limited electric conductivity of conducting polymers, the kinetics of charge carrier transfer within these materials could not be neglected, and should be taken into account by considering the net kinetics of electrocatalytic processes at conducting polymer modified electrodes.

At indefinitely high rate of charge carrier transfer, the reaction occurs at an outer polymer/solution interface, whereas at a limited mobility of charge carriers the reaction should occur within the conducting polymer film. The mean depth of the reaction zone in this case should depend greatly on the conductivity of the film, and on reaction variables like the concentration of diffusing species, the rate of a chemical redox interaction, etc. Apart from a theoretical consideration, the location of a mean reaction zone is of a great practical interest related to optimization of the parameters of electrocatalytic system for its best performance. Thus, the choice between the two reaction mechanisms, i.e., “metal-like catalysis”, where the process occurs at a modifier/solution interface, and “a redox catalysis” with the process occurring within the modifier layer, has been a subject of investigation. Electrocatalytic reduction of benzoquinone has been claimed to proceed at an outer polyaniline/electrolyte interface in an acidic solution, whereas, at a higher pH, the reduction occurs within polyaniline film because of a decreased electric conductivity of this polymer at higher pH [5]. For hydroquinone/benzoquinone and $\text{Fe}^{2+}/3+$ redox couples, the occurrence of electrocatalytic processes either at an outer interface, or within polyaniline film has been shown, depending on the electrode potential applied [6]. Electrocatalytic oxidation of coenzyme NADH within polyaniline film has been shown to proceed with the use of a rotating electrode [7]. Direct evidences for the location of electrocatalytic redox conversion of various species at electrodes, modified with polyaniline and some of its derivatives, have been obtained by using transmission UV-Vis spectroelectrochemical [8–10] and in situ Raman spectroelectrochemical techniques [11].

The present study has been aimed to mathematical modeling of electrochemical processes occurring at electrodes covered with a thin film of a conducting polymer.

2. The model and approximations

All four simple processes outlined in Section 1 have been taken into account for modeling of electrocatalysis at conducting polymer coated electrode. It is assumed that a flat surface of electrode is covered with a uniform layer of a conducting polymer of a definite thickness d . Three values for d have been taken into consideration, viz. 10^{-6} , 10^{-5} , and 10^{-4} m (i.e., 1, 10, and 100 μm). In the most experimental works published, the thickness of a polymer layer varies exactly within this range. This modified electrode is supposed to be immersed into a reactant solution of unlimited volume, ensuring that no reduction of reactant concentration proceeds in the bulk of solution during its electrocatalytic conversion. It is also supposed that there is no concentration gradient neither for reactant nor for reaction product outside of a polymer layer in the course of

electrocatalytic process. In a technical sense, this means that the process proceeds under ideal stirring conditions.

The Ficks law describes the diffusion of reactant into a polymer layer:

$$\frac{\partial R}{\partial t} = D \frac{\partial^2 R}{\partial x^2}, \quad (1)$$

where R means the concentration of reactant, t is a time, x is a space coordinate, and D is the diffusion coefficient for reactant.

By applying of a suitable electrode potential, electrochemical conversion of a reactant into product proceeds. This conversion means either anodic oxidation (i.e., withdrawing of electrons from reactant), or cathodic reduction (i.e., addition of electrons to reactant). For many real reactant/product pairs, electrochemical oxidation or reduction is accompanied by protonation/deprotonation processes, or even more complex perturbation in a molecular structure. For the seek of simplicity, all these processes are neglected in the present model. Thus, strongly speaking, the present model could be well applied for electrochemical conversion of simple metal ions, where no accompanying processes occur except for electron exchange between the electrode and reactant, like, e.g., $Fe^{2+/3+}$ redox couple. However, the model should be well applicable also to a wider range of reactant/product couples, where other accompanying processes do not limit an overall kinetics of the electrode process. The electrochemical charge transfer process is described by a single equation:



where R and P are reactant and reaction product, respectively, and n is a charge carrier, i.e., an electron for cathodic reduction, or a hole for anodic oxidation processes.

The rate of this reaction is described by a simple equation of chemical kinetics:

$$\frac{dP}{dt} = -\frac{dR}{dt} = kRn, \quad (3)$$

where k is a second-order rate constant for the chemical reaction, and R and n are mean concentrations of reactant and charge carrier, respectively.

