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Quasi-equilibrium voltammetric curves resulting from the existence of two immobile charge carriers within electroactive polymer films

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ABSTRACT

In the paper, we have considered possible causes responsible for the fact that CV-curves of electrodes modified by polymer metal complexes with the Schiff bases possess some shoulders or split into two peaks, while the total electrode process has a one-electron character. This study includes a quantitative analysis of voltammetric responses of electrodes, the modifying films of which contain, beside mobile charge carriers (counter-ions), two kinds of immobile ones. Three cases of polymer films are the object of the corresponding description, namely systems combining such charge carriers formed either independently of each other or due to some conversions between them. The obtained results are in a qualitative agreement with those observed in experimental conditions.

1. Introduction

Polymer transition metal complexes with tetradentate N_2O_2 Schiff base ligands derived from salicylaldehydes and aliphatic diamines and often denoted as poly[M(Schiff)] can be formed easily on inert electrode surfaces via oxidative electrochemical polymerization of corresponding Schiff base monomers in moderately/weak donor solvents [1]. Schiff base metal polymer-modified electrodes have been studied by several groups [2,3]. These studies have considered such fundamental issues, as electropolymerization process, polymer structure, identification of the surface redox couples, and the mechanism of charge transport.

Despite intensive investigations, some properties of poly[M(Schiff)] films have still remained unclear. In particular, there is some inconsistency between the observed voltammetric response of the polymer in the potential range from 0 to 1.3 V and one-electron character of the polymer redox-switching. For example, Fig. 1 shows the cyclic voltammograms of polymer complexes as with unsubstituted Schiff base ligands, as well with the ligands containing methoxy substituents in their aromatic parts [4–7]. Various authors have found that the redox switching of these polymers in a specified range of potentials is carried out using 0.7–1.2 electron per one polymer fragment. This was established with the use of thin-layer voltammetry [8], coulometry [9,10], and EQCM [4–7]. At the same time, voltammograms of the polymers are characterized by two sets of relatively broad peaks. In the case of polymers with unsubstituted ligands, the first pair of peaks appears as weak shoulders; introduction of methoxy groups in the ligand environment results in splitting the curves into two distinct voltammetric waves (see Fig. 1).

Different views on the nature of poly-[M (Schiff)] voltammetric response have been published. Goldsby et al. [11], noting the one-electron nature of the process, supposed that having two pairs of waves is due to the presence in the polymer film some traces of the initial monomer, remaining after polymerization procedure. This assumption has extensively been tested and disproved [1]; carefully removing residues of the parent compound from the polymer does not lead to significant changes in the shape of voltammograms. Peters [8] in the study of poly-[Ni(SalEn)] explained the complex voltammetric responses by "cross-linking" of polymer stacks following the oxidation of the metal center. However, subsequent studies of polymers of different compositions have shown that this explanation is not universal; two pairs of redox waves are observed at more negative potentials than those, at which there is a "cross-link". Freire et al. believe that the presence of two pairs of waves

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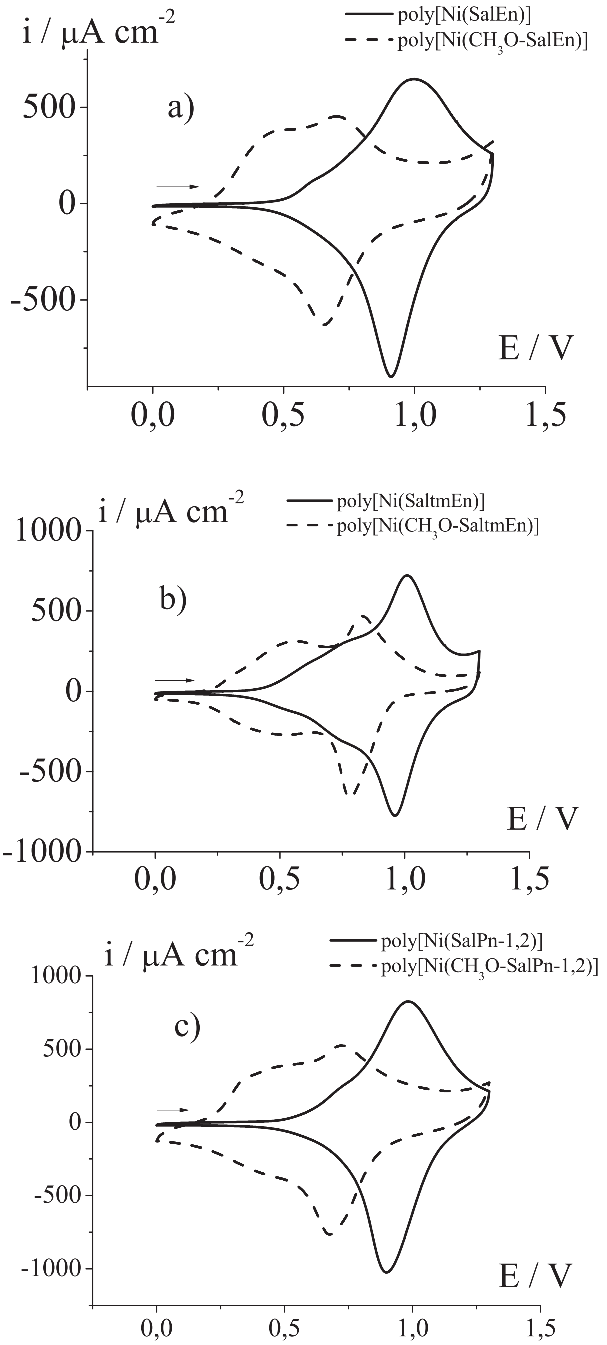

