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# ACCEPTED MANUSCRIPT

# Double Layer Structural Effects in Cyclic Voltammetry Curves Complicated with Non-Equilibrium Injection of Charge Carriers into Redox Polymer Films

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#### **ABSTRACT**

An expressed asymmetry of cyclic voltammetry curves of electrodes modified with redox and conducting polymers is often considered as a consequence of slow injection of charge carriers into/out of polymer films. The Butler-Volmer equation is usually applied to quantitative treatment of the rates of such injection processes. It is generally considered that the above equation does not take into account the influence of the double layer structure on the rates of electrode processes and, hence, one can assume that its use might lead only to a qualitative explanation of the observed asymmetry effect. Using different models of film double layers (at the film/electrode substrate and film/adjacent electrolyte interfaces) and the proper kinetic equations that include the so-called Frumkin correction, we have calculated the corresponding voltammetric curves in case of electrodes modified with redox polymer films. As expected, a good agreement between the data calculated and the results followed from the Butler-Volmer equation takes place only for the Helmholtz model of the both interfacial regions, while significant quantitative differences in such curves appear with using the Stern and Gouy models of film double layers.

### Key words:

Cyclic voltammetry, Redox polymers, Charge carriers injection, Asymmetry of cyclic curves, Peak currents, Double layer, Frumkin's correction.

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#### 1. Introduction

Cyclic voltammetry of electrodes modified with electroactive polymer films is the most Page 1 of 37 commonly used method to study charge transfer processes in such objects. With the

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