TARTU UNIVERSITY

DOUBLE LAYER AND ADSORPTION AT SOLID ELECTRODES

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Tartu 1991

GENERATION OF VARIABLE SIGN SPACE CHARGE IN A DIFFUSION LAYER FOR ELECTRODE PROCESS WITH SUBSEQUENT HOMOGENEOUS REACTION

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It is known that during electric current passing, a space charge region arises in diffusion layer, whose distribution density does not decrease exponentially as it was in diffuse layer, but gradually /1/. When the current density tends to its limiting value, the space charge density in the vicinity of the electrode increases abruptly, coinciding in sign with that for electroactive ions.

Here we present the results of imeetigation of space charge distribution in diffusion layer for reduction of cations $A^{z+} + 2e^- \rightarrow A^0$, and parallel oxygen reduction $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ with subsequent recombination reaction of OH^- and H^+ ions in diffusion layer: $OH^- + H^+ \rightarrow H_2O$. This reaction scheme was analyzed in detail in ref. /2/, in which the mechanism of migration current exaltation effect in acidic solution was theoretically investigated.

The set of electrodiffueion equations describing the distributione of components' concentrations and the potential in diffusion layer may be written as

$$\frac{dc_1}{dx} + c_1 \frac{d\Psi}{dx} = \frac{i_1 L}{FD_1 c^0} , \qquad \frac{dc_2}{dx} - c_2 \frac{d\Psi}{dx} = 0 , \qquad (1)$$

$$D_3 \frac{dc_3}{dx} - c_3 \frac{d\Psi}{dx} - D_4 \frac{dc_4}{dx} + c_4 \frac{d\Psi}{dx} = -\frac{i_2 L}{Fc^0} = -D_3 j_2 , \qquad (2)$$

$$c_3 c_4 = K_0 , \qquad\qquad c_z + c_3 = c_1 + c_4 . \qquad (3)$$

Here c_1, c_2, c_3 and c_4 are dimensionless concentrations of cations A^+, anions, OH^- ions and H^+ ions, c_o is the dimensional concentration of A^+ ions in the eolution bulk, $\Psi = F\varphi/RT$ is the dimensionless electric potential, x is di-

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meneionless coordinate ($0 \le x \le 1$), L is the thickness of the Nernst diffusion layer, i_1 and i_2 are current densities for cation's discharge and oxygen reduction, K_0 - the ionic product for water, the boundary conditions at $x = 1$ can be written as $c_1(1) = 1$, $c_2(1) = 1 + k$, $c_3(1) = 0$, $c_4(1) = k$, $\Psi(1) = 0$.

Taking into account that the recombination reaction for water is very fast and the equilibrium constant satisfies inequality $K_0 \ll 1$, we can suppose that in the diffusion layer either ions OH^- of H^+ ions can exist simultaneously. Correspondingly, the recombination of reaction plane x=0 splits the diffusion layer into two regions, $0 \le x \le \theta$ and $\theta \le x \le 1$ We can put $c_4 > 0$ and $c_3 \approx 0$ in the region spaced to the right of the point $x = \theta$ and $c_3 > 0$ and $c_4 \approx 0$ in the region spaced to the left of the point $x = 0$. These approximatione make it possible to determine the potential distribution $\Psi(x)$ and then using the Poisson equation, to find apace charge distribution $\rho = -\varepsilon RT\Psi''/F$.

Calculated $\rho(x)$ distributions for series of parameters j_1, and fixed j_2 and k values are shown in Figure 1.
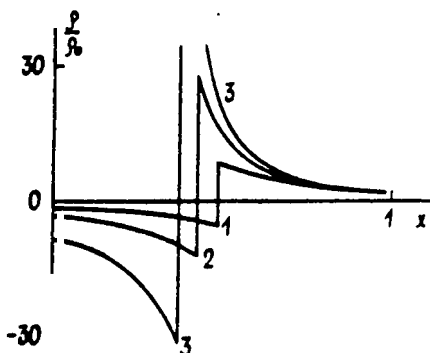

Fig. 1 Spece charge distribution for $D_3/D_4 = 0.56$; k $= 0.8$; $j_2 = 4$, and j_1: $1 - 2$; $2 - 2.5$; $3 - 2.7$; $\rho_0 = 2ec^0 \cdot (l_D/L)^2$; l_D is the Debyey length.

The analysis shows that as e result of recombination

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reaction inside the diffusion layer some interesting peculiarities in space charge distribution arise. At the point of homogeneous reaction localization $x = \Theta$ and under the condition $D_3 j_2 \quad kD_4 j_1$ an abrupt change of the sign and absolute value of $\rho(x)$ takes place. In the discussed model due to high value of rate constant of recombination reaction its reaction layer had practically zero thickness. In a more general case of moderate reaction rates there must exist some transition region in which space charge varies from positive to negative values. Qualitatively the obtained result can be explained as follows. We can present the plane of recombination reaction localization as some electrode plane at $x = \theta$, which is on the one hand brought into contact with H^+ ions, and on the other hand with OH^- ions. Then in the region $\theta \leqslant x \leqslant 1$ where H^+ ions exist we have positive space charge distribution ae usual in electrolyte. And in the region $0 \leqslant x \leqslant \theta$ where OH^- exists we have correepondingly negative apace charge distribution.

We note in conclusion that the peak in space charge distributions including also a change in the sign of charge was earlier predicted in refs. /3,4/ for the systems in which besides movable carriers of charge also fixed charges exist.

References

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