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Cyclic voltammetry of electrodes modified by pristine and metal-composite polymer films

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The Laviron equation of a quasi-equilibrium reaction proceeding in a compact film adsorbed onto an electrode

- Cyclic voltammetry is probably the most frequently used method of electrochemical research. A great influence on its application to studying the electrode reactions that proceed in an adsorbed state of reacting particles has had brilliant works by Laviron. His widely known equation

$$i = \frac{(nF)^2 A v \Gamma_m \eta}{RT(1 + \eta)^2}$$

- where $\eta = exp\{nF(E - E_p)/RT\}$ and $E = E_i - vt$ (v, the rate of potential change; E_i, the initial value of E in linear potential sweep voltammetry), was derived for reversible reaction $O + ne \leftrightarrow R$ proceeding in a compact film adsorbed onto an electrode of surface A. A series of inferences from this equation, namely: (1) the appearance of peak current i_p at potential value $E = E_p$ (i.e. $\eta = 1$); (2) the equality of adsorption densities of reduced (Γ_R) and oxidized forms (Γ_O) to each other at peak (or formal) potential E_p ($\Gamma_O(E_p) = \Gamma_R(E_p) = \Gamma_m/2$); (3) symmetry of $i(E)$-curves with respect to the peak potential and (4) the fact that "the width of the peak at mid-height δ is equal to 90.6/n mV" is considered as a complex of experimental criteria that can be used to establish the absence of specific (short-range) interactions between particles forming such films (or the Langmuir type of adsorption in case of monolayer films).

Is it possible to reformulate the Laviron's criteria of the absence of short-range interactions within polymer films?

- To perform such reformulation is necessary due to the fact that the Laviron's consideration had been performed for monolayer films of adsorbed particles O and R, whereas modifying polymer films have a phase character; they are so thick, that the electroneutrality condition takes place practically for their entire interior. This means that the charge consumed to reduce/oxidize the film fragments (Q_f) is strictly compensated by the opposite one of counter-ions entering/leaving such films. The concentration of these ions, C_m, and, hence, charge

$$Q_f = - z_m F \int C_m \, dz \qquad\qquad 0 \leq z \leq L$$

- (here, L is the film thickness; z_m is the charge of counter-ions) is determined by electric potential Φ_0 of the film bulk. As potential Φ_0 differs from electrode one E , the derivative of the film charge with respect to time t or potential E (taking into account that $dt = \pm dE/v$ in the conditions of cyclic voltammetry) should contain derivative $d\Phi_0/dE$, which changes the final result for passing current i as compared to that given by the above Laviron's equation.

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Electroneutrality condition for p- and n-doped polymers

**Thus, one can conclude that the electroneutrality condition plays the key role for the further consideration of red/ox processes Red - e ↔ Ox, which are accompanied with entering/leaving the counter-ions of charge Z_m.**

Three following cases will be considered below

I. **(I.1) Charge Z_0 of the oxidized form equal to 1 and $Z_0 = -1$ (*p*-doped film, the polaron formation); (I.2) $Z_0 = 0$, $Z_m = 1$ (*n*-doped film)**

II. **(II.1) Charge $Z_0 = 2$, $Z_m = -1$ (polaron / bipolaron system; (II.2) $Z_0 = -1$, $Z_m = 1$ (*n*-doped film)**

III. **(III.1) Charge $Z_0 = 1$, $Z_m = -1$ (*p*-doped film), but the oxidation process is accompanied with binding the formed polarons into ionic associates with counter-ions: P + A ↔ PA; (III.2) $Z_0 = -1$, $Z_m = 1$ (*n*-doped film) and the reduction process is also accompanied with ionic associate formation**

The electroneutrality condition: $Z_0 C_{Ox} + (Z_0 - 1) C_{Red} + Z_m C_m = 0$

Here, C_K are the concentrations of corresponding species (K = Ox, Red, m)

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const $= \dfrac{vF^{2}ALk_{m}C_{0}}{RT}$
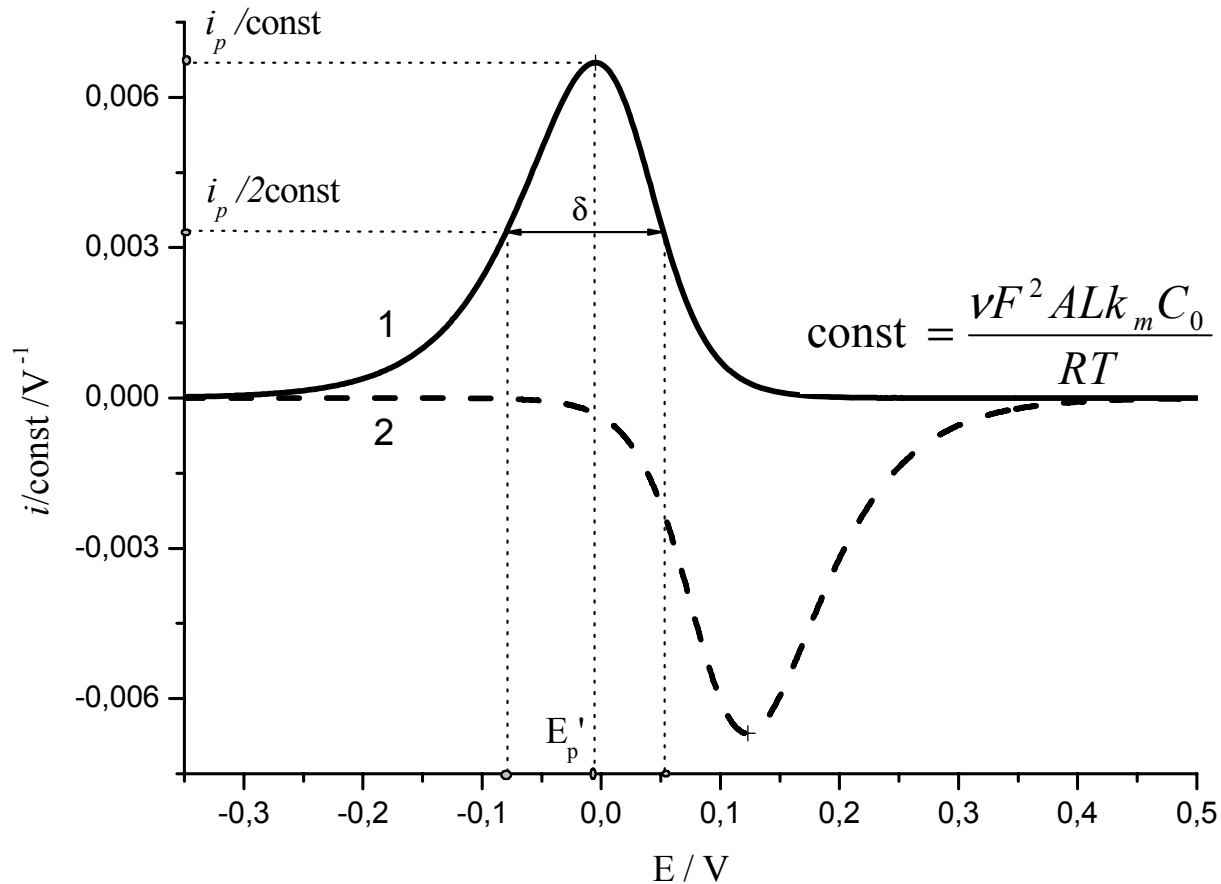
- **Quasi- equilibrium CV-curves of electrodes modified by p-doped (curve 1) and n-doped (curve 2) polymer films at z_0 =1, 0, correspondingly**

- v, the velocity of scanning the electrode potential; A, the electrode area; L, the film thickness; k_m, the partition coefficient of counter-ions; C_0, their concentration

- δ is a semi-width of CV-curves that, in the case considered, is equal to 5.1RT/F (131 mV at room temperature)

