

Modeling of electrocatalysis at polyaniline-modified electrodes: autoacceleration of the process by the reaction product

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Abstract We extend our previous model taking into account a possible autoacceleration mechanism of electrochemical processes. It is supposed that protons generated in an electrochemical oxidation of ascorbate are responsible for an increase of electric conductivity of polyaniline. Accordingly, the current–time profiles have been calculated taking into account a “threshold” value for proton concentration to increase the electric conductivity of polyaniline by one or more orders of magnitude. Different kinds of corresponding profiles, including ones with a sigmoid character and possessing sharp current flashes as well, were obtained and analyzed.

Keywords Modeling · Electrocatalysis · Reaction–diffusion · Sensor · Modified electrode

1 Introduction

Electrocatalysis plays an important role in electrochemistry-related fields of technology like electrosynthesis, electroanalysis, batteries, and electrochemical sensors or biosensors. Among many electrocatalytic systems and materials suitable for these systems, conducting polymers and related organic materials have been intensively

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studied during the past two or more decades due to their unusual and interesting properties [1,2]. As distinct from usual metal- and carbon-based electrode materials used in electrocatalytic systems, conducting polymers possess limited electric conductivity and thus belong rather to semiconductors. Therefore, the rate of electron or hole transport within the layer of conducting polymer placed at an electrode surface can limit the overall efficiency of electrocatalytic redox process. Recently, with the use of in situ Raman spectroelectrochemistry, it was demonstrated that both oxidized and reduced forms of electrode modifier are present within its layer during intense electrolysis of solution species, showing the importance of charge propagation rate within the modifier layer. This phenomenon seems to be of a common nature for many semiconducting electrode modifiers like electropolymerized organic redox mediators Meldola blue [3], Neutral red [4], or Toluidine blue [5], inorganic hexacyanoferrate complex Prussian blue [6], and polyaniline or its derivatives [7].

It is well known that an electrode coated with a thin layer of polyaniline can be used as an amperometric sensor for ascorbic acid in pH-neutral solutions. In this case, ascorbate chemically reduces an oxidized form of polyaniline. At an appropriate electrode potential, polyaniline is re-oxidized, and the resulting anodic current appears to be proportional to ascorbate concentration. In a pH-neutral solution, a sigmoid-shaped profile for current growth upon addition of ascorbate into solution has been observed at a polyaniline modified electrode [8]. This profile appears to be unusual since it differs drastically from usually observed hyperbolic profiles and cannot be predicted based on diffusion-limited electrochemical kinetics. The phenomenon was explained in [8] in terms of variable electric conductivity of polyaniline. Initially, at a relatively high pH of solution (around 7) and in absence of ascorbate, the conductivity of this polymer is low because polyaniline occurs in its deprotonated (nondoped) form. At a progressive electrochemical oxidation of ascorbate, protons are expelled, and pH of the adjacent solution diminishes gradually. Accordingly, polyaniline turns gradually into its protonated and conducting form. This causes a facilitated electron flow through a polymer layer to the reaction zone, resulting in a greater amperometric response. Somewhat later, this mechanism was indirectly confirmed with the use of different polymer poly(*N*-methylaniline), which possesses different dependence of electric conductivity on solution pH [9].

In a series of our preceding works [10–12], we considered various aspects of electrode processes taking place at conducting polymer modified electrodes. In all these publications, however, the electric conductivity of a polymer layer has been assumed to be constant and not influenced by reaction variables. Therefore, the phenomenon presented above cannot be explained based on a set of parameters taking into account in our preceding modeling. The present study has been aimed to expand our previous model, taking into account the dependence of electric conductivity of a polymer layer placed at electrode surface, on solution acidity.

2 The model and approximations

Similarly to our previous works, the model implies that a flat surface of electrode is covered with a uniform layer of conducting polymer of a definite thickness d [10–12].