By combining the diffusion equation (1) with kinetic equation (3), the rate equations for R , P , and n could be expressed as follows:

$$\frac{\partial R}{\partial t} = D \frac{\partial^2 R}{\partial x^2} - kRn, \quad (4)$$

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} + kRn, \quad (5)$$

$$\frac{\partial n}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} - kRn, \quad x \in]0, d[, t > 0. \quad (6)$$

Let $x = 0$ represents the electrode/polymer film boundary while $x = d$ is the thickness of a polymer layer. The electrocatalytic processes starts when the reactant appears over the surface of a polymer layer. This is used in the initial conditions ($t = 0$)

$$R(0, x) = \begin{cases} R_0, & x = d, \\ 0, & x \in [0, d[, \end{cases} \quad (7)$$

$$P(0, x) = 0, \quad n(0, x) = n_0, \quad x \in [0, d].$$

Consequently, the boundary conditions are ($t > 0$)

$$\begin{aligned} \frac{\partial R(t, 0)}{\partial x} &= 0, & R(t, d) &= R_0, \\ \frac{\partial P(t, 0)}{\partial x} &= 0, & P(t, d) &= 0, \\ n(t, 0) &= n_0, & \frac{\partial n(t, d)}{\partial x} &= 0. \end{aligned} \quad (8)$$

The density $I(t)$ of the current at time t can be obtained explicitly

$$I(t) = n_e F D_n \frac{\partial n(0, t)}{\partial x}, \quad (9)$$

where n_e is the number of electrons involved in a charge transfer, F is Faraday constant, $F \approx 9.65 \times 10^4 \text{ l/mol}$. We assume, that the systems (4)–(8) approaches a steady-state as $t \rightarrow \infty$

$$I_\infty = \lim_{t \rightarrow \infty} I(t).$$

I_∞ is assumed as the steady-state current.

The problems (4)–(8) were solved numerically using the finite difference technique [12].

For simplicity, the diffusion coefficients for R and P have been chosen to be equal and a value of $D=10^{-9} \text{ m}^2/\text{s}$, typical for small molecules, has been taken for calculations. The model used implies that the movement of charge carriers within the polymer film could be treated as a simple diffusion and described by the Ficks law. For usual electrode materials like metals or graphite, it is common accepted that the movement of either electrons or holes within the bulk electrode material proceeds at an indefinitely high rate. The electric conductivity of conducting polymers, however, is lower than that of metals or graphite, thus, the diffusion of charge carriers should be taken into account, proceeding at a finite rate. For modeling, three values for the diffusion coefficient of charge carriers D_n of 10^{-9} , 10^{-8} , and $10^{-7} \text{ m}^2/\text{s}$, have been used. The lower limit of D_n chosen coincides with D for reactant or product species, whereas the upper limit of D_n has been chosen as being two orders of magnitude higher. Further extension of D_n towards higher values should lead to the case with indefinitely high mobility of

Table 1
Numerical values for parameters, taken into consideration.

Parameter	Dimension	Numerical values
d (thickness of a polymer layer)	(m) (μm)	$10^{-6}, 10^{-5}, 10^{-4}$ 1, 10, 100
D (diffusion coefficient for reactant and product)	(m^2/s)	10^{-9}
D_n (diffusion coefficient for charge carrier within polymer film)	(m^2/s)	$10^{-9}, 10^{-8}, 10^{-7}$
k (second-order reaction rate constant)	($\text{m}^3 \cdot \text{mol}/\text{s}$) ($\text{l} \cdot \text{mol}/\text{s}$)	$10^1, 10^0, 10^{-1}, 10^{-2}$ $10^4, 10^3, 10^2, 10^1$
R (concentration of reactant in the bulk solution)	(mol/m^3)	$10^2, 10^1, 10^0$
n (initial concentration of charge carriers within polymer film)	(mol/l) (mol/m^3) (mol/l)	0.1, 0.01, 0.001 4×10^3 4

charge carriers, resembling the behavior, typical for metal electrodes. In this case, the process follows usual electrochemical kinetics and thus will not be considered here.

There is scarce information in the literature regarding the value of a second-order reaction rate constant k , however, a wide variety for this constant should be considered because of a wide variety of possible electrocatalytic reactions taking place at conducting polymer modified electrodes. A value of 6.4×10^3 l/mol/s has been reported for the electron cross-exchange between poly(N-methylaniline) and hydroquinone, based on rotating disc electrode experiments [12]. Electrocatalytic oxidation of hydroquinone is known to be one of the fastest reactions taking place at conducting polymers, thus, lower values for k should be taken into consideration. Table 1 summarizes most possible or interesting values for parameters, used in the present modeling.

3. Results and discussion

Most probable numerical values for parameters have been chosen as presented in table 1. Combining of all possible values gives a huge number of combinations, thus, only most characteristic cases are considered as below.

3.1. Space- and time-resolved concentration profiles for reactant

The concentration profile for reactant is one of the most prominent characteristics for the efficiency of electrocatalytic reaction. In an ideal case, at a very high-electric conductivity of a conducting polymer layer, the reactant concentration (R) drops to a zero level in a very thin layer of conducting polymer at the polymer/solution interface. In reality, however, the electric conductivity of nearly all known conducting polymers is not high enough, thus, the reactant concentration does not drop to a zero level in a thin layer.

