

# Voltammetry of electrodes modified with pristine and composite polymer films; theoretical and experimental aspects



V.V. Malev<sup>a,b,\*</sup>, O.V. Levin<sup>a</sup>, V.V. Kondratiev<sup>a</sup>

<sup>a</sup> Department of Chemistry, St. Petersburg State University, Universitetsky prospekt, 26, 198504 St. Petersburg, Russian Federation

<sup>b</sup> Institute of Cytology, Russian Academy of Sciences, St. Petersburg, Russian Federation

## ARTICLE INFO

### Article history:

Received 6 July 2013

Received in revised form

26 September 2013

Accepted 28 September 2013

Available online 18 October 2013

To the memory of Prof. Veniamin Levich.

### Keywords:

Voltammetry

Conducting polymers

Porosity

Charge transfer

Rotating disk electrode

## ABSTRACT

Specific features of voltammetric studies with modified electrodes are subject of the consideration performed in the review. Basing on the approaches developed in preceding works, three groups of problems are discussed. The first one concerns a regular treatment of quasi-equilibrium cyclic voltammograms of modified electrodes. It is emphasized that singular points of such curves and their form depend on the system parameters (charges of immobile charge carriers, binding of counter-ions with the film fragments). As regards the second group of problems, its existence results from possible effects of the film porosity on the rates of reduction/oxidation processes with participation of particles capable to react on the film/solution interface. The main conclusion followed from the performed discussion is in the possibility of appearing the limiting currents not controlled with tested particles diffusion within the adjacent electrolyte. In scope of the third group of problems, the tested particles reactions on the electrodes covered with metal-containing polymer films are considered. As follows from the proper analysis, the current–voltage curves of these processes are described with the well-known equations of the electrochemical kinetics. Validity of the obtained conclusions is illustrated with the corresponding experimental results.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Charge transfer in modified electrodes is a promising direction of electrochemical research due to the prospects of the practical use of electroactive polymers, in addition to the scientific significance of such studies. The mixed ion–electron (polaron) nature of the film conductance, the presence of two interfaces and, hence, two processes of charge carriers injection into a modifying film, and the evident dependence of the conductance on structural peculiarities of these films significantly complicate a quantitative interpretation of the results obtained with such systems. The so-called “hopping” mechanism of electron (polaron) transfer between two immobile neighbouring redox centres



accompanied by diffusion of mobile counter-ions is in the base-ment of the corresponding description [1,2]. For the partial case of

a homogeneous film and the presence of only two kinds of charge carriers in its volume, the following set of balance equations

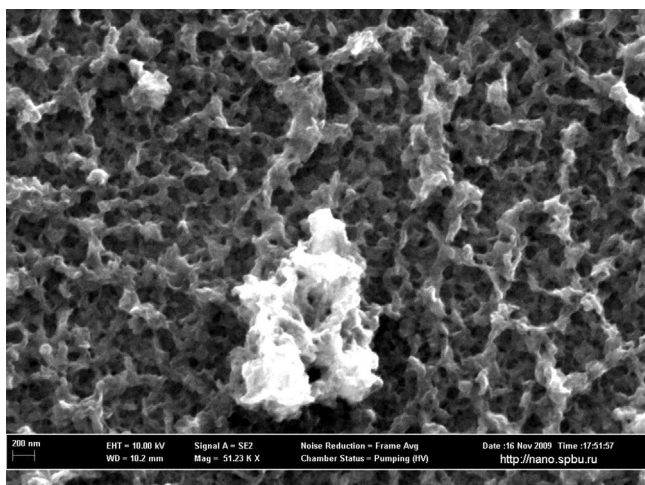
$$\begin{aligned} \frac{\partial C_R}{\partial t} &= D_{\text{im}} \left( \frac{\partial^2 C_R}{\partial z^2} - \frac{\partial \left( C_R (1 - \theta_R) \left( \frac{\partial \Phi}{\partial z} - a \frac{\partial \theta_R}{\partial z} \right) \right)}{\partial z} \right) \\ \frac{\partial C_m}{\partial t} &= D_m \left( \frac{\partial^2 C_m}{\partial z^2} + \frac{\partial \left( z_m C_m \frac{\partial \Phi}{\partial z} \right)}{\partial z} \right) \end{aligned} \quad (2)$$