For simplicity, the value of d has not been varied and assumed to be 10^{-5} m ($10\ \mu\text{m}$). It is supposed that this modified electrode is immersed into an ideally stirred solution and no concentration gradient for reactant is present outside of a modifier layer. The diffusion of a reactant into a modifier layer is determined by the Fick's law:

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

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

Electrochemical conversion of the reactant to the reaction product P means either anodic oxidation (i.e., withdrawing of electrons from the reactant), or, adversely, cathodic reduction (i.e., addition of electrons), and can be simply described by the general equation



where R and P are the 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 first-order equation of chemical kinetics

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

where k is a second-order rate constant of chemical reaction, and R and n are 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 can be expressed as follows:

$$\begin{cases} \frac{\partial R}{\partial t} = D \frac{\partial^2 R}{\partial x^2} - kRn, \\ \frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} + kRn, \\ \frac{\partial n}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} - kRn, \\ x \in]0, d[, \quad t > 0. \end{cases} \quad (4)$$

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

$$\begin{aligned} R(0, x) &= \begin{cases} R_0, & x = d, \\ 0, & x \in [0, d[, \end{cases} \\ P(0, x) &= 0, \quad n(0, x) = n_0, \quad x \in [0, d]. \end{aligned} \quad (5)$$

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

$$\frac{\partial R(t, 0)}{\partial x} = 0, \quad R(t, d) = R_0,$$

$$\begin{aligned} \frac{\partial P(t, 0)}{\partial x} &= 0, & P(t, d) &= 0, \\ n(t, 0) &= n_0, & \frac{\partial n(t, d)}{\partial x} &= 0. \end{aligned} \tag{6}$$

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

$$I(t) = -n_e F D_n \frac{\partial n(t, 0)}{\partial x}, \tag{7}$$

where $n_e = 1$ is the number of electrons involved in a charge transfer, F is Faraday constant, $F \approx 9,65 \times 10^4$ l/mol. We assume that system (4)–(6) approaches a steady state as $t \rightarrow \infty$,

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

I_∞ is assumed to be the steady-state current.

Problem (4)–(6) was solved numerically using the finite difference technique [13].

Unlike our previous works, the value of D_n has been varied as a function of the local concentration of reaction product P :

$$D_n = \begin{cases} 10^{-9} & \text{if } P(t, x) \leq \alpha, \\ D_n^* & \text{if } P(t, x) > \alpha, \end{cases}$$

where α of $10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}$, and 10^{-5} mol/m³ were taken, and four values for the diffusion coefficient of charge carriers D_n^* of $10^{-6}, 10^{-7}, 10^{-8}$, and 10^{-9} m²/s were used.

We used the following values of parameters: $D = 10^{-9}$ m²/s was taken, as well as the only value for $n_0 = 4 \times 10^3$ mol/m³ (4 mol/l), $R = 1$ mol/m³ (10^{-3} mol/l, or 1 mmol/l), and the reaction rate constant $k = 10^0, 10^{-1}, 10^{-2}$, and 10^{-3} m³ mol⁻¹ s⁻¹ (i.e., $10^3, 10^2, 10^1$, and 10^0 l mol⁻¹ s⁻¹, respectively).

3 Results and discussion

The main assumption of the present work is that the diffusion coefficient for charge carriers D_n is considered to be dependent on solution acidity. It is well known that polyaniline shows its electric conductivity only in its protonated (or “proton-doped”) state. When polyaniline is used as a modifier layer at electrode, this implies that the surrounding solution should be acidic enough to protonate the polymer layer. It has been noted in a high number of works that the transformation between insulating (or, more precisely, semiconducting) and conducting forms of this polymer occurs around pH=3 or 4. Above this value, polyaniline occurs in its deprotonated nonconducting form, whereas below this value, its electric conductivity increases by a few orders of magnitude. In the present work, the lowest limit for D_n has been chosen as equal to D of a reactant (10^{-9} m²/s). For a “better conducting” form of polyaniline, D_n values of $10^{-8}, 10^{-7}$, and 10^{-6} m²/s were taken into consideration. The values chosen cover a

wide range of charge carrier mobility and thus of electric conductivity. Also, we tried to cover a wide range of threshold value of solution acidity, ranging from 10^{-5} through 10^{-4} , 10^{-3} , 10^{-2} , to 10^{-1} mol/m³ (corresponding to 10^{-8} , 10^{-7} , 10^{-6} , 10^{-5} , and 10^{-4} mol/l, respectively). The lowest values of this parameter correspond to pH-neutral or even slightly alkaline solutions with pH of 8 or 7, whereas the highest value corresponds to mild acidic conditions (pH = 4).