Figure 1 presents some characteristic simulated time- and space-resolved profiles for reactant concentration. In case of a fast chemical redox reaction between reactant and charge carriers ($k=10^4$ l/mol/s), the equilibrium establishes in a short time, whereas R drops within the polymer film nearly exponentially to almost zero at the electrode/polymer interface (figure 1, top left). Significant changes occur by lowering the reaction rate constant k . At a constant thickness of a reaction layer and a constant reactant concentration in solution, the decrease of k results in a slower establishment of equilibrium conditions, whereas R does not drop to zero within the modifier layer. Figure 1, top left and right, compares two cases, as obtained for the highest and lowest k values taken for simulation, respectively. It is seen that, for the lowest k value of 10^1 l/mol/s, the reactant concentration at the electrode/polymer boundary appears to be almost as high as at the polymer/solution interface. By varying of k value between 10^4 and 10^1 l/mol/s, intermediate profiles have been obtained (not shown). In terms of efficiency of electrocatalytic conversion, the results obtained show that, at a given reactant concentration in a solution (0.01 mol/l), and at a constant thickness of a polymer layer (1 μ m), an efficient conversion proceeds at the highest k value, i.e. full conversion of reactant to reaction product is achieved within the thinnest polymer film taken into consideration. For the lowest k value, however, the electrocatalytic conversion proceeds inefficient. For practical purposes, care should be taken to enhance the efficiency in this case, like the thickening of a polymer layer.

Thickening of a polymer layer results in drastic changes of profiles studied (cf. top, middle and bottom rows in Figure 1, where the thickness differs by an order of magnitude). Again, a fast establishment of steady state conditions occurs at a high-reaction rate constant, whereas full conversion of reactant occurs in a thin polymer layer near the polymer/solution boundary. In practice-oriented terms, the results obtained show that, at a high reaction rate, an increase of polymer layer thickness over 1 μ m does not increase the efficiency of electrocatalytic conversion. As expected, lower values of k taken for simulation result in lower efficiency (figure 1). For the lowest k , a drop of reactant concentration up to *ca.* one half along the polymer layer occurs with 10 μ m polymer film, whereas almost full conversion