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Comparison between CV-curves corresponding to different values of charge z_0 of the reduced film fragments
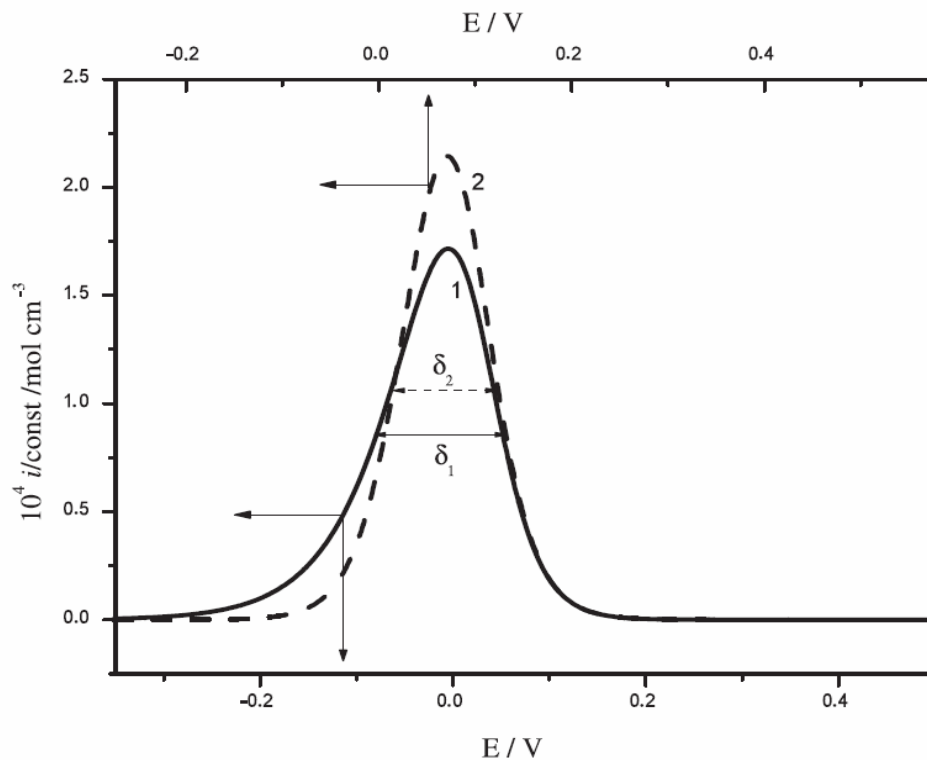
Reduced CV-curves in case of p-doped polymer at different charges z_0 of its oxidized fragments, const = $\nu F^2 AL/RT$. Curves 1 and 2 correspond to $z_0 = 1$ and $z_0 = 2$, respectively. $\delta_1 = 131$ mV and $\delta_2 = 108$ mV, the mid-width of curves 1 and 2. Both curves were calculated at $k_e = k_m = 0.1$, $C = C_0 = 10^{-3}$ mol/cm^3.

Influence of binding the counter-ions with reduced fragments of polymer films
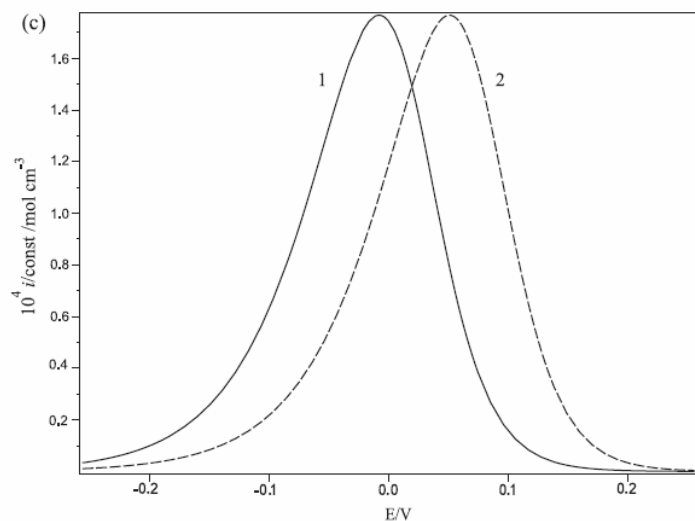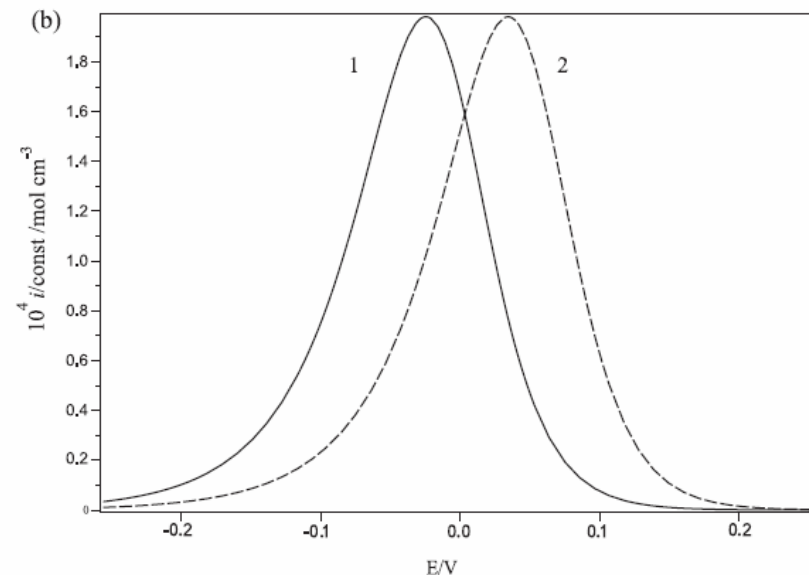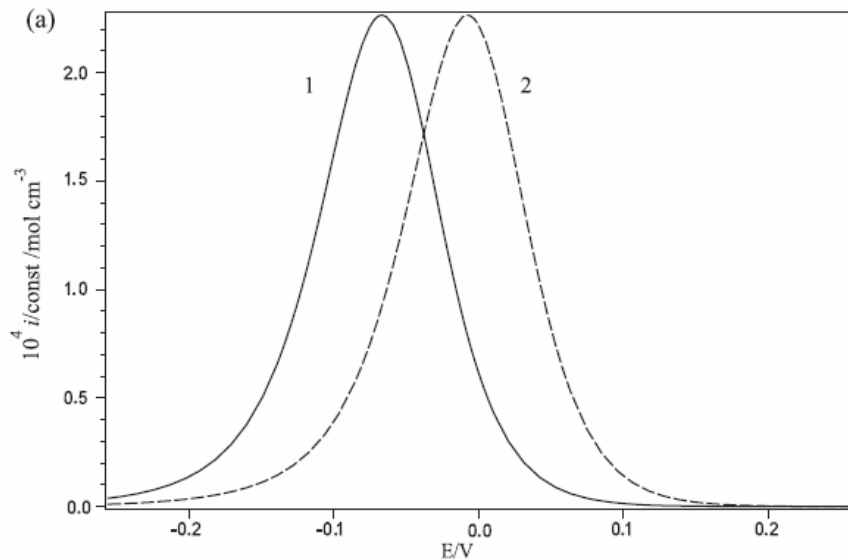
Reduced CV-curves in case of p-doped polymer in the presence of ionic association between counter-ions and charged film fragments, const = $v F^2 AL/RT$. (a) $k_p = 1000$, $k_1 = 1$, $k_m = 1$ (curve 1) and $k_m = 0.1$ (curve 2), the obtained mid-width value $\delta = 3.80 RT/F$; (b) $k_p = 100$, other parameters are the same as those of figure a, the obtained mid-width value $\delta = 4.32 RT/F$; (c) $k_p = 10$, other parameters are the same as those of figure a, the obtained mid-width value $\delta = 4.93 RT/F$.

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## *Conclusions from the above consideration of quasi-equilibrium CV-curves*
(*Electrochimica Acta 80 (2012) 426-431*)

- 1. Current and potential values in singular points of CV-curves, as well as the semi-widths of such curves depend on charges of red / ox film fragments and counter-ions, and binding of the film fragments with counter-ions.

- 2. This means that any general formulation of the only set of criteria of the absence of short-range interactions within polymer films is impossible, since the shape of CV-curves of modified electrodes changes with variations in the system parameters.

- 3. Cyclic voltammetry is, therefore, only a primary method of studying charge transfer processes in modified electrodes and should be used in a combination with other instrumental methods.

Obviously, the question arises whether there exists an optimum combination. In some cases indicated further on, such combination might be indicated.

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Problems of modeling the electrode processes in pristine and composite films of electroactive polymers

- Modified electrodes are often used for electroanalytical determinations of different substances inclusive of biologically active ones. Meanwhile, details of the corresponding processes underlying such applications have mostly remained to be unclear.

- As it is known, real polymer films are porous systems (see the next slide). This, in particular, means that reactions of the determined particles can proceed not only on the visible ("outer") film surface, but also on an "inner" surface of pores penetrating completely or partly such films.

- The same situation probably takes place for electrode reactions in composite films, the metal inclusions of which are predominantly settled in film pores.

