

# Modeling of reactant concentration in electrocatalytic processes at conducting polymer modified electrodes

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**Abstract.** This research presents a mathematical model analyzing of electrochemical processes occurring at electrodes covered with a thin film of a conducting polymer. 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 aim of this work was to find the location of a mean reaction zone that is of a great practical interest related to optimization of the parameters of electrocatalytic system for its best performance. It has been shown that electrocatalysis of solute species at conducting polymer modified electrodes proceeds within the polymer film rather than at the outer polymer/solution interface.

*Keywords:* modeling, electrocatalysis, reaction-diffusion, conducting polymer.

## 1. Introduction

Conducting polymers are novel synthetic materials, which possess unique properties, differing them from nearly all organic materials ever synthesized [1–3]. The ability to catalyze some electrochemical oxidation and/or reduction processes of solution species is potentially useful in important fields of applied electrochemistry like electrosynthesis and electroanalysis [4]. 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.

The problem of the location of the reaction zone during electrochemical redox process should be solved for the successful application of conducting polymers in electrocatalytic systems. Any electrocatalytic conversion of solute species at a conducting polymer covered electrode should be considered as consisting of a few simple processes [4] (Fig. 1). 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 polymer layer into the bulk of solution.

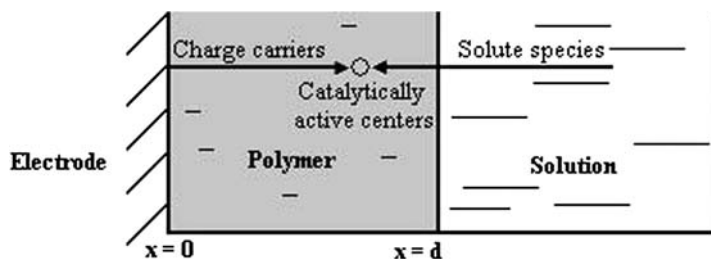


Fig. 1. Processes of electrocatalytic conversion of solute species at a conducting polymer covered electrode.

Actually, except for the diffusion of charge carriers within polymer film, all remaining processes are characteristic for any electrocatalytic process, occurring at electrode/solution interface. 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. 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.

The present study has been aimed to mathematical modeling of electrochemical processes accruing 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  $d$ . This modified electrode is supposed to be immersed into reactant solution of unlimited volume. It is supposed that process proceeds under ideal stirring conditions.

The Fick 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.

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.,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  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 charge carrier, i.e., an electron for cathodic reduction, or a hole for anodic oxidation processes.

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

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

where  $k$  is 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 [5]:

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

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

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

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 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 ( $t > 0$ )

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

The problems (4)–(8) were solved numerically using the finite difference technique [6].

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 calculation. 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 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.

### 3. Results and discussion

Combining of all possible values gives a huge amount of combinations, thus, only most characteristic cases are considered.

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. In this model, it was calculated the thickness of polymer layer when reactant concentration equals half of the reactant concentration in solution ( $R = (1/2) \times R_0$ ) at the beginning of the process. The results show, where at the polymer layer the chemical redox reaction between reactant and charge carriers proceeds.

Fig. 3 presents some characteristic simulated thickness of a modifying layer and reaction rate constant for reactant mean concentration. The results obtained by changing reaction rate constant and calculating thickness of a modifying layer when reactant concentration is  $R = (1/2) \times R_0$ . In case of a fast chemical redox reaction between reactant and charge carriers ( $k$  shifts from 1 to  $10 \text{ m}^3 \times \text{mol/s}$ ), the mean of  $R$  remains within the polymer film near polymer/solution interface (Fig. 3, top left). Significant changes occur by lowering the reaction rate constant  $k$ . When thickness of a reaction layer  $d$  and reactant concentration in solution  $R_0$  are constants, the decrease of  $k$  (shifts from 0.01 to  $0.1 \text{ m}^3 \times \text{mol/s}$ ) results the mean of reactant concentration  $R = (1/2) \times R_0$  drops within the polymer film to  $\sim 2 \times 10^7 \text{ m}$ , thus, the reaction proceeds near the electrode/polymer interface.

Fig. 3, top left and right, compares two cases, as obtained for the highest and lowest range of values of  $k$  taken for simulation, respectively. It is seen that, for the lowest range of  $k$  values (from 0.01 to  $0.1 \text{ m}^3 \times \text{mol/s}$ ), the half of the reactant concentration is  $\sim 2 \times 10^7 \text{ m}$  and it appears near electrode/polymer interface. In terms of efficiency of electrocatalytic conversion, the results obtained show that, at a given reactant concentration in a solution  $R_0$  ( $10^1 \text{ mol/m}^3$ ), and at a constant thickness of polymer layer  $d$  ( $10^{-6} \text{ m}$ ), an efficient conversion proceeds at the highest range of  $k$  values.