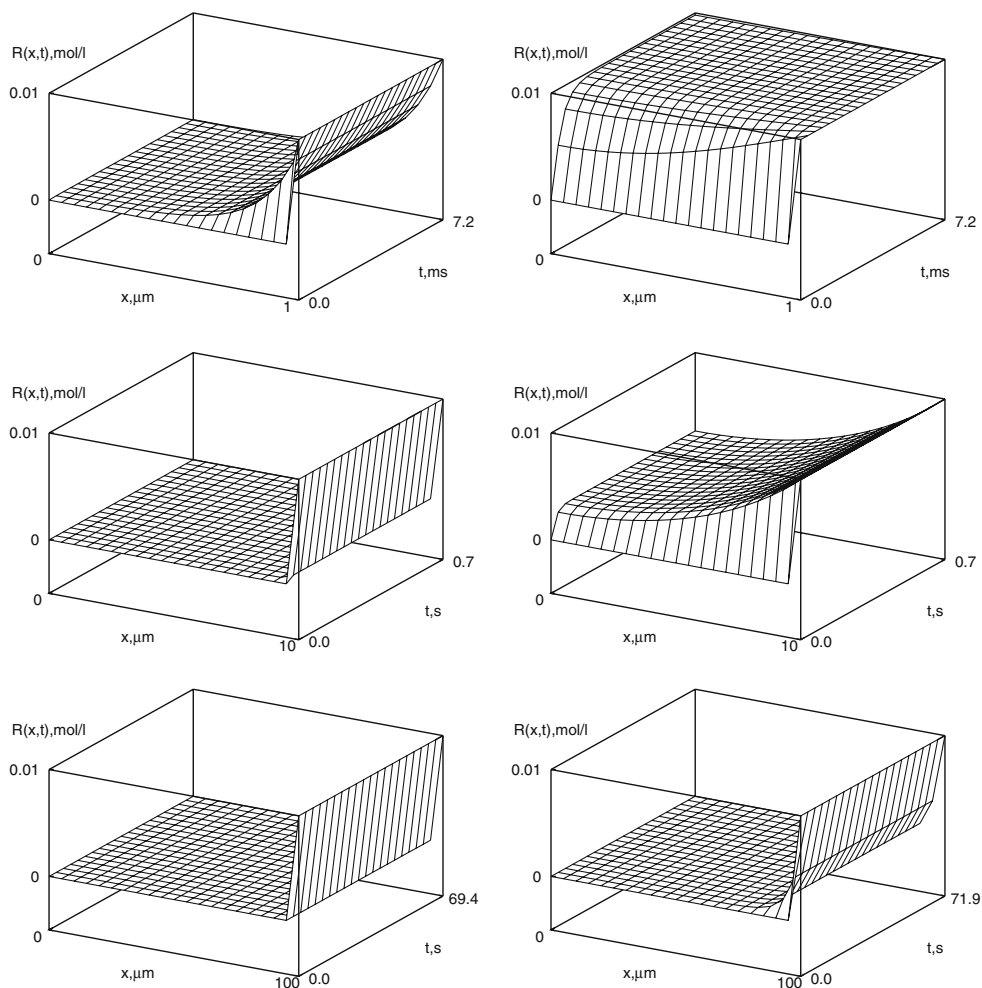


Figure 1. 3D-profiles for reactant (R) concentration within the conducting polymer film. The vertical axes represent reactant concentration, horizontal left axes – the thickness of a modifying layer, and horizontal right axes – reaction time. Other conditions are as follows: reactant concentration in solution 0.01 mol/l, diffusion coefficient for charge carrier $D_n = 10^{-8}$ m²/s, reaction rate constant $k = 10^4$ (left column), or 10 l/mol/s (right column), thickness of a polymer layer $d = 1$ (top row), 10 (middle row), or 100 μm (bottom row). The values of D and n are as in table 1.

of reactant occur with the thickest film of 100 μm (*cf.* right column of figure 1). The simulation results obtained show that, for practical purposes, a slow chemical redox reaction between the reactant and reaction centers within a polymer film could be compensated by an increase of the film thickness to get a maximum conversion of reactant into reaction product. A close-related set of simulation data has been also obtained for varying concentration of reactant between 0.001 and 0.1 mol/l (not shown). As it could

be expected, a slower drop of reactant concentration occurs at a higher R in solution, and *vice versa*. Thus, thicker films should be used for higher reactant concentration to get a sufficiently high efficiency of electrocatalytic process.

3.2. Space- and time-resolved concentration profiles for charge carriers

Similarly, like for reactant, the concentration profiles for reaction product and for charge carriers have been calculated. From these, profiles for charge carriers are considered below. Within the frame of the present model, charge carriers are supposed to be reactive centers within the polymer structure, which are capable to donate/accept electrons or holes to/from reactant according equation (2). After this chemical redox reaction, the reactive centers gain the electrons or holes from electrode, whereas the transport of charge carriers is supposed to proceed at a finite rate characterized by appropriate diffusion coefficient as given in table 1.

Figure 2 presents selected time- and space-resolved profiles for concentration of charge carriers. In all cases, the initial concentration of charge carriers drops at the polymer/solution boundary to a definite level, which depends on D , D_n , k and R , whereas no drop occurs at the electrode/polymer boundary. Figure 2 presents the profiles depending on the most interesting parameters – k and d , whereas other variables (D and D_n) are kept constant. For thin polymer layer, a negligible drop of n occurs for low reactant concentration, reaching *ca.* 0.3% from its initial value for $R = 0.01$ mol/l. An increase of R by one order of magnitude causes a proportional increase of n drop up to 3% (cf. top row of Figure 2). Increase of a polymer layer thickness, again, causes increase of n drop. At a constant $R = 0.01$ mol/l, increase of d from 1 to 10 and 100 μm results in an increase of n drop from 0.3 to 4.5 and 18%, respectively (as presented in the left column of figure 2). For each d value, again, the drop of n depends on the thickness of a polymer layer, being higher for thicker films. For some selected combinations of parameters like a high-reactant concentration and a thick polymer film, a drop of n almost to zero value occurs (right column of figure 2).

3.3. Dependence of electric current on system variables

The most prominent characteristic for efficiency of any electrocatalytic process is electric current that yields electrons or holes to reactant. Below, some of the most characteristic dependencies of current on variables taken for simulation are considered. Figure 3 presents the dependence of a relative current (I_{rel}) on the concentration of reactant. For the fast charge carrier transport ($D_n = 10^{-7}$ m²/s), a linear dependence between I_{rel} and R has been obtained in double logarithmic coordinates, irrespective of reaction rate constant. This