During electrochemical oxidation of ascorbate, protons are expelled into the solution in an equimolar quantity. This causes a local acidification of a modifier layer. As a result, polyaniline turns into its conducting form within this small local domain. By progressive electrooxidation of ascorbate, the conducting domains should grow and expand to a direction, coinciding with the diffusion flow of ascorbate. Therefore, adding of ascorbate into surrounding electrolyte causes the rise of small (most probably, of nanometer size) conducting domains at a solution–polyaniline interface. At a continuing diffusion of ascorbate into a polyaniline layer and thus at a continuing electrooxidation of ascorbate and acidification of a reaction zone, the conducting domains grow in size and probably compose a frontier of a conducting zone, moving from the solution–polyaniline interface through the polymer layer to polyaniline–metal interface. By reaching this interface, an entire layer of polyaniline becomes conducting, and electrocatalytic process turns now into steady-state conditions, characterized by the balance of the rate of ascorbate diffusion, its redox interaction with polyaniline, and diffusion of charge carriers through the polyaniline layer. This balance should result in a steady-state electric current.

Following this supposed consequence of processes, three parameters have been chosen for analysis, having the most significant influence to current–time profiles. These are:

1. The threshold value for a local concentration of protons generated in a chemical redox interaction of ascorbate and polyaniline α . Although the most expected value for α should be 10^{-4} or 10^{-3} mol/l (or 10^{-1} and 10^0 mol/m³), we varied it within a broad range of 10^{-8} to 10^{-4} mol/l. It is clear that, at a zero or even very low value of α , the system should obey a simple rise of current as it was analyzed in our previous publications [10–12] because a low value for α means nearly no significant changes in the conductivity at a progressing reaction.
2. The diffusion coefficient for charge carriers D_n . Its lowest value chosen (10^{-9} m²/s) equals to D for ascorbate (reactant) and means that no increase of electric conductivity proceeds upon protonation of polyaniline at the expense of protons produced in a chemical redox interaction. For modeling of an increase of electric conductivity, an increase of D_n by 1, 2, and 3 orders of magnitude has been chosen.
3. Reaction rate constant for the chemical redox interaction of ascorbate with polyaniline k . Although it is clear that the higher values of k should result in a faster growth of current, the exact influence of this important parameter cannot be simply predicted, even in a rough qualitative manner. Thus, the value for k has been varied within three orders of magnitude, ranging from 1 (denoting slow reaction) to 10^3 l/mol s (for the fastest reaction).

Below, we analyze the results related to variation of all of these parameters. The lowest value of α taken into account (10^{-5} mol/m³, or 10^{-8} mol/l) corresponds to solution

