Quasi-equilibrium voltammetric curves of polaron-conducting polymer films

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A B S T R A C T

This article continues modeling of the polaron conductance of polymer films in the general case of an arbitrary number of polymer repeat units included into the polaron structure. The main feature of the proposed approach is stipulated by the introduced definition of reduced quasi-particles as species that contain only one repeat unit of polymer chains, but not the same their quantity (usually, 3-6 units) included into polaron species according to the previously accepted description of polaron-containing polymer films. For a homogeneous population of polarons, every one of which contains the same number of repeat units, the analytical dependence of CV shape on such number m has been derived with a use of the proposed approach. The case of the simultaneous existence of two polaron kinds including different numbers of repeat units is also considered in scope of the applied method. The performed consideration leads to the following results. The quasi-equilibrium voltammetric curves derived with this approach are in a better agreement with experimental CV of conducting polymers than those calculated according to the approach accepted previously. In particular, the mid-widths of CV peaks calculated even without accounting for the so-called short-range interactions result in proximity to the actual values observed for various conducting polymers. In addition, such peculiarities of the real voltammetric curves, as the existence of several peaks or shoulders in their shape and the appearance of a plateau-like tail at high positive electrode potentials can be obtained with using simple assumptions.

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1. Introduction

Conducting polymers (CPs) are organic π-conjugated polymers, which conduct electricity by delocalized electrons or holes. CPs are also capable of forming modifying layers on electrode substrates, which makes them be prospective materials for applications in batteries, sensors, microelectronics, etc. The vast spectrum of such applications has brought about their extensive research during the last years. In particular, many works have been devoted to syntheses of such new materials with improved electrochemical properties (for example, see [1,2]). However, despite this profound research, some issues have still remained unclear especially questions concerning quantitative description of these objects, in particular their electrochemical properties.

It is widely known that delocalized cation-radicals (polarons) and dications (bipolarons) play the role of charge carriers within the most CP films [3,4]. Quantum mechanics methods are usually applied to describe properties of such quasi-particles. This approach allows one to calculate a series of such characteristics, as molecule geometry, electron density distribution, polaron/bipolaron formation energy, etc [5,6]. At the same time, it does not allow to predict electrochemical properties of the real CPs films because of structural irregularities of these objects. Therefore, electrochemical behavior of polymer films, in particular a current reply of polymer-modified electrodes on electrode potential changes, is usually treated in scope of the thermodynamic approach [7,8]. According to this approach, it is assumed that polymer films have a phase character, i.e. they are so thick that their interior is subject to an electroneutrality condition. The film phase is assumed to be in equilibrium conditions and its bulk to contain the oxidized and reduced fragments of equal sizes, which treated as different quasi-particles. Charge transfer in such systems is described as electron translocation from a reduced quasi-particle to a neighboring oxidized one.

However, there are some peculiarities in CPs properties, which can hardly be explained by the given approach. For example, as indicated in review [9], CV curves of poly-dimethoxibitiophene

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films have a long plateau and several peaks. Also, according to the accepted approach, the mid-width of CV curves of quasi-equilibrium process of film charging/discharging must be equal to 131 mV [8], rather than around 500 mV, as indicated in the review mentioned above. These peculiarities cannot be treated quantitatively even if one accounts for the existence of short-range interactions between film fragments or non-zero scan rate values. Such impossibility seems to be still more obvious for the case of electrodes modified by PEDOT films and immersed into aqueous electrolyte solutions, where the corresponding voltammetric curves have a practically rectangular form in a wide potential range [10]. Although, as it was noticed in the cited review, the registered charging/discharging processes should probably be treated as sequences of separate but overlapping redox steps, no quantitative description of the observed peculiarities of such CV curves has been given in scope of the above thermodynamic approach even further on.