- Such porous character of polymer films in some extent complicates a quantitative description of electrode processes in these objects. The problem seems to be more complex in case of composite films. However, the problems have their solutions in some cases, at least.
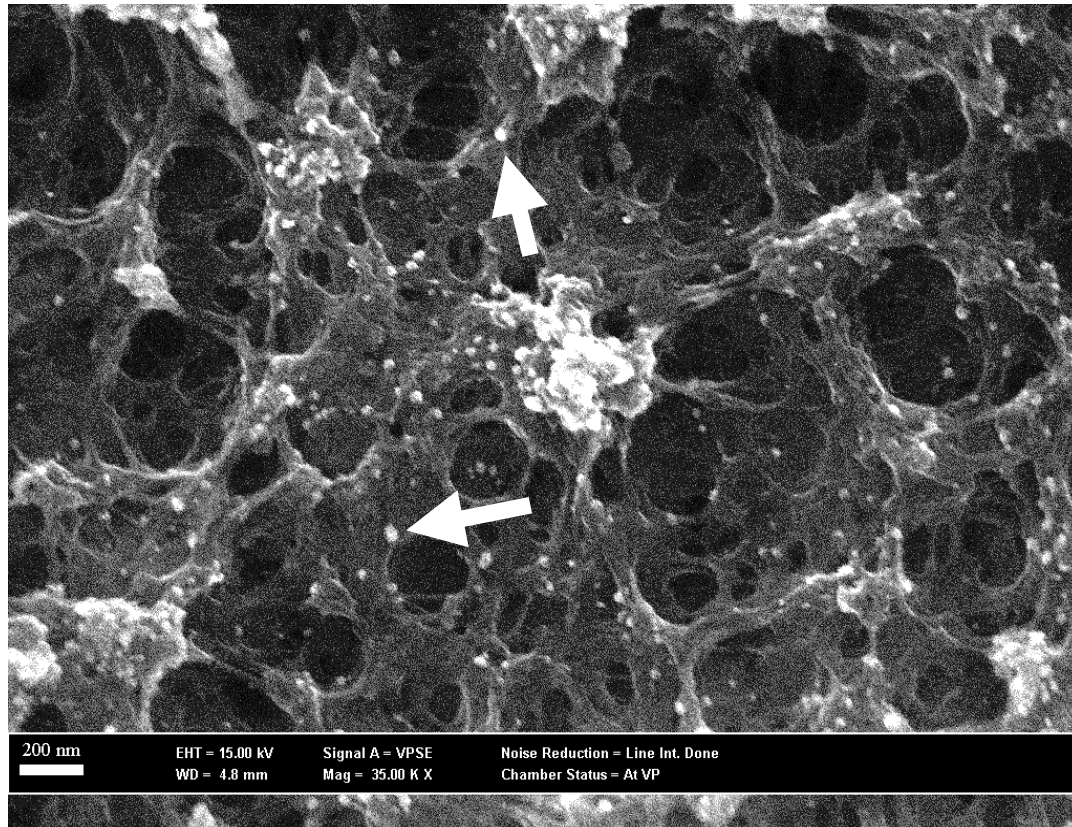
SEM-image of a PEDOT/Pd film.

Pd particles are deposited by dipping of previously reduced polymer . film for 60 s into $5 \cdot 10^{-3}$ M $PdCl_2$ / 0.1 M H_2SO_4 solution. Separate palladium clusters are indicated by arrows.
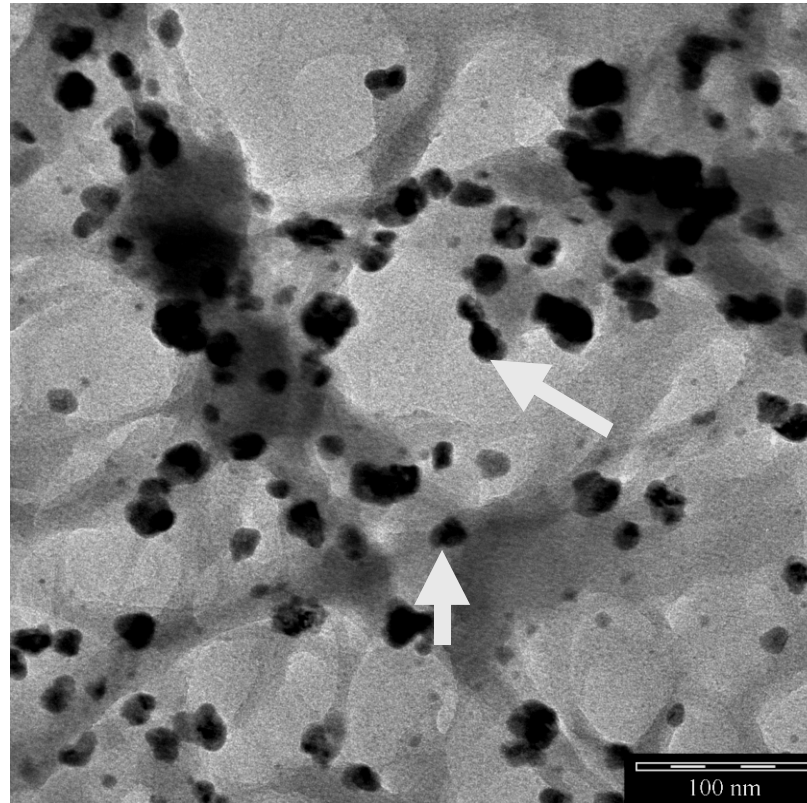
TEM-image of a PEDOT/Pd film.

Pd particles are deposited by dipping the previously reduced polymer film for 120 s into ***$5 \cdot 10^{-3}$ M PdCl$_2$ / 0.1 M H$_2$SO$_4$*** solution. Separate palladium clusters are indicated by arrows

substrate | film | solution
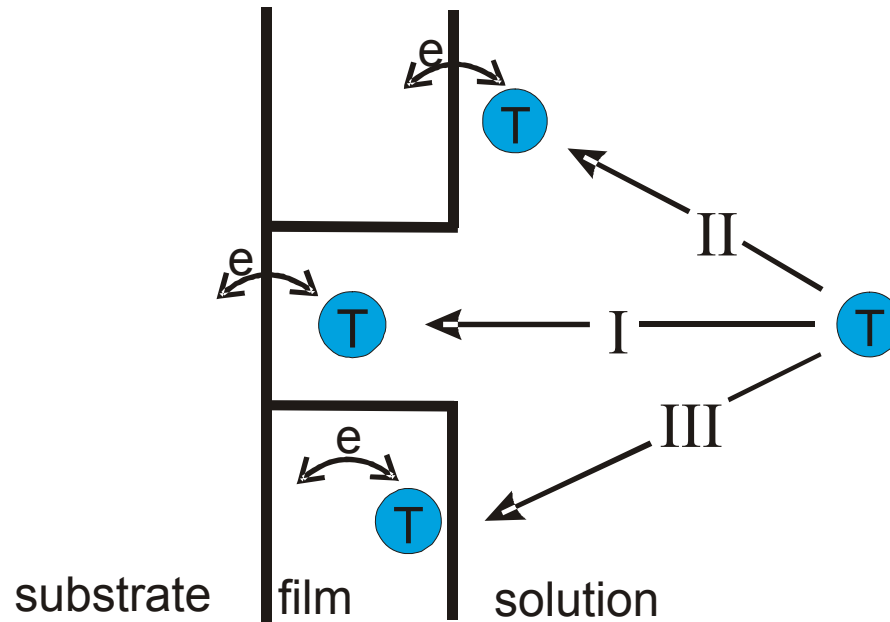
Possible paths of tested particles' diffusion