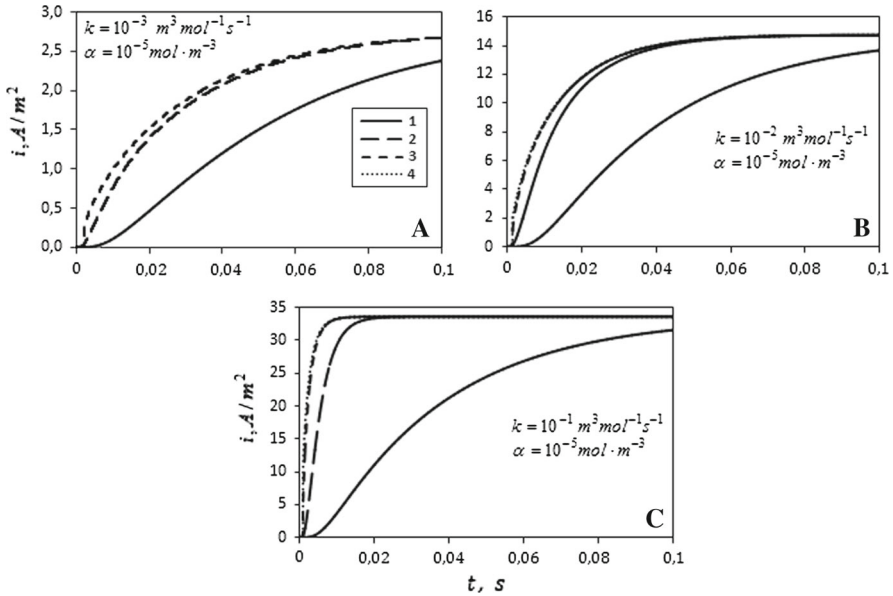


Fig. 1 Dynamics of the sensor current at four values of the diffusion coefficient of charge carriers $D_n^* = 10^{-9}$ (1), 10^{-8} (2), 10^{-7} (3), 10^{-6} (4) m^2/s for different k at $\alpha = 10^{-5} \text{ mol}/\text{m}^3$

pH within the reaction zone around 8. Roughly speaking, this means that the electric conductivity of a modifier layer or, more precisely, the D_n value practically does not depend on chemical conversion of ascorbate taking place within a layer under the “normal” reaction conditions taken into account. For this case, the calculated current–time profiles are displayed in Fig. 1. In all cases, the current reaches its steady-state value in less than 1 s. Also, in all cases the current grows faster at a faster chemical interaction of ascorbate with reaction centers within the layer, i.e., at higher k values. The current growth rate depends also on charge carriers diffusion rate: an increase in D_n^* from its lowest value of $10^{-9} \text{ m}^2/\text{s}$ by one order of magnitude results in a sharp (more than tenfold) increase of growth rate, whereas further increase of D_n^* results in lower increase, and almost no changes of current increase rate are noted at the fastest diffusion of charge carriers, i.e., by changing of D_n^* from 10^{-7} to $10^{-6} \text{ m}^2/\text{s}$ (Fig. 1). A specific sigmoidal form of current–time transients should be noted, best seen at the slowest diffusion of charge carriers. In a physical sense, this means that it takes some time for charge carriers, initially generated in a chemical interaction at an outer solution–modifier boundary, to diffuse through the modifier layer to the surface of electrode. It is also well seen from Fig. 1 that the steady-state current depends on chemical interaction rate constant. An increase of k from 1 $\text{l}/\text{mol s}$ by one and two orders of magnitude results in an increase of a maximum current from about 3 to 15 and 33 A/m^2 , respectively (Fig. 1). It is worth noting that no linear dependence of steady-state (maximum) current and a chemical reaction rate constant is obtained.

Significant changes are observed by increasing α . Figure 2 presents similar current–time profiles for somewhat higher $\alpha = 10^{-7} \text{ mol}/\text{l}$. This means that the local pH within the reaction zone should drop to 7 to start the faster diffusion of generated

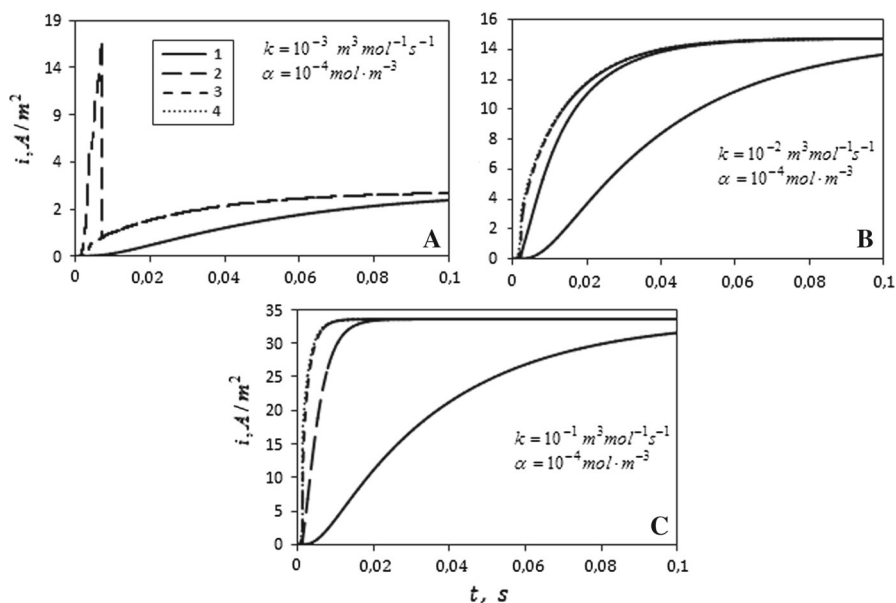


Fig. 2 Dynamics of the sensor current at four values of the diffusion coefficient of charge carriers $D_n^* = 10^{-9}$ (1), 10^{-8} (2), 10^{-7} (3), 10^{-6} (4) m^2/s for different k at $\alpha = 10^{-4} \text{mol}/\text{m}^3$

