Modelling of Partially Blocked Electrodes under Linear Potential Sweep Conditions

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This report presents a model for efficient computer simulation the electrochemical behaviour of partially blocked electrodes under linear potential sweep and cyclic voltammetry conditions. The model involves a resist layer of the inactive site of the electrode surface. The effect of the thickness of the resist layer on the behaviour of partially blocked electrodes is investigated.

THEORETICAL

A simple redox-electrode reaction, involving two soluble species O and R, is considered. The electrochemical process includes exchange of current and diffusion. It was assumed that mass transport obeys a finite diffusion regime within a Nernst layer from the electrode/electrolyte boundary [1].

A lot of circular active regions are arranged in a rigid hexagonal array at the surface of partially covered electrode (Fig. 1). Due to the symmetric distribution of the active sites, the diffusion space adjustment to the electrode surface may be divided into equal hexagonal regular prisms. For simplicity, a circle of radius b, whose area is equal to that of the hexagon, is considered, and one of the cylinders is regarded as a unit cell of the diffusion space. Due to the symmetry, we consider only a quarter of the cylinder. The thickness of the Nernst layer (δ_{R}, δ_{O}) was assumed to be different for species R and O. The mass transport is regular in the entire diffusion space.

Taking into consideration the resist layer of thickness h, the model of the redox reaction for partially blocked electrodes, was written in cylindrical coordinates (r, z) by a system of partial differential equation of the diffusion type with initial and boundary conditions [2]. The problem was solved numerically using the finite-difference technique for the discretization of the model.

RESULTS

Several model electrodes were used in physical experiments and numerical simulation [2]. The electrodes varied in the blocking degree $\theta = 1 - a^2/b^2$, where a is the radius of the active site. The influence of the thickness of the resist layer on current dynamics was investigated. Results of calculation are depicted in Fig. 2 and 3 at sweep rate of 20 mV/s.

Fig. 2 shows, that in modelling of the partially blocked electrodes, the resist layer of thickness of 1 μm should be taken into consideration to obtain an satisfactory agreement between the experimental data and numerical solution.

We introduce the normalized cathodic k_{c} and anodic k_{a} peak current, determined by the ratio of the corresponding peak current at thickness $h = 1\,\mu$m to the peak current at $h = 0$. Fig. 3 shows, that the influence of the resist layer on the cathodic and anodic normalized peak current increases with the increase of blocking degree. It it highly necessary to consider the resist layer of thickness $h = 1\,\mu$m only for highly blocked electrodes ($\theta >\approx 0.8$). Additional calculation showed the similar variation of k_{c} and k_{a} vs. blocking degree also at the sweep rate of 100 mV/s.

REFERENCES

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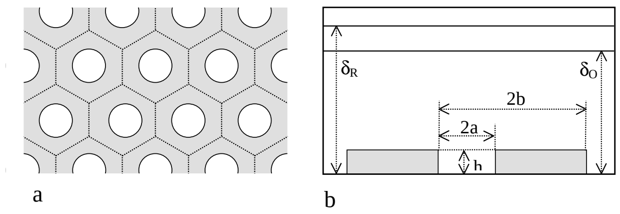

Figure 1

A principal structure of (a) partially blocked electrode and (b) the profile at z plate. Shaded areas indicate the resist layer of thickness h.

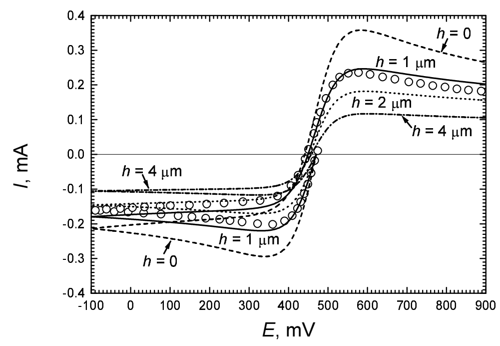

Figure 2

Evolution of the current at $a = 2.5$, $b = 23.6\,\mu$m, $\theta = 0.989$, $h \in \{0, 1, 3, 4\}\,\mu$m. Circles show experimental data, and the lines are numerical ones.

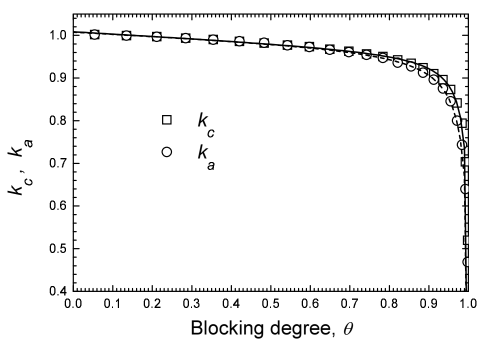

Figure 3

The normalized cathodic (k_{c}) and anodic (k_{a}) peak current vs. the blocking degree θ.