is usually applied to describe the charge transport within modifying films. Here,  $D_{\text{im}}$  and  $D_m$  are the diffusion coefficients of immobile and mobile charge carriers;  $\theta_R = C_R/C_T$  is the occupancy of the lattice fragments by their red-form, where constant  $C_T$  is the total concentration of such fragments;  $a$  is the dimensionless (in  $RT$  units) attraction constant related to the site interaction energies;  $\Phi(z) = F\varphi(z)/RT$ , the dimensionless electric potential;  $C_m$ , the concentration of counter-ions; and  $z_m$ , their charge.

Strictly speaking, set (2) was formulated initially for redox polymers and then extended without essential premises to conducting polymers, the unit polaron charge of which is distributed over three–five neighbouring monomer units of polymer chains. At this

\* Corresponding author at: Department of Chemistry, St. Petersburg State University, Universitetsky prospekt, 26, 198504 St. Petersburg, Russian Federation. Tel.: +7 812 2731359; fax: +7 812 4286900.

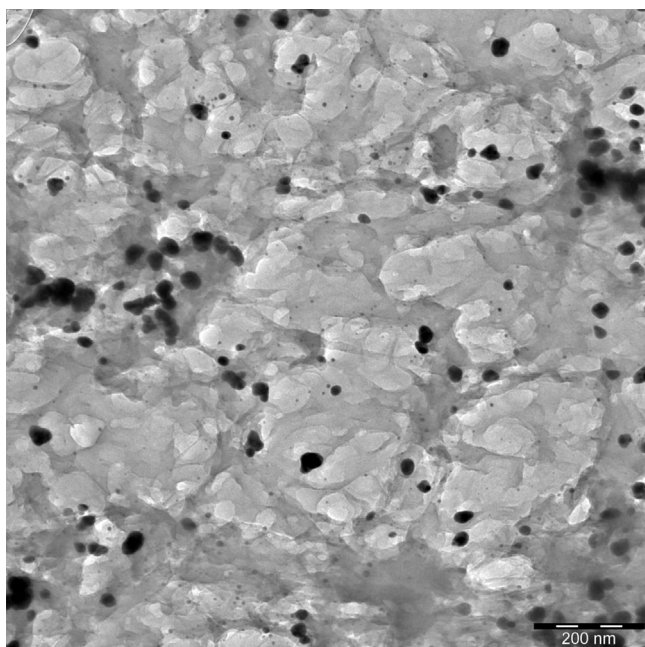
E-mail addresses: [elchem@rbcm.ru](mailto:elchem@rbcm.ru), [valerymalev@gmail.com](mailto:valerymalev@gmail.com) (V.V. Malev).



**Fig. 1.** Typical SEM-image of a PEDOT (poly(3,4-ethylenedioxythiophene)) film. An irregular porous structure of the film is seen from the figure. The predominant sizes of pores (dark spots on the figure) are in the limits of 50–200 nm.

stage, we only note that such generalization needs some corrections, as will be explained later. One more disadvantage of the above approach is in the assumption of homogeneity of modifying films, though it is well known that they are inhomogeneous systems and possess an expressed porosity (see Fig. 1). The necessity of accounting for the film inhomogeneity becomes obvious in the case of composite films containing, for example metal or metal oxide inclusions (see Fig. 2), which provide a catalytic activity of such systems with respect to some chosen electrochemical reactions.