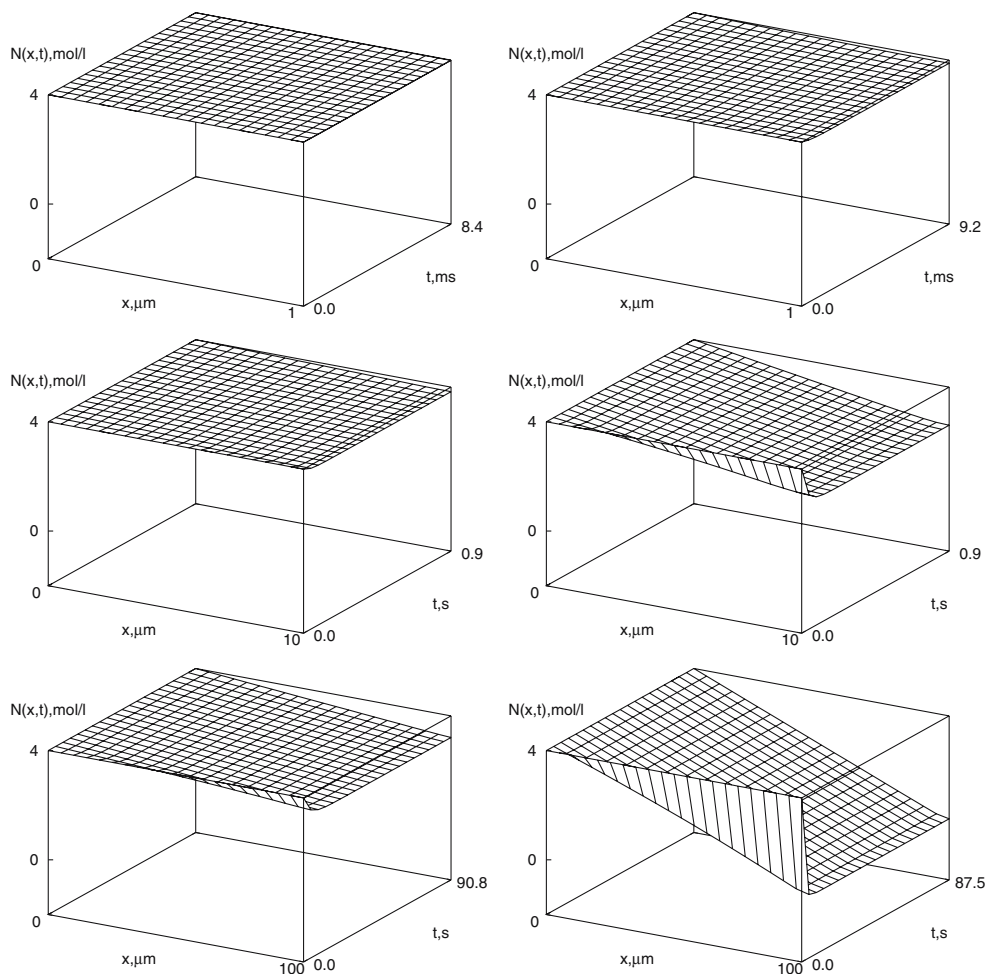


Figure 2. 3D-profiles for charge carrier concentration (n) within the conducting polymer film. The vertical axes represent charge carrier concentration, horizontal axes are same as in Figure 1. Other conditions: diffusion coefficient for charge carrier $D_n = 10^{-9} \text{ m}^2/\text{s}$, reaction rate constant $k = 10^3 \text{ l/mol/s}$, thickness of a polymer layer $d = 1$ (top row), 10 (middle row), or $100 \text{ }\mu\text{m}$ (bottom row), reactant concentration in solution $R = 0.01$ (left column), or 0.1 mol/l (right column).

means that charge transfer rate does not limit the overall rate of electrocatalytic process. For slower charge transfer, however, a deviation from the linearity is observed at higher concentrations of reactant. For the highest R of 0.1 mol/l , and the highest k of 10^4 l/mol/s , the steady-state appears to be 2.39 times lower for the lowest D_n of $10^{-9} \text{ m}^2/\text{s}$, as compared to the highest D_n of $10^{-7} \text{ m}^2/\text{s}$. Thus, at a high concentration of reactant, charge transfer rate becomes a limiting factor of an overall rate of the process. For lower reaction rate, however, the deviation from linearity at lower D_n appears to be less evident (*cf.* representative dependencies of figure 3). The relative current grows with increasing chemical

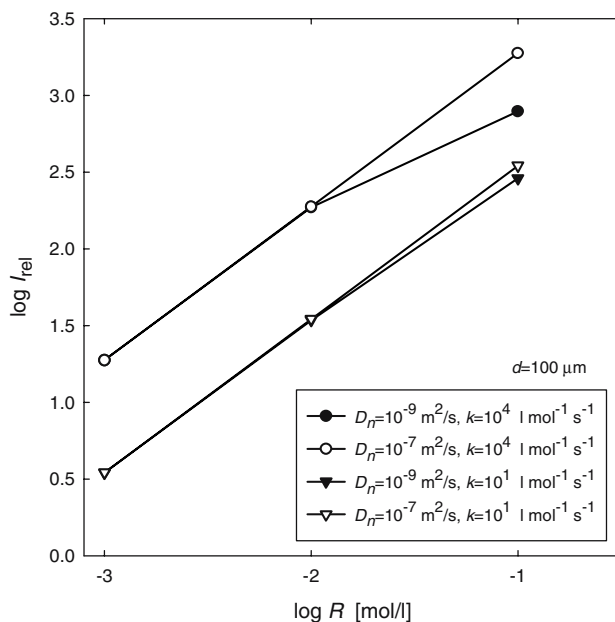


Figure 3. Simulated dependence of relative current on reactant concentration in double logarithmic coordinates, as obtained for $d = 100 \mu\text{m}$, and varying D_n and k (as indicated).

reaction rate constant. However, no linear dependence of I_{rel} on k is observed. Indeed, an increase of k by three orders of magnitude, from 10^1 to 10^4 l/mol/s, causes only a 5.4-fold increase of relative current. Some practice-oriented generalization could be made from the dependences obtained. First, at a low concentration of reactant, no attempts should be paid to increase the conductance of a conducting polymer layer, since an efficient redox reaction proceeds even at a relatively low conductance. In addition, there is a little or almost no need to enhance the rate of chemical redox interaction between reactant and conducting polymer. At a high reactant concentration, however, the conductivity of a polymer layer becomes more important.