charge carriers. Here, for the fast chemical interaction, characterized by k of 10 or 100 $\text{l}/\text{mol s}$, the current–time profiles almost do not differ from those obtained for $\alpha = 10^{-8} \text{mol}/\text{l}$, as presented above in Fig. 1. However, drastical changes are observed for the slow chemical reaction in combination with fast diffusion of charge carriers (D_n^* of 10^{-7} and $10^{-6} \text{m}^2/\text{s}$) (Fig. 2a). After a very short period, a fast increase of current is observed, exceeding at its maximum approximately 6 times the steady-state current, observed at lower D_n^* values (10^{-8} and $10^{-9} \text{m}^2/\text{s}$). Then, the current drops to its “normal” value and follows the dynamics characteristic for higher values of D_n^* . As a result, an unexpected sharp maximum (flash) at the current–time profiles is observed.

The interpretation of physicochemical processes that are responsible for this maximum may be as follows. At an initial stage of the process, ascorbate diffuses into an outer layer of a modifier film, where slow chemical redox interaction begins. As a result, ascorbate becomes oxidized, whereas an outer layer turns into its reduced state, i.e., it becomes rich in electrons. Because the deeper layers of a modifier film are still nonconducting (since the concentration of protons there is still low), the electrons cannot move toward the electrode. At progressing redox reaction, its front and thus the threshold concentration of protons moves into the deep of a modifier film toward the electrode. Correspondingly, the front of high conductance (i.e., high D_n^*) moves toward the electrode. When it reaches the electrode, the reduced state of the film discharges immediately, i.e., the electrons accumulated into it at the expense of a chemical reaction flow to the electrode. As a result, a sharp flash of electroic current (anodic current) is observed. After that, because the concentration of protons exceeds the threshold value through the entire layer, and thus the modifier occurs in its con-

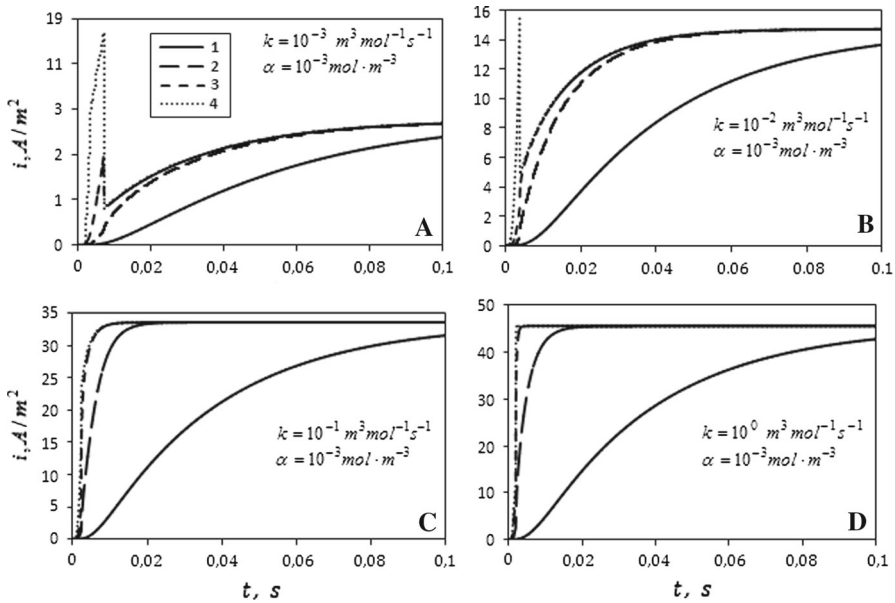


Fig. 3 Dynamics of the sensor current at four values of the diffusion coefficient of charge carriers $D_n^* = 10^{-9}$ (1), 10^{-8} (2), 10^{-7} (3), 10^{-6} (4) m^2/s for different k at $\alpha = 10^{-3} \text{mol}/\text{m}^3$

ducting form, the time-evolution of current follows its usual profile. We did not yet observe the phenomenon described here experimentally, most probably because of its shortness, not exceeding 0.01 s. For its experimental observation, special experimental care should be taken regarding the measurement of short electric pulses; however, there are no principal invincible obstacles to observe this interesting phenomenon.