I.   Reaction on the electrode substrate

II. Reaction on the film/solution interface including the "inner" surface of pores

III. Reaction within the film volume (the case of metal-composite films)
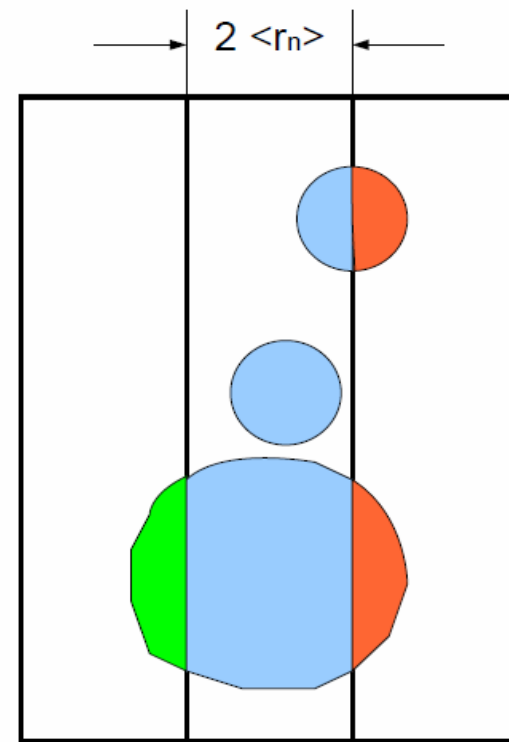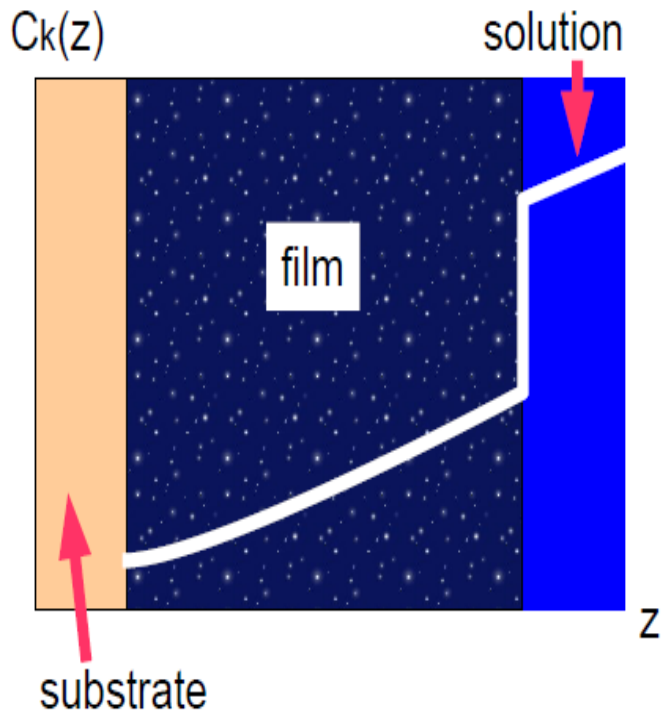
Left figure: open points within the film correspond to metal clusters. White line of the figure represents the tested particles' distribution.
Right figure: metal clusters included partly or completely into an arbitrary film layer of the thickness equal to 2<r>, where <r>, the mean radius of film clusters

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Cylindrical and slit pores

- LEFT: r_i is the radius of cylindric pores of the *i*-th kind

- RIGHT: r_j is the width of slit pores of the *j*-th kind
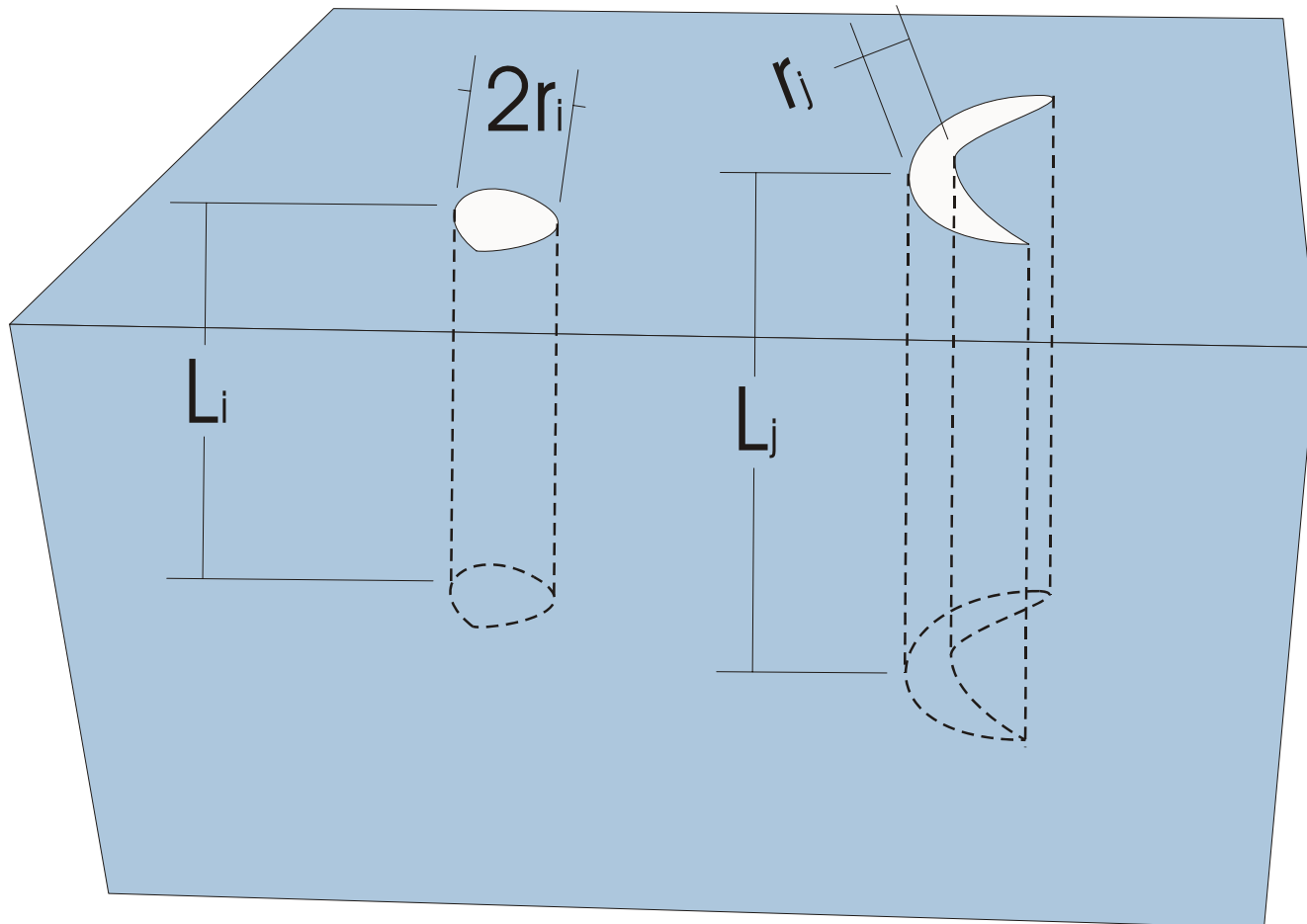
Description of electrode processes with participation of tested particles

In the three cases considered, the concentration C_k of tested particles satisfies the following equation:

$$\partial C_k / \partial t = D_k\, \partial^2 C_k / \partial z^2 - K(z, r_i)C_k \;,$$

where D_k, the diffusion coefficient of tested particles; $K(z, r_i)$ is some effective rate constant (see *V.V. Malev, O.V. Levin , Electrochimica Acta 56 (2011) 3586-3596; Russian J. Electrochemistry (2012)*).

The final equation for current **I** resulted from the reduction/oxidation of tested particles on film surface $A_{tot} = (A_{in} + A)$ is as follows

$$-AC_k^0 / \textbf{\textit{I}} = 1/K_k(1 + A_{in}/A) + \textbf{\textit{I}}_{lim}/D_k \;,$$

where A_{in} , the total inner surface of all possible kinds of pores (cylindrical, conic, slit, wedge-shaped, and so on); $\textbf{\textit{I}}_{lim} = 0.62nF\, AD_k^{2/3}\omega^{1/2}v^{-1/6}C_k^0$ *is the limiting current to a rotating disc electrode of surface A; K_k is the rate constant of the reaction $K \pm ne \rightarrow K_{red}$ or K_{ox}. Definitions of constant K_k are given in the next slide.*

# *Continuation of the preceding slide*

- *In all the cases considered, K_k is a potential dependent quantity that tends to a constant value in the limit of $|E| \rightarrow \infty$ (sign of E depends on the electrode reaction nature). Though the above Levich-Koutecky 's representation is valid for arbitrary values of electrode potential E, I'll further consider only the cases of limiting currents, which have a different nature in different cases.*

- *Case I: through pores and the tested species' reaction on the electrode substrate. In this case, $A_{tot} \equiv A$, while constant K_k is determined by the film porosity and equal to*

- *$K_k = D_k\eta/L$, where η, the substrate surface fraction free of a modifying film; L and D_k, the film thickness and the diffusion coefficient of tested particles.*

- *Case II: reaction on the film physical border (including lateral surface of pores). In this case, $A_{tot} \geq A$, while constant K_k is determined by both the concentration of red- or ox-fragments of the film and the electric potential drop on the film/solution interface. As the latter in the limit of high electrolyte concentrations is practically equal to zero, the intercept of the dependence $(AC_k{}^0/\textbf{I}(\omega^{1/2}))$ gives the reversal product of three quantities: $K_k{}^0C (1 + A_{tot}/A)$, where $K_k{}^0$, the true value of the constant and C, the total concentration of film fragments.*