Figure 4 shows the dependence of a relative current on the reaction rate constant. In all cases studied, no direct proportionality between I_{rel} and k is observed. In addition, for the low k values, a higher slope of I_{rel} on k is observed, as compared to high k values. Again, nearly coinciding (independent on the conductivity of polymer layer) dependencies of I_{rel} on k have been obtained for low reactant concentration, whereas higher slopes are observed for higher D_n at high-reactant concentration. For example, an increase of k value from 10^1 to 10^4 l/mol/s results in 5.41-fold increase of I_{rel} for $D_n = 10^{-7}$ m²/s, and in 2.73-fold increase for $D_n = 10^{-9}$ m²/s at the highest reactant concentration studied (0.1 mol/l). The data presented in Figure 4 again show a relatively little dependence of an overall efficiency of electrocatalytic process on

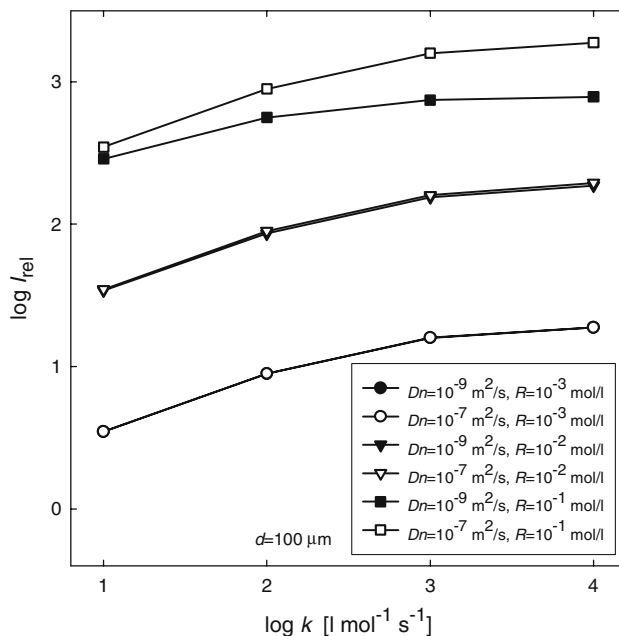


Figure 4. Simulated dependence of relative current on reaction rate constant in double logarithmic coordinates, as obtained for $d = 100 \mu\text{m}$, and varying D_n and R (as indicated).

the conductivity of polymer layer within its limits taken into consideration, especially for low-reactant concentration.

Somewhat unexpected dependencies of I_{rel} on the thickness of a polymer layer have been obtained (figure 5). For slow chemical reaction (with k values ranging from 10^1 to 10^2 l/mol/s), an increase of I_{rel} by thickening of a polymer film from 1 to $10 \mu\text{m}$ is followed by a decrease of I_{rel} by thickening of polymer layer to $100 \mu\text{m}$ (Figure 5). For the fast chemical reaction (with k values of 10^3 and 10^4 l/mol/s), a decrease of I_{rel} is observed, e.g., a drop of I_{rel} by the factor of *ca.* 6.3 has been obtained for the highest reaction rate constant taken into account. Similar dependencies have been obtained for other combinations of R and D_n as well (different from those presented in Figure 5).

3.4. Current-time profiles

From practical point of view, the time required to establish steady-state conditions of electrocatalysis, is of a great importance. The kinetics of current growth depends on many variables, and ranges within a broad window. Some typical current–time dependencies are shown in figure 6.

For a combination of thick polymer films ($d = 100 \mu\text{m}$) and slow diffusion of charge carriers ($D_n = 10^{-9} \text{m}^2/\text{s}$), a slow rise of current is observed: it takes