Further increase of α by an additional order of magnitude up to $\alpha = 10^{-6} \text{mol}/\text{l}$ causes a similar appearance of a current flash, however, now under a wider variety of conditions (Fig. 3). A close similarity in shape, magnitude, and in its position on the time scale current flash is now observed at a higher conductivity of the modifier layer, i.e., at $D_n^* = 10^{-6} \text{m}^2/\text{s}$ (instead of $10^{-7} \text{m}^2/\text{s}$ as in the previous case) for the same rate constant of chemical interaction (see Figs. 2a, 3a). This shows a specific kind of a “compensation effect”: an increase of α means a proportional increase in D_n^* to be necessary for the same effect. In the present case, somewhat lower in magnitude current flash appears also for slower diffusion of charge carriers, characterized by $D_n^* = 10^{-7} \text{m}^2/\text{s}$ (Fig. 3a). Also, a flash of a considerably high magnitude, although at a shorter time of about 0.005 s appears also for a faster chemical interaction with $k = 10 \text{l mol}^{-1} \text{s}^{-1}$ (Fig. 3b).

Even more combinations of parameters for the appearance of this specific current flash presents a higher value of $\alpha = 10^{-5} \text{mol}/\text{l}$, as depicted in Fig. 4. In a physical sense, this higher value of α means that the concentration of protons should increase to a higher (by one order of magnitude, as compared to the previous case) degree to turn the modifier layer into its conducting state. In other words, the chemical reaction should proceed to a higher extent to make the polyaniline layer more conducting,

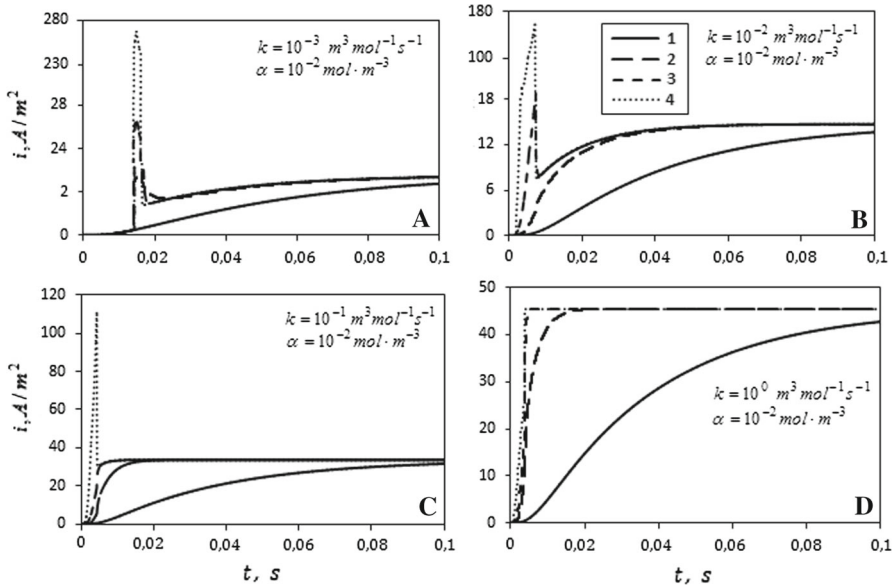


Fig. 4 Dynamics of the sensor current at four values of the diffusion coefficient of charge carriers $D_n^* = 10^{-9}$ (1), 10^{-8} (2), 10^{-7} (3), 10^{-6} (4) m^2/s for different k at $\alpha = 10^{-2} \text{ mol}/\text{m}^3$