Despite these and other possible remarks, the approach summarised above is typically used in studies related to the modified electrodes topic. Although the approach allows one to treat the results of such non-stationary methods, as low amplitude chronoammetry [3] and electrochemical impedance spectroscopy [4,5], in most studies along the indicated topic, researchers restrict themselves only to cyclic voltammetry method, by supposing it be



**Fig. 2.** Typical TEM-image of a composite PEDOT/Au film. Dark spots of the figure correspond to gold clusters. Gold deposition was performed from a  $5 \times 10^{-4}$  M  $\text{HAuCl}_4 + 0.1$  M  $\text{H}_2\text{SO}_4$  solution; deposition time was equal to 60 s.

sufficient to characterize the studied objects. The last method is probably the most frequently used one in electrochemical research and its application in case of modified electrodes seems reasonable. At the same time, in such applications, specific features of modified electrodes should be taken into account, since their presence determines essential differences of the obtained current responses as compared to those known, for example for electrode reactions proceeding in compact monolayer films adsorbed onto metal electrodes [6,7]. In particular, a phase character of electroactive polymer films is their most important feature that differentiates these objects from adsorbed monolayer films. It means that the electroneutrality condition occurs within the interior of polymer films and this circumstance is responsible for peculiarities of current responses of the systems discussed in this paper [8].

In connection with using the modified electrodes as sensors on different substances inclusive of biologically active ones, there appears to be a series of questions. As was mentioned above, real electroactive polymer films are porous systems and, hence, reactions of particles capable to reduce/oxidize on the electrodes covered with these films can occur not only on their visible (“outer”) surface, but also on an “inner” surface of pores penetrating the films completely or partially. Should one observe any influence of the film porosity on the rate of tested particles reactions? Questions of the similar kind might also be posed in case of composite films if reactions of tested particles exclusively proceed on the surface of film inclusions. In these conditions, the evident questions are as follows. Is it possible to analyse such reactions with the help of classical equations of the electrochemical kinetics? If so, how do the rate constants of the proceeding reactions depend on the amount of inclusions loaded into the film, and whether they are dependent on the distribution of inclusions within the film interior? All these questions might be formulated in a more general form; namely, whether there exist any differences in electrochemical behaviour of the considered systems and solid electrodes formed from the material of the film inclusions?

It is necessary to say that the preceding remarks and the questions posed were not generated initially, but have appeared during searching the corresponding information and subsequent studies. In our view, at least a relative clarity in the above points has been achieved, and we will try to show this in the given review. The latter includes a short discussion of both the obtained theoretical conclusions and their experimental illustrations, including a limited number of those not published previously. We therefore give below some experimental details concerning mainly procedures of syntheses of the electrodes studied; additional information can be found in the references cited further on.

## 2. Experimental

Electrochemical synthesis of poly-*o*-phenylenediamine films was conducted in a potentiodynamic mode on a polished glassy-carbon disk 0.3 cm in diameter from solutions containing 0.05 M *o*-phenylenediamine and 0.5 M perchloric acid at the electrode potential cycled from  $-200$  to  $1200$  mV by using the procedure of [9]. Measurements on a rotating disk were conducted as described in [10].

The polyaniline/rhodium (PANI/Rh) composite films were synthesized by simultaneous deposition of polyaniline and rhodium from solutions containing 1 M  $\text{HNO}_3$ , 0.1 M aniline, and  $\text{Na}_3\text{RhCl}_6$  in different concentrations ( $2 \times 10^{-3}$ ,  $4 \times 10^{-3}$ , and  $8 \times 10^{-3}$  M), as described in [11]. The kinetics of the  $\text{H}_2\text{O}_2$  electroreduction on PANI/Rh films was studied in 1 M  $\text{HNO}_3$  solutions deaerated with argon at room temperature ( $20 \pm 2^\circ\text{C}$ ) [12].

PEDOT films were synthesized by electropolymerization on glassy carbon (GC) substrate under galvanostatic conditions

Download English Version:

<https://daneshyari.com/en/article/186315>

Download Persian Version:

<https://daneshyari.com/article/186315>

[Daneshyari.com](https://daneshyari.com)