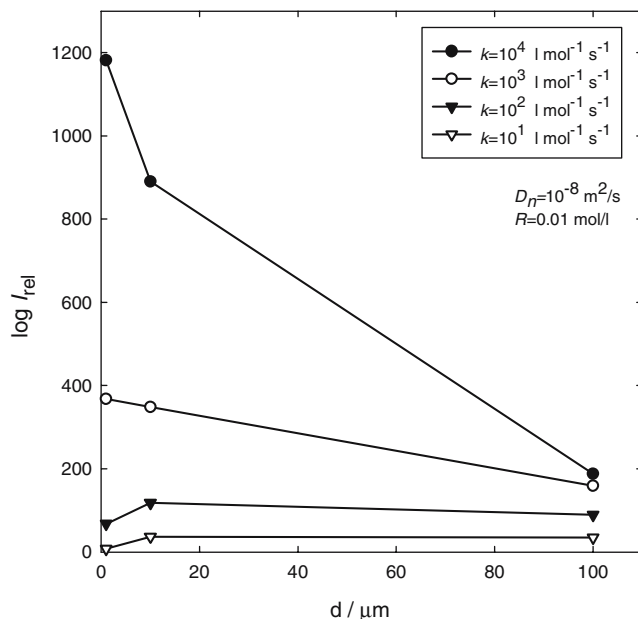


Figure 5. Simulated dependence of relative current on thickness of a polymer layer, as obtained for $D_n = 10^{-8} \text{ m}^2/\text{s}$ and $R = 0.01 \text{ mol/l}$, and varying k (as indicated).

ca. 20 s to reach the steady-state current (figure 6, top). A characteristic feature in this case is a sigmoid shape of the current–time transients. This feature manifests itself more strongly for thickest polymer film, and lowest electric conductivity of a modifier layer. Much more faster growth of current is observed for thin polymer films, especially in a combination with a fast diffusion of charge carriers (figure 6, bottom). In some cases, the rise time (up to steady state) of 1 ms has been obtained. For the latter combination of parameters, almost no sigmoid shape of current–time transients has been obtained.

In order to compare the kinetics of current growth for different combinations of variables, the current rise time up to 99% of its maximum value (τ_{99}) has been calculated. Some characteristic results thus obtained are displayed in figure 7. It is seen that, for thin polymer films ($d = 1 \mu\text{m}$) and slow diffusion of charge carriers ($D_n = 10^{-9} \text{ m}^2/\text{s}$), τ_{99} of ca. 2 ms has been obtained, which almost does not depend on the rate of a chemical reaction (whereas k has been varied within four orders of magnitude), and the reactant concentration (whereas R has been varied within three orders of magnitude). For the slow reaction ($k = 10^1 \text{ l/mol/s}$, an increase of film thickness by an order of magnitude causes an increase of τ_{99} by two orders (figure 7, top), reaching ca. 20 s. For thicker polymer films, again, τ_{99} does not depend on reaction rate constant at lower reactant concentration (0.001 or 0.01 mol/l), whereas lower values of τ_{99} have been obtained for the high concentration at a high reaction rate constant.

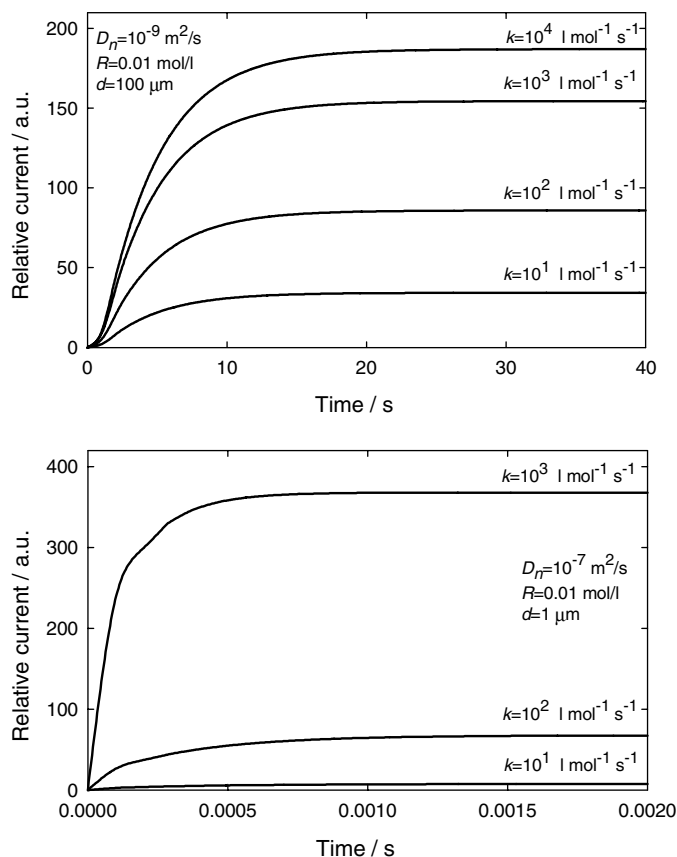


Figure 6. Simulated time profiles of relative current, as obtained for $D_n = 10^{-9} \text{ m}^2/\text{s}$, $R = 0.01 \text{ mol/l}$ and, $d = 100 \text{ }\mu\text{m}$ (top), or $D_n = 10^{-7} \text{ m}^2/\text{s}$, $R = 0.01 \text{ mol/l}$, and $d = 1 \text{ }\mu\text{m}$ (bottom), and varying k .