Fig. 1. Voltammograms of polymer films on GC electrode (BAS MF 2012, diameter 3 mm) registered in acetonitrile (AN) solutions of 0.1 mol/l (Et$_4$N)BF$_4$ at scan rate v = 0.05 V/s. Polymerization conditions: 5 polymerization cycles at v = 0.05 V/s in the potential range 0–1.2 V (vs. AgCl/Ag reference electrode) in 0.1 mol/l (Et$_4$N)BF$_4$/AN solution, containing 1×10^{-3} mol/l of the corresponding monomer. Designations: [Ni(SalEn)] = N,N-ethylenebis(salicylideneaminato) nickel(II), [Ni(CH3O-SalEn)] = N,N-ethylenebis(3-methoxysalicylideneaminato) nickel(II), [Ni(SaltmEn)] = N,N-2,3-dimethylbutane-2,3-dyil-bis(salicylideneiminato) nickel(II), [Ni(CH3O-SaltmEn)] = N,N-2,3-dimethylbutane-2,3-dyil-bis(3-methoxysalicylideneiminato) nickel(II), [Ni(SalPn-1,2)] = N,N-propane-1,2-dyil-bis(salicylideneiminato) nickel(II), [Ni(CH3O-SalPn-1,2)] = N,N-propane-1,2-dyil-bis(3-methoxysalicylideneiminato) nickel(II).

within the general one-electron nature of the redox processes may be due to the presence of two types of charge carriers – polarons and bipolarons [9,10].

Practically the same representations (without indications on the nature of charge carriers) are used by us in the forthcoming paper [12]. The main objective of the given one is a quantitative consideration of a series of simple models, explaining complex voltammetric responses of poly-[M(Schiff)] one-electron redox switching at the positive potentials. To achieve this aim, we shall, in essence, use the same approach that was applied previously in [13].

2. Theory

We will consider below three partial electrode systems corresponding to the presumed existence of three kinds of charge carriers within a polymer film, two types of which are immobile, while the third one conforms to mobile carriers, namely counter-ions entering/leaving the film during its charging/discharge. The simplest system obviously corresponds to a film containing two kinds of immobile carriers that are not capable to transform each other. We determine this case as a “mechanical mixture of two immobile charge carriers” to distinguish it from others; we assume that the scope of this case does not include some special conversions between such carriers. The second system to be analyzed includes a polymer film, in which the polaron/bipolaron conversion takes place. As to the third system, the concrete type of the charge carriers’ conversion proceeding within the film interior will be defined further on.

2.1. Mechanical mixture of two immobile charge carriers

In the case of polymer films without significant short-range interactions but containing three kinds of charge carriers, it is necessary to operate with three flux equations written as follows:

$$J_1 = -D_1\left(\frac{\partial C_1}{\partial z} - C_1(1-\theta_1)\frac{\partial \Phi}{\partial z}\right) \qquad (1)$$

$$J_2 = -D_2\left(\frac{\partial C_2}{\partial z} - C_2(1-\theta_2)\frac{\partial \Phi}{\partial z}\right) \qquad (2)$$

$$J_3 = -D_3\left(\frac{\partial C_3}{\partial z} + z_3 C_3\frac{\partial \Phi}{\partial z}\right) \qquad (3)$$

and three mass conservation ones:

$$\frac{\partial C_k}{\partial t} + \frac{\partial J_k}{\partial z} = 0, \quad \text{where index} \quad k = 1, 2, 3 \qquad (4)$$

According to these equations and the above definition of the system considered, the electron transfer is assumed to proceed along different chains including red/ox forms of different film fragments in such way, that the electron exchange between these chains is absent. The notations used above are determined by the following definitions: $C_1(z,t)$, $C_2(z,t)$ are the concentrations of red-forms of the first and second kind, respectively; $C_3(z,t)$, the counter-ion concentration; $\Phi(z,t) = F\varphi(z,t)/RT$, the dimensionless electric potential ($\varphi(z,t)$, its value in electrical units (here V)); D_k, the diffusion coefficient of the kth species; J_k, their flux; z_3, the charge of counter-ions; z and t are the distance from the substrate/film interface and time variable, correspondingly.

If film thickness L is much higher than that of the diffuse layers formed at the film interfaces, the electroneutrality is achieved for practically all the film volume. To write the corresponding condition, we shall suppose that the total concentrations of red- and