In that respect, the approach proposed initially in [11,12] and generalized later for the case of non-equilibrium conditions [13] appears more promising for such explanations than the approach discussed above [7,8]. The main discrepancy between the compared approaches is in the used treatment of reduced quasi-particles of polymer films. In particular, the proposed approach assumes any reduced (undoped) repeat unit (single fragment) of polymer chains to be a separate quasi-particle, while, in frames of the preceding approach, the role of such particle plays a complex of neighboring reduced units containing the same number, m, of fragments, as that included in polaron (bipolaron) species. The indicated difference in the definitions naturally leads to the assumption that electron transfer (or polaron movement) along the length of a polymer chain proceeds in a "step by step" way including consecutive acts of charge transfer from a polaron to the nearest and single reduced chain fragment. This means that a single polaron translocation length is most probably equal to one polymer fragment size but not the total length of m fragments included into polaron quasi-particles, as assumed in scope of the approach used earlier. Thus, this corrected approach allows one to consider the polaron motion within CPs films as a hopping process that consists of consecutive acts of polaron translocations from the extreme fragment included into a polaron to the neighboring repeat unit provided the latter is in the undoped state. Such step by step consideration of polaron motion inevitably leads to the subsequent definition of each undoped chain fragment as a separate quasi-particle. In particular, we will further assume such quasi-particle to be a conjugated chain fragment that is planar one and has a full π-electron delocalization in its undoped state [9,14]. In the most cases, this definition corresponds to one monomer fragment, for example one thiophene or pyrrol ring in poly-thiophenes or polypyrrols, but might have a different meaning in polymers like poly(p-phenylene vinilene), where several double bonds are present in monomer precursors.

Using this novel treatment, a quasi-equilibrium voltammetric curve has been calculated in [11,13] for the case of polarons containing two monomer units. As has been established, the mid-width value of such curve appears be equal to 181 mV (at room temperature), which exceeds about 1.4 times the value calculated previously in scope of the traditional approach (131 mV, see [8]). Moreover, it has been shown that the above reformulation of polaron translocations leads also to quantitative changes in the corresponding impedance equations as compared to those followed from the preceding approach, and these changes become more pronounced the greater number m of fragments included into the polaron structure [13]. Taking into account the established fact that, in the real systems, number m is in between three and six [15], it is of interest to get a more complete knowledge on specific features of polaron-containing films (in particular, their quasi-

equilibrium voltammetric curves) in case of arbitrary number m of polaron fragments.

This article deals with analysis of changes in voltammetric curves at variations in number m of polaron fragments. In addition, the simultaneous existence of two polaron kinds containing different numbers of polymer fragments is considered below. The calculated quasi-equilibrium cyclic voltammograms (CVs) seem to be in a better accord with the experimental curves of electrodes modified with polaron-containing films than CV curves followed from the traditional description. In particular, the obtained mid-width of such curves increases monotonically with rising number m and grows up to 330 mV for the case of polarons consisting of six fragments. Moreover, some tendency to the formation of a current plateau and several peaks (or shoulders) that are characteristic for the real CV curves has been traced as a result of the performed calculations.

2. Results

Applying the proposed approach, we will analyze below CV curves of different systems, which consist of an electrode substrate, conducting polymer film, and adjacent electrolyte solution. The first case to be considered corresponds to the existence of only one kind of polarons within a polymer film, namely polarons including the same but arbitrary number m of repeat monomer units. The second case corresponds to a film, which contains two types of polaron species, in particular polarons formed with m neighboring monomer fragments and those containing one lesser (m-1) of such fragments.

2.1. Polymer film containing one type of polaron species

In scope of the traditional approach (see [7,8]), the reaction of polaron formation is assumed to be of a view:

$$R(f) \rightleftarrows P^+(f) + e, \tag{1}$$

where symbols R, P^+, and e are assigned to reduced quasi-particles, polarons, and electrons, correspondingly. This obviously means that the number of repeat units included into the reduced quasi-particles and polarons is the same and, hence, its concrete value should not have any significance for the subsequent consideration and might formally be equated to unity.

In contrast to such treatment, the above corrected approach accounts for a simultaneous participation of m neighboring repeat units considered as separate quasi-particles in acts of polaron formation:

$$mR(f) \rightleftarrows P^+(f) + e(sb) \tag{2}$$

Here, letters (f) and (sb) point to the presence of corresponding particles in the film and electrode substrate phases, respectively. The phase character of the polymer film in question means it is necessary to take into account the counter-ions (A^-) presence in both the film interior (f) and the adjacent electrolyte bulk (s), i.e. their entering/leaving the film according to the reaction:

$$A^-(s) \rightleftarrows A^-(f), \tag{3}$$

in order to provide electroneutrality of the film during the subsequent consideration. As mentioned above, the latter was performed in [13] basing on the Gibbs equilibrium principle [16] applied to Reactions (2) and (3) and not accounting for non-ideality of the considered system (i.e. assuming the absence of the so-called short-range interactions). This led to the equations:

$$\frac{\theta_P}{(1 - \theta_P)^m} = K_P \exp\left(\frac{FE}{RT} - \frac{F\Phi}{RT}\right); \tag{4}$$