- *Case III: reaction on the metal clusters' surface. In this case, quantity $(1 + A_{tot}/A)$ should be treated as the ratio of the clusters' surface to the visible electrode one if all clusters are of the same radius, r_0. At this condition, $K_k = D_k/r_0$; more complicated expressions for these quantities are valid in the general case of different r_i .*

# Experimental results; poly-o-phenylenediamine + hydroquinone (case I of through pores)
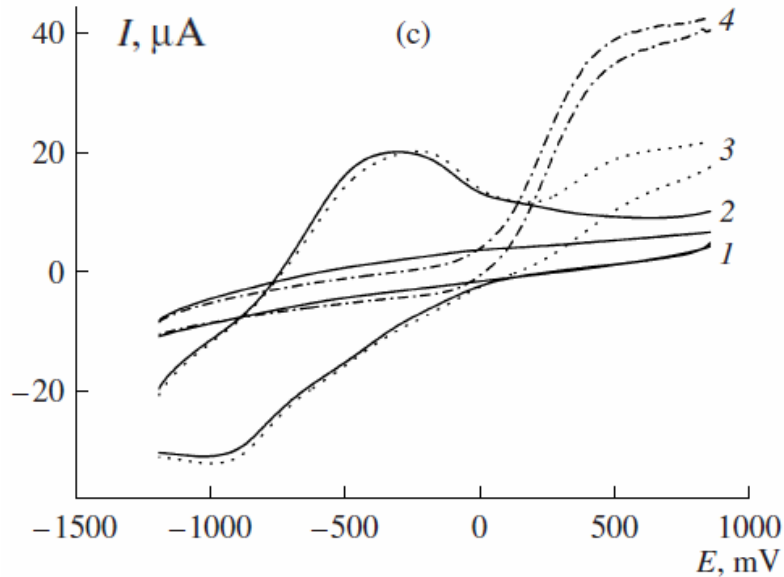
Effects of the PPD film on the oxidation wave of hydroquinone. 0.01 M $Na_2B_4O_7 \cdot 10H_2O$ was used as electrolyte;
(1) pure glassy-carbon disk without any hydroquinone additions, (2) glassy-carbon disk coated with a PPD film without any hydroquinone additions, (3) glassy-carbon disk coated with a PPD film in solutions with hydroquinone at concentrations indicated below, and (4) pure glassy-carbon disk in solution with hydroquinone at 6×10^{-4} M
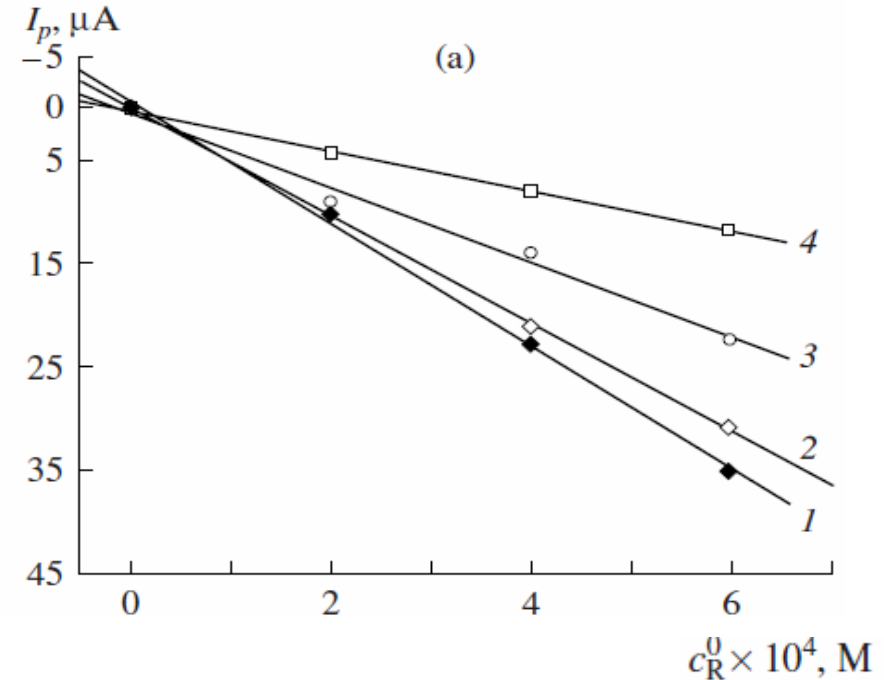
Dependences of the limiting penetration current on the hydroquinone concentration (1) pure glassy-carbon electrode and (2)–(4) PPD- coated electrode for film thicknesses L (nm) of (2) 150, (3) 330, and (4) 390

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Experimental results; poly-o-phenylenediamine + hydroquinone (case I of through pores)
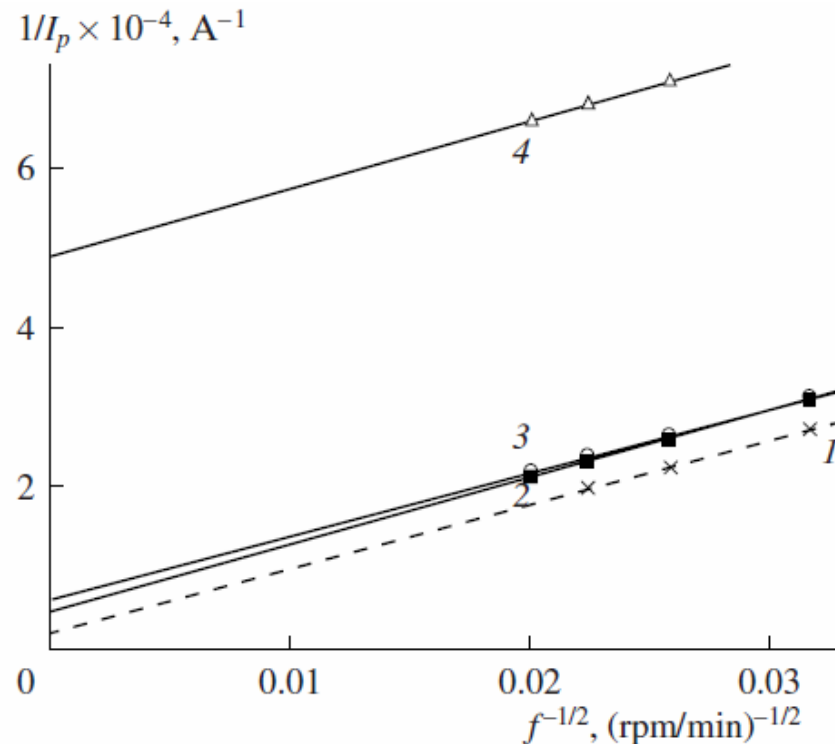
The Levich-Koutecky representation of the dependences of the limiting penetration current on the RDE frequency.

The hydroquinone concentration is 6×10^{-4} M; (1) pure glassy-carbon electrode, (2)–(4) PPD-coated electrode, film thickness L, nm: (2) 150, (3) 330, (4) 390.