ensuring fast transfer of charge carriers. At the lowest value of k , the current flash is observed for all values of D_n^* , except for the lowest one (Fig. 4a). In this case, the longest period for current flash is observed. Surprisingly, the magnitude of current flash drastically exceeds (by the factor of about 15) that observed for lower $\alpha = 10^{-6} \text{ mol}/\text{l}$ (cf. Figs. 3a, 4a), although the steady-state current, achieved at longer time period, remains roughly on the same level. An increase in rate constant of reaction leads to a gradual decrease of current flash. For $k = 100 \text{ l}/\text{mol} \cdot \text{s}$, the current flash is observed only for the fastest diffusion of charge carriers (Fig. 4c). At the highest value of $\alpha = 10^{-4} \text{ mol}/\text{l}$ taken into consideration in this study, some different dependencies were obtained, as depicted in Fig. 5. Here, the highest value for current flash (within the frames of the present study) has been observed for a definite combination of parameters (Fig. 5c). Also, the greatest width of current flash on the time scale and thus the greatest integral for (i, t) -dependencies, which means the greatest electric charge passed, were observed for the fastest diffusion of charge carriers (Fig. 5c, d). Somewhat different in their shape (i, t) -dependencies are obtained for the slowest chemical interaction (Fig. 5a). Initially, the sigmoidal growth of current does not depend on D_n^* within the entire range used in calculations. However, a drop of current is then observed after a definite time period for all values of D_n^* , except for the lowest one.

4 Conclusions

The present study has been provoked by the sigmoidal character of current–time dependencies, observed experimentally for polyaniline modified electrode used as

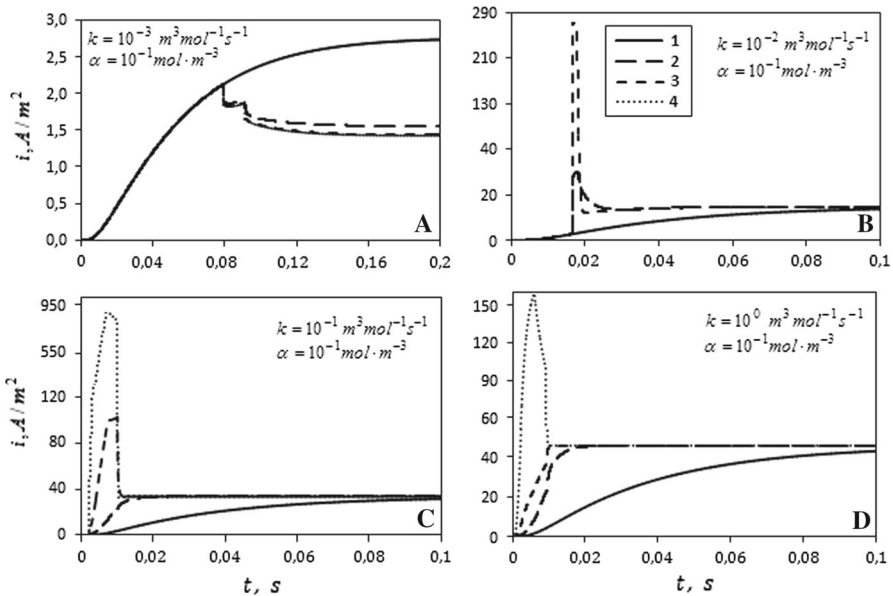


Fig. 5 Dynamics of the sensor current at four values of the diffusion coefficient of charge carriers $D_n^* = 10^{-9}$ (1), 10^{-8} (2), 10^{-7} (3), 10^{-6} (4) m^2/s for different k at $\alpha = 10^{-1} \text{mol}/\text{m}^3$

an amperometric ascorbate sensor. An assumption on the specific autocatalytic character of the processes responsible for this behavior has been modeled here, assuming that the electric conductivity of polyaniline layer increases by one or more orders of magnitude when the concentration of protons (a side product of electrochemical oxidation of ascorbate) reaches some definite threshold value. Depending on the reaction parameters chosen, different current–time profiles were obtained, both of sigmoidal and nonsigmoidal shape. In some cases, sharp current flashes were observed. Phenomenological interpretation of the dependencies observed is presented.

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