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ON THE MECHANISM OF THE MIGRATION CURRENT EXALTATION EFFECT IN ACID SOLUTIONS

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The Problem of diffusion - migration ionic transport in parallel Processes of cation reduction and molecular oxygen reduction is theoretical studied. For the case of acid solutions the recombination reaction of H^+ ions and OH^- ions generated at the electrode due to oxygen reduction is taken into account. It is shown that at rather high H^+ ions concentration in the bulk solution, when their flux to the electrode is high the recombination reaction takes place in the narrow region close to the electrode. Therefore in this case the Process of oxygen reduction proceeds with participation of H^+ ions. At moderate H^+ ions concentration in the bulk solution the process of H^+ and OH^- ions recombination is localized due to high rate of recombination process in a narrow region inside the diffusion layer which is much less than the thickness of Nernst diffusion layer. Diffusion layer consists in this case of two regions. In the first one spaced near the electrode the H^+ ions are practically absent and the corresponding system of electrodiffusion equations coincides with that used in the theory of migration current exaltation (1). In the second region the OH^- ions are practically absent and the corresponding system of electrodiffusion equations coincides with that used in the theory of correlation exaltation of migration current (1).

It is shown that the limiting current of cations discharge increases with the growth of oxygen reduction current, this increase being most pronounced at low H^+ concentrations. For rather acid solutions the unusual limiting diffusion - migration current of cations discharge must be realized due to the decrease of their concentration to zero inside the diffusion layer (2).

The anomalous character of space charge density distribution is found in the region of the H^+ and OH^- ions recombination where the abrupt change of electric field takes place.

(1) Yu.I.Kharkats, *Elektrokhimiya*, 1978, 14,1716, 1840.

(2) A.V.Sokirko, Yu.I.Kharkats, *Elektrokhimiya*, 1989, 25, 232.

THE THEORY OF HIDDEN LIMITING DIFFUSION CURRENTS.

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The phenomenon of hidden limiting current is observed in systems where the product of electrochemical reaction irreversibly interacts in the solution with the depolarizaton of another parallel electrochemical reaction (1). As a result of such interaction the diffusion flux to the electrode of reactant of second reaction depends on the rate of first reaction, i.e. both Processes are not independent.

Let, for example, two substances A and B are reduced at the electrode, $A + ne \rightarrow pA^*$, $B + me \rightarrow rB^*$. If in solution bulk reaction, $pA^* + qB \rightarrow A_p^*B_q$ takes place, then according to definition given in (1) the hidden limiting current $\Delta i = i_B - i_B'$ is the difference of limitine current of B reduction in the absence of A i_B' , and in its presence i_B .

The theoretical analysis of hidden limitine currents described in (1) was valid only for the case of infinitely high rate of homogeneous reaction.

In the Present work a theory of hidden limiting currents is developed which is valid for arbitrary values of rates of homogeneous Process (2). The distributions of reactant B and reaction product A^* in diffusion layer are described by equation

$$D_A^* \frac{d^2 C_A^*}{dx^2} - K C_A^* C_B = 0, \quad D_B \frac{d^2 C_B}{dx^2} - K C_A^* C_B = 0,$$

Here D_A^* and D_B are corresponding diffusion coefficients, K is the rate constant of homogeneous reaction, x is coordinate.

The analytical solution of the problem has been derived for the cases: 1) high or slow rates of homogeneous reaction: 2) the fluxes of substance A are large or small. At intermediate values of these parameters the problem was solved numerically.

(1) W.Kemula, Z.R.Grabowski, Roszn.Chem.,1952, 25, 516.

(2) A.V.Sokirko, Yu.I.Kharkats, Elektrokimiya, 1989, 25, 34.