Thickening of a polymer layer results in drastic changes of profiles studied (cf. top, middle and bottom rows in Fig. 3, where the thickness differs by an order of magnitude). Again, a half conversion of reactant  $R$  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  $10^{-6} \text{ m}$  does not increase the efficiency of electrocatalytic conversion very much. As expected, lower values of  $k$  taken for simulation result in lower efficiency (Fig. 3). For the lowest values of  $k$ , half conversion of reactant  $R$  occurs in a  $10^{-5} \text{ m}$  polymer layer near (polymer thickness  $\sim 8 \times 10^{-5}$ ) the polymer/solution interface, whereas almost full conversion of reactant occurs with the thickest film of  $10^{-4} \text{ m}$  (cf. right column of Fig. 2). The simulation results obtained show that, for practical purpose, 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 maximum conversion of reactant into reaction product.

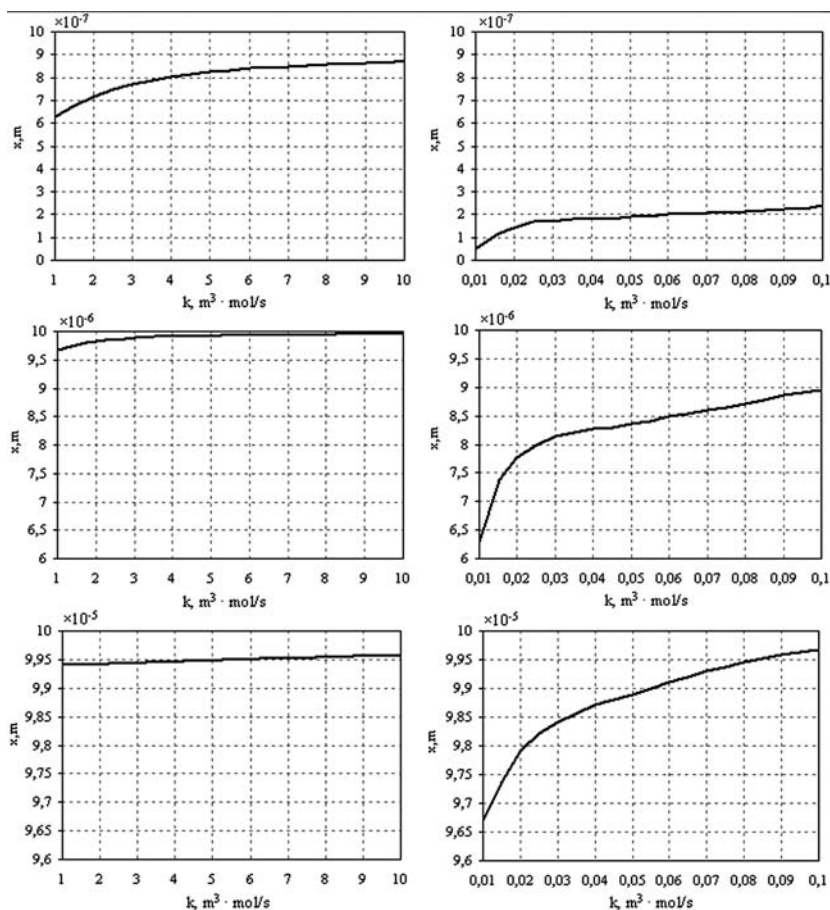


Fig. 2. 2D-profiles for reactant mean concentration ( $R = (1/2) \times R_0$ ) within the conducting polymer film. The vertical axes represent the thickness of a modifying layer and horizontal axes – second-order reaction rate constant. Other conditions are as follows: reactant concentration in solution  $R_0 = 10 \text{ mol/m}^3$ , diffusion coefficient for charge carrier  $D_n = 10^{-8} \text{ m}^2/\text{s}$ , reaction rate constant change from  $k = 1$  to  $10 \text{ m}^3 \times \text{mol/s}$  (left column), or from  $k = 0.01$  to  $0.1 \text{ m}^3 \times \text{mol/s}$  (right column), thickness of a polymer layer  $d = 10^{-6} \text{ m}$  (top row),  $10^{-5} \text{ m}$  (middle row), or  $10^{-4} \text{ m}$  (bottom row).

#### 4. Conclusions

In conclusion, the presented results 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. Based on the proposed model, optimization of reaction system parameters could be made for any particular case to get an optimum efficiency or reaction to product conversion.

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### REZIUMĖ

**V. Jasaitis, A. Malinauskas, F. Ivanauskas. Elektrokatalizės procesų (reagento koncentracijos) elektrai laidžiuose polimeruose kompiuterinis modeliavimas**

Šiame straipsnyje pristatomas elektrokatalizės procesų (reagento koncentracijos) elektrai laidžiuose polimeruose kompiuterinis modeliavimas. Modelis įtraukia tirpalo junginių difuziją polimeru, krūvininkų difuziją polimeru nuo elektrodo paviršiaus ir elektrocheminę redukcijos/oksidacijos reakciją polimero viduje. Tyrimo tikslas – rasti reakcijos vietą polimere, kai reagento koncentracija pasiekia pusę pradinės koncentracijos keičiant modelio parametrus. Straipsnyje parodoma, kad tirpalo junginių elektrokatalizės reakcija vyksta polimero plokštelės viduje, o ne išoriniame polimero/tirpalo paviršiuje kaip metalų katalizės atveju.