Russian Journal of Electrochemistry, 2008, Vol. 44, No. 1, pp. 98–103 18

Experimental results; PB+H_2O_2 (case II: reaction on the real physical film surface)
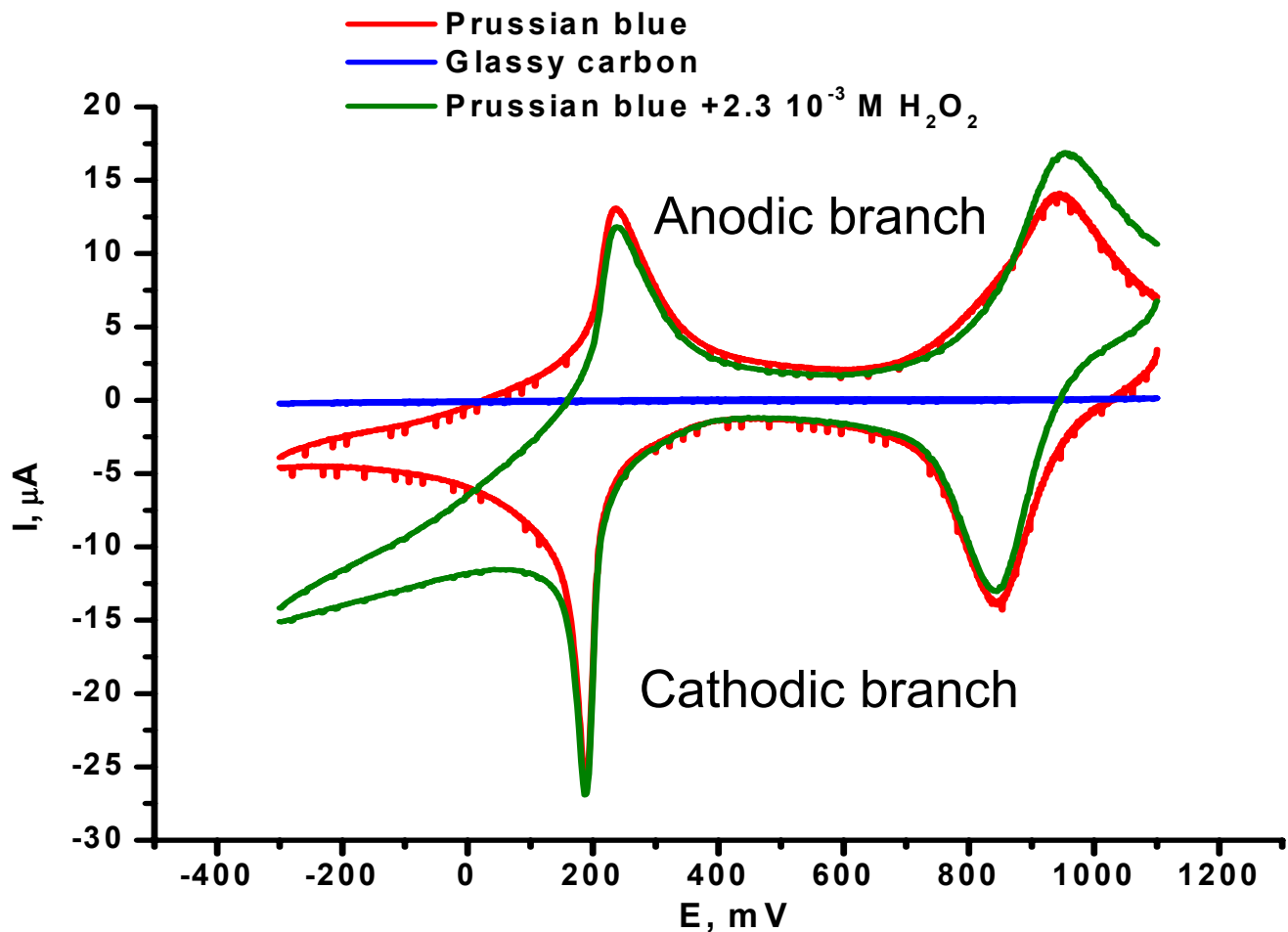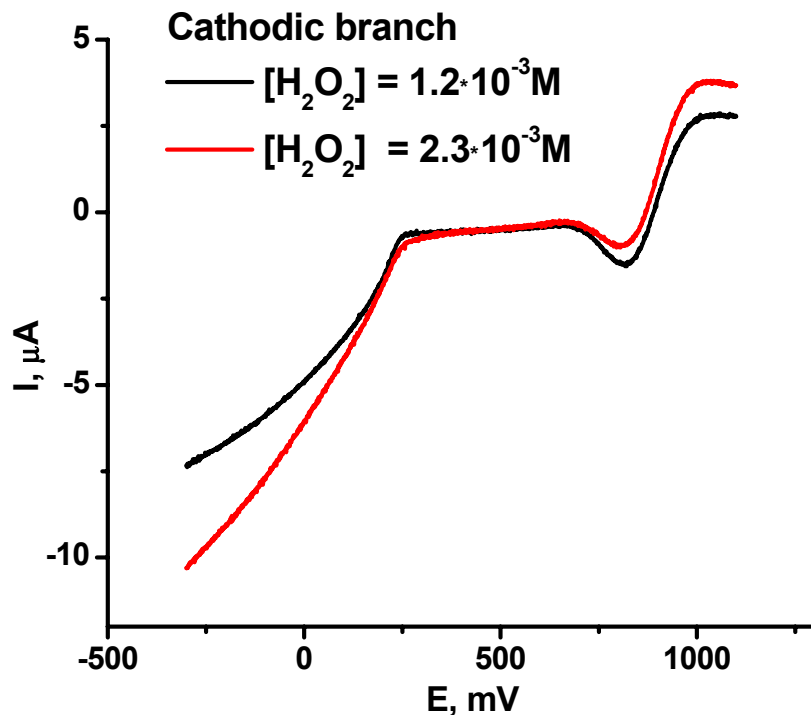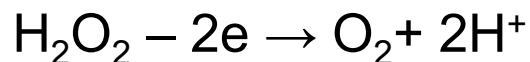
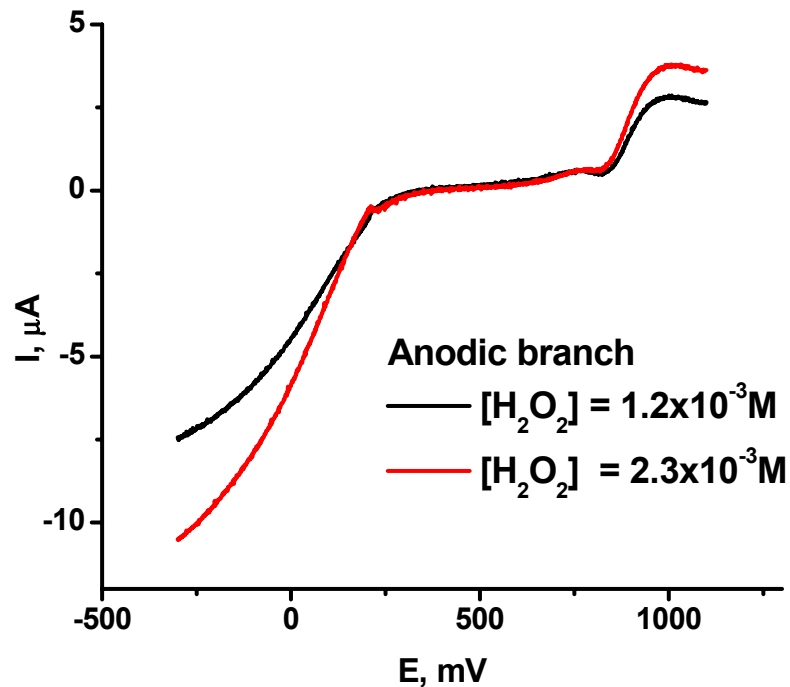Cyclic voltammograms of glassy carbon and PB-modified electrodes with hydrogen peroxide added.

C_{H2O2} = 2.3·10^{-3} M, v=20 mV/s

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Experimental results; PB+H$_2$O$_2$ (case II: reaction on the real physical film surface)

Anodic limiting current at **1.1 V** :

$$H_2O_2 - 2e \rightarrow O_2 + 2H^+$$

Cathodic 'limiting' current at **- 0.3 V** :

$$H_2O_2 + 2e + 2H^+ \rightarrow 2H_2O$$

Cathodic branch
— [H$_2$O$_2$] = 1.2*10^{-3}M
— [H$_2$O$_2$] = 2.3*10^{-3}M

Anodic branch
— [H$_2$O$_2$] = 1.2x10^{-3}M
— [H$_2$O$_2$] = 2.3x10^{-3}M
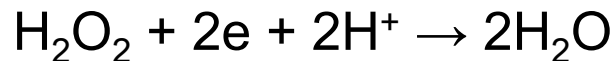
0.1 M KCl, pH=3

Partial currents of the hydrogen peroxide electroreduction/electrooxidation on a PB modified electrode at different concentrations of H$_2$O$_2$ (Unpublished data).
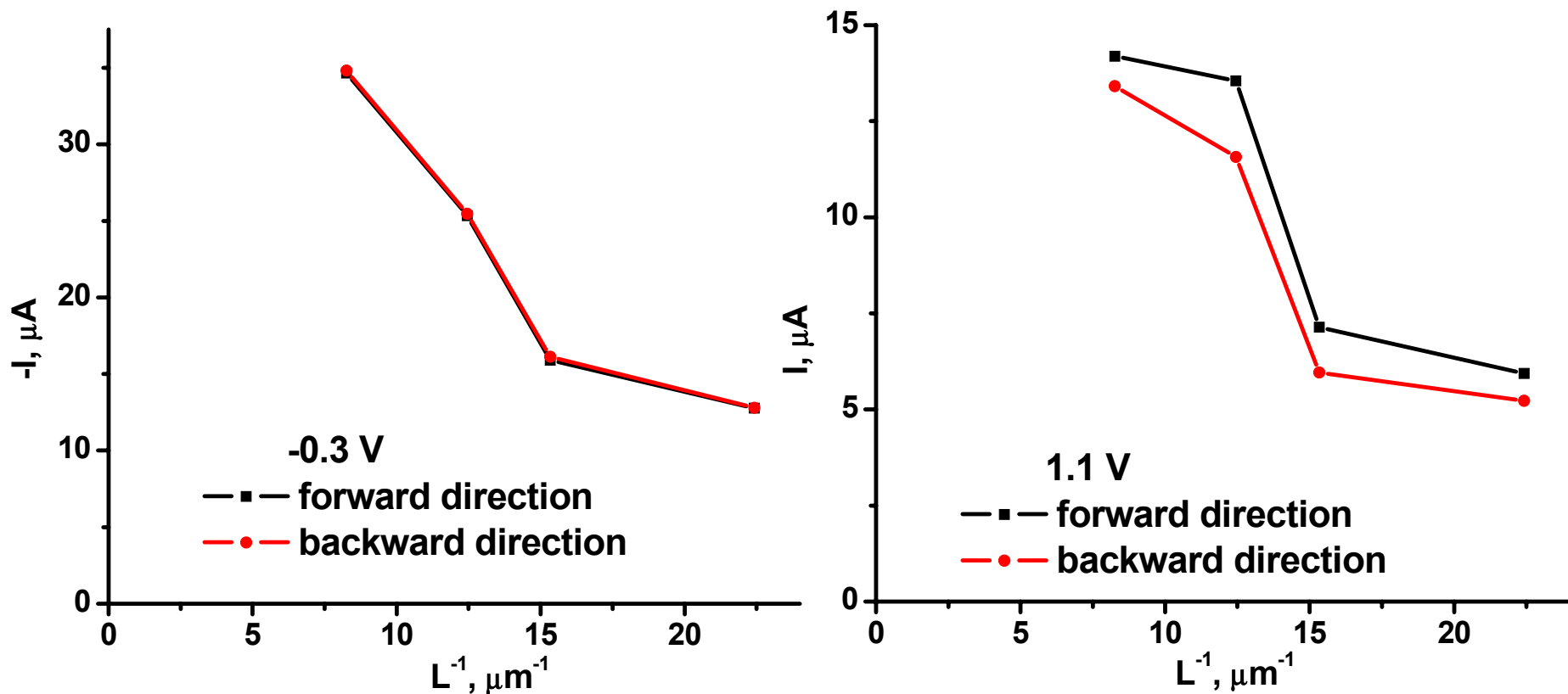
Experimental results; PB+H$_2$O$_2$ (case II: reaction on the real physical film surface)

f	Calculated current, Icalc, A$\cdot 10^5$ (C (H$_2$0$_2$)= 1.2 $\cdot 10^{-3}$M)	Calculated current, Icalc, A$\cdot 10^5$ (C (H$_2$0$_2$) = 2.3$\cdot 10^{-3}$M)	Experimental current, Iexp, A$\cdot 10^5$ (C (H$_2$0$_2$)=1.2 $\cdot 10^{-3}$M) E=-0.3 V	Experimental current, Iexp, A$\cdot 10^5$ (C (H$_2$0$_2$) =2.3 $\cdot 10^{-3}$M) E=-0.3 V	Experimental current, Iexp, A$\cdot 10^5$ (C (H$_2$0$_2$)=1.2 $\cdot 10^{-3}$M) E=1.1 V	Experimental current, Iexp, A$\cdot 10^5$ (C (H$_2$0$_2$)=2.3 $\cdot 10^{-3}$M) E=1.1 V
2500	±16	±31	-1.1	-1.4	0.7	1
2000	±14.5	±28	-1.1	-1.4	0.6	1
1500	±12.5	±24	-1.0	-1.3	0.7	1
1000	±10	±20	-0.9	-1.2	0.6	0.9

Comparison between the experimental limiting currents and those calculated according to the Levich equation
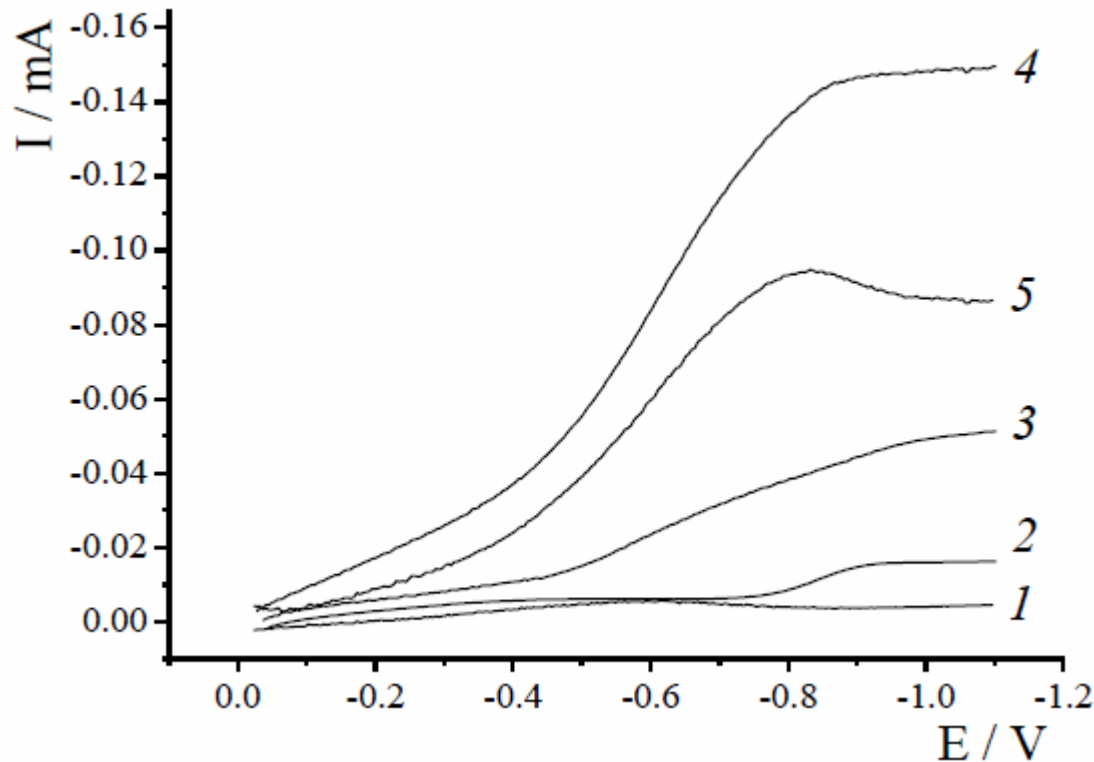
Experimental results; PB+H$_2$O$_2$ (case II: reaction on the real physical film surface)

**Current change with increasing the film thickness in 1.2·10^{-3} M H$_2$O$_2$**

Similar results were published by U. Scharf and E. W. Grabner (Electrocatalytic oxidation of hydrazine at a Prussian blue-modified glassy carbon electrode / Electrochimica A. (1996), 41, 233)

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RDE voltammetry curves of GC/PEDOT electrode in solution of PBS in the absence (1) and presence (3) of 0.001 M H_2O_2 and those of GC/PEDOT/Au electrode in PBS solution in the absence (2) and presence (4) of 0.001 M H_2O_2 (substrate - GC disk of 0.07 cm², f =2500 rpm, scan rate 10 mV s^{-1}). Duration of gold loading from solution of $1 \cdot 10^{-3} M$ HAuCl$_4$ + 0.1M H$_2$SO$_4$ is 60 s

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# Experimental results; PEDOT/Au + H_2O_2 (case III of metal-composite films)
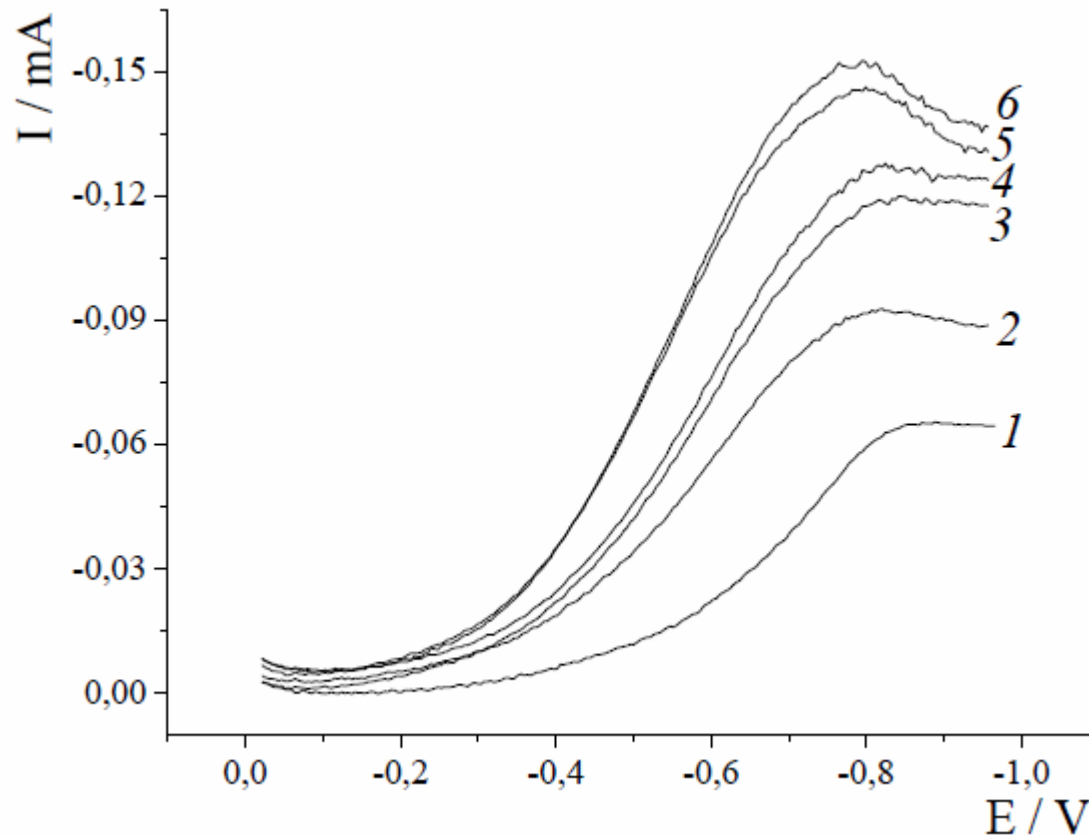
Partial RDE voltammetry curves for the hydrogen peroxide reduction on Au-particles in PBS solution plus $1·10^{-3}$ M H_2O_2. Durations (s) of gold loading from solution of $1·10^{-3}$M $HAuCl_4$ +0.1M H_2SO_4 are as follows: **1 -** 60, **2 -** 150, **3 -** 240, **4 -** 330, **5 -** 560, **6 -** 720.

Experimental results; PEDOT/Au + H_2O_2 (case III of metal-composite films)
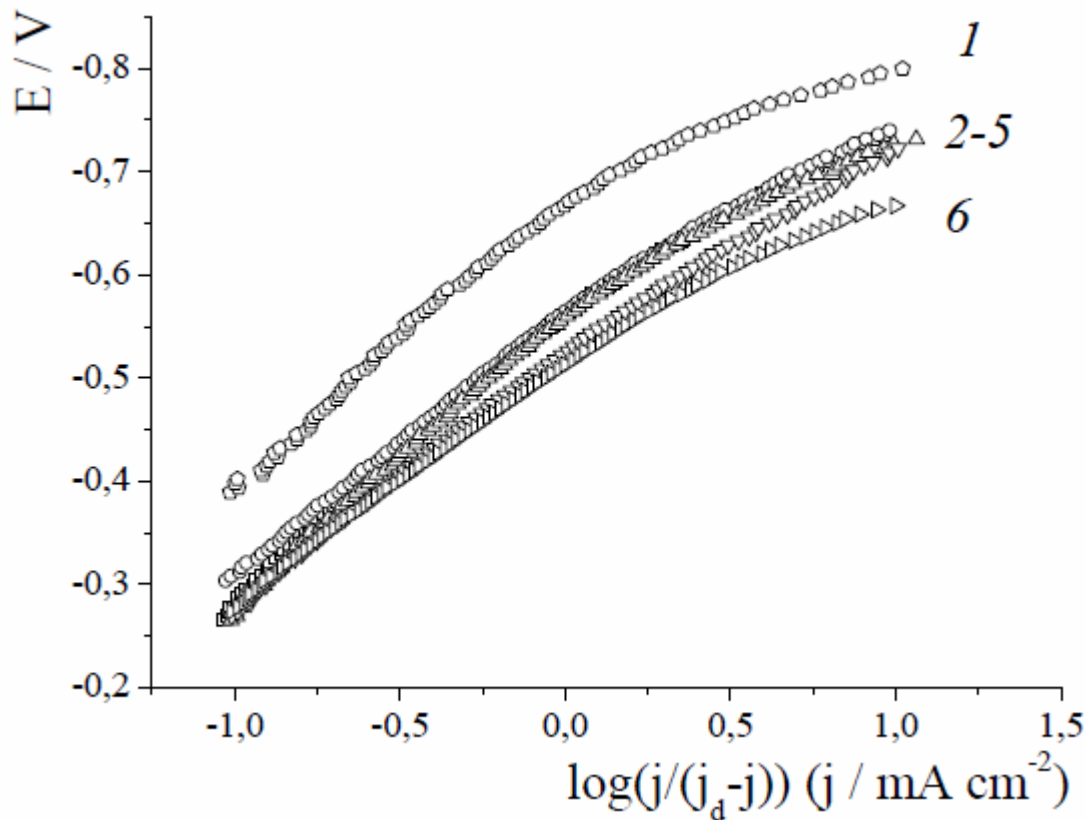
Mass-transfer corrected Tafel plots for the hydrogen peroxide reduction on Au-particles in PBS solution plus $1 \cdot 10^{-3}$ M H_2O_2 at different durations of gold loading, s: **1 -** 60, **2 -** 150, **3 -** 240, **4 -** 330, **5 -** 560, **6 –** 720.

PEDOT/Au + H$_2$O$_2$ (case III of metal-composite films)
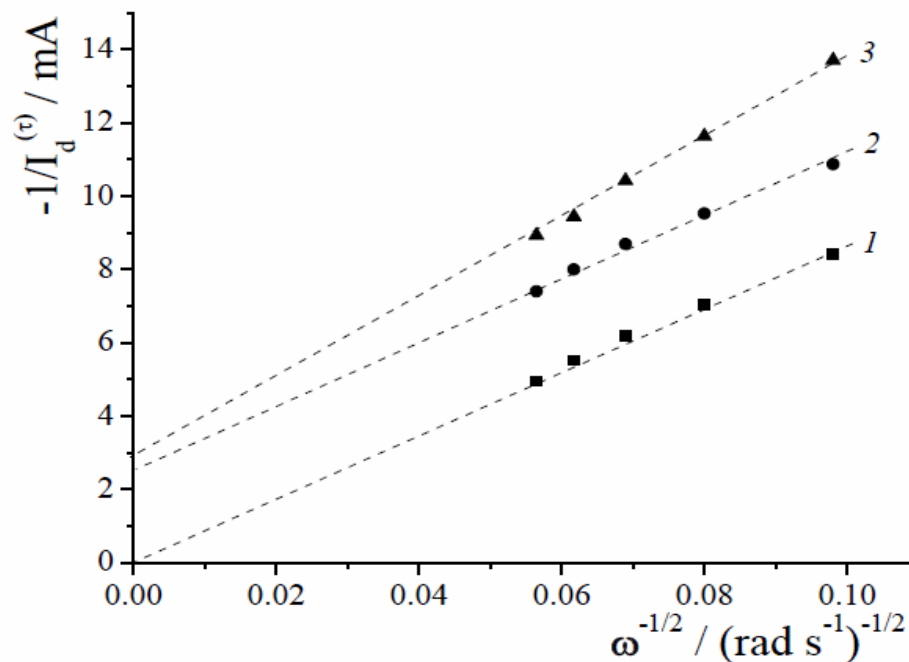
Koutecky-Levich plots of $1/I_d^{(\tau)}$ vs. $\omega^{-1/2}$ for the hydrogen peroxide reduction on composite PEDOT/Au film in PBS solution plus $1 \cdot 10^{-3}$ M H$_2$O$_2$ at different durations of gold loading from solution of $1 \cdot 10^{-3}$ M HAuCl$_4$, s: **1** - 720, **2** – 60, **3** – 60 (partial currents). Curve **3** represents partial limiting currents of H$_2$O$_2$ reduction on gold particles.

Acknowledgements:

Thank you for attention