An increase of D_n by one or two orders of magnitude results in a decrease of τ_{99} by one or two orders, respectively. For the combination of the highest values of $D_n = 10^{-7} \text{ m}^2/\text{s}$ and $k = 10^4 \text{ l/mol/s}$, taken into consideration, the shortest current rise time τ_{99} of less than 0.1 ms has been obtained for the thinnest polymer film of $1 \text{ }\mu\text{m}$. In contrast to the case of a slow charge carriers diffusion, τ_{99} appears to depend on reaction rate constant for high values of D_n , especially for the thin films. So, for $d = 1 \text{ }\mu\text{m}$ and $D_n = 10^{-7} \text{ m}^2/\text{s}$, τ_{99} drops from *ca.* 1.7 to 0.09 ms by increasing of k from 10^1 to 10^4 l/mol/s . At the same time, τ_{99} do not depend on k for thick polymer films (figure 7, bottom). Noteworthy, τ_{99} do not depend on the reactant concentration within the range studied at $D_n = 10^{-7} \text{ m}^2/\text{s}$, in contrast to lower values of D_n (*cf.* figure 7, top and bottom).

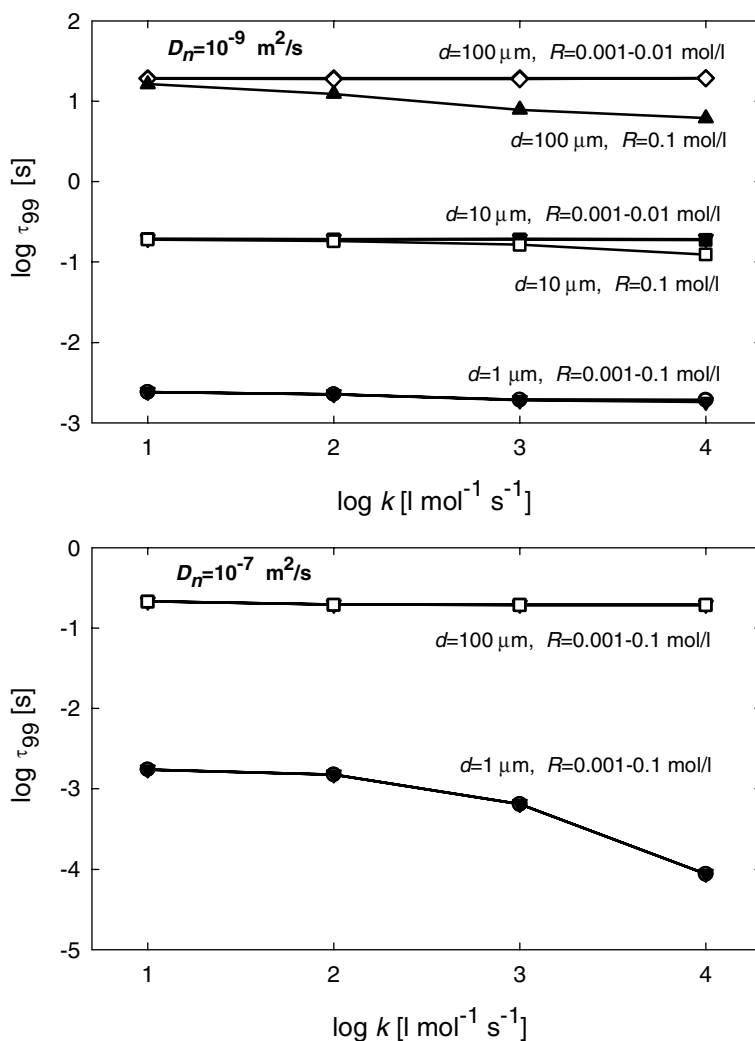


Figure 7. Simulated dependence of current rise time on reaction rate constant in double logarithmic coordinates, as obtained for $D_n = 10^{-9} \text{ m}^2/\text{s}$ (top) or $D_n = 10^{-7} \text{ m}^2/\text{s}$ (bottom), and varying other parameters (as indicated).

4. Conclusions

In general, the data obtained show that, even at a relatively fast diffusion of charge carriers within the conducting polymer film, exceeding the diffusion rate of reactant by two orders of magnitude, electrocatalysis of solute species at conducting polymer modified electrodes proceeds within the polymer film rather than at the outer polymer/solution interface, i.e., electrocatalytic conversion follows a redox-mechanism rather than metal-like one. Time- and space-resolved

concentration profiles for reactant and charge carrier obtained show that the depth of a reaction zone varies within a broad range depending on the thickness of a polymer layer, reactant concentration, and chemical redox reaction rate constant. Based on the simulations made, optimization of reaction system parameters could be made for any particular case to get an optimum efficiency or reactant to